DYNAMICS AND FRACTIONATION OF HEAVY METALS IN THE UPPER REACHES OF MUVATTUPUZHA - A TROPICAL RIVER

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Certificate

This is to certify that the thesis entitled ***"Dynamics and Fractionation of Heavy Metals in the Upper Reaches of Muvattupuzha - A Tropical River"*** *is an authentic record of the research carried out by Josekutty J. Ozhukayil under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology in partial fulfilment of the requirements for the Ph.D degree of the Cochin University of Science and Technology under the faculty of Marine Sciences and no part of this work has been submitted before for the award of any other degree, diploma or associateship in any university.*

Kochi-16
March 2015

Dr. N. Chandramohanakumar

Declaration

I hereby declare that the thesis entitled ***"Dynamics and Fractionation of Heavy Metals in the Upper Reaches of Muvattupuzha - A Tropical River"*** *is an authentic record of the research carried out by me under the supervision of Dr. N. Chandramohanakumar, Professor, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology in partial fulfilment of the requirements for the Ph.D degree of the Cochin University of Science and Technology under the faculty of Marine Sciences and that no part of this work has been submitted before for the award of any other degree, diploma or associateship in any university.*

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Preface

Heavy metal contamination in aquatic environments is one of the major environmental concerns owing to its toxicity, persistence and ecological risks. The transport, fate and biogeochemical cycling of trace metals in rivers are based on partitioning with water, suspended particulate matter and sediments. Trace metals released into river waters are bound to the suspended particulate matter by adsorption or precipitation reactions, which get settled along with various carrier phases and become incorporated into bottom sediments. Thus, environmental impacts and ecological risks arising out of trace metal contamination depend on various chemical forms by which they are associated in riverine sediments. Understanding the dynamic metal interactions in and between different compartments like water, suspended particulate matter and sediments is vital for assessing the environmental impacts of heavy metal pollution.

The study region for the present investigation is the Muvattupuzha River basin, located between north latitudes 9°45' – 10°05' and east longitudes 76°22' – 76°50'. This River which acts as a major source of fresh water which carries contaminant discharges (pollution load) from municipal (urban) towns and agricultural areas that debouches into the northern Vembanad Lake near Vaikom. Even though a few reports on trace metal distribution in the sediments from the lower reaches of the Muvattupuzha River and adjoining Cochin backwaters are available to a certain extent, no systematic study have been conducted on the upstream freshwater zones of the Muvattupuzha River to assess its distribution, toxicity and bioavailability in water, suspended particulate matter and sediments. The present study depicts the spatial and seasonal variations of trace metals in the dissolved

phase, particulate phase and that bound among various sedimentary geochemical phases from upstream areas of Muvattupuzha River.

The entire thesis is presented in seven chapters. Chapter 1 gives a general introduction stating the necessity of studying trace metals in riverine systems. Review of relevant literature along with aim, scope and objectives of the present investigation are also given in Chapter 1.

Chapter 2 deals with the materials and methods adopted for the work. The field work consists of bi-monthly sampling of water and sediments are discussed in detail. Moreover, the analytical procedures adopted for the estimation of relevant hydro-chemical parameters and trace metal analysis using an Atomic Absorption Spectrophotometer is also discussed.

Chapter 3 presents the spatial and seasonal variations of hydro-chemical parameters like pH, temperature, dissolved oxygen, chemical oxygen demand and chloride content in the water column. It also covers with the spatial and seasonal variations of organic carbon and textural characteristics of the sediments.

Chapter 4 deals the spatial and seasonal variations of dissolved and particulate metals in the water column. The geochemical behaviour of trace metals in the water column is addressed based on the partition coefficient values obtained for each metal.

Chapter 5 reports the spatial and seasonal variations of total metal contents in sediments. The current pollution status in sediments was assessed by means of geo-statistical tools like enrichment factor, contamination factor, geo-accumulation index and pollution load index are also included.

Chapter 6 depicts with the fractionation of trace metals in sediments. The spatial and seasonal variations of trace metals in the five geochemical phases like exchangeable fraction, carbonate fraction, Fe-Mn oxide fraction, organic fraction and residual fraction in sediments are included in Chapter 6.

The summary of the study and the major conclusions drawn are given in Chapter 7. The list of references cited is given at the end of each chapter.

Contents

Chapter 1

INTRODUCTION

1. Introduction

1.1. Environmental settings of the rivers draining into the Vembanad Lake

The state of Kerala is characterised by short and swift west flowing monsoon fed 41 perennial rivers, which originate from the Western Ghats mountains that support the life and greenery of the region and drain into the Lakshadweep Sea either via. the estuaries or kayals/lakes. The most conspicuous feature of Kerala coast is the wide spread distribution of estuaries and lagoons, which is thought to be the remnants of the receding sea (Nair, 1996). The Vembanad Lake (Latitude. 09°00'–10°40' N and Longitude. 76°00'–77°30' E) bordered by Alappuzha, Pathanamthitta, Kottayam and Ernakulam districts is the largest lake in Kerala, covering an area of about ~ 365 km^2 and its breadth varies from 500 m to 4000 m, is the longest lake in India extending to a length of ~ 113 km in a NW-SE direction from Azhikode

in the north to Alappuzha in the south. The lake catchment is drained by seven small westward flowing rivers (i.e. rivers with catchment area <10,000 km^2) viz., Chalakudy, Periyar, Muvattupuzha, Meenachil, Manimala, Pamba and Achankovil rivers which originate from the Western Ghats. This region exhibits a tropical humid climate and receives an annual rainfall of about 3500 mm which brings in approximately 20,000 Mm^3 of fresh water run-off into the Vembanad Lake (Soman, 1997). Of the total rainfall, southwest monsoon (June–September) contributes to about 75% and the remaining by northeast monsoon (October–December) and summer showers. The percentage contribution of river discharge into the Cochin backwaters from Periyar, Muvattupuzha, Pampa, Manimala, Meenachil and Achenkovil were 33 %, 24.2 %, 19.7 %, 8.8 %, 8.3 % and 5.8 % respectively (Srinivas, 2000).

Hydrological characteristics of the Vembanad Lake are governed by the seawater intrusion by micro-tides (≤ 1.0 m) through the Cochin barmouth and influx of freshwater discharges from seven perennial major rivers like Chalakkudi, Periyar, Muvattupuza, Meenachil, Manimala, Pamba, and Achenkovil. Among these rivers, Periyar and Muvattupuzha discharge into the northern and southern-central part of the Cochin backwater system hence play an active role on the prevailing hydrography of the northern Vembanad Lake (*Figure 1.1.1.*). The major hydrological variable is salinity (~ 0.20 to 30.00 ppt) which typically divides the lake into two distinct segments as a freshwater dominant southern zone and a salt-water dominant northern zone and these salinity gradients supports a diverse species of flora and fauna that tolerates oligohaline, mesohaline or marine conditions (Menon et al. 2000).

The anthropogenic activities in the region commence from the second part of 19^{th} century onwards and remain high to the present day. The environmental consequences of various human interventions during the last 5

decades have resulted in drastic alterations in the length and breadth of the Vembanad Lake. Indiscriminate reclamation of the Vembanad Lake and its adjoining wetlands for agricultural expansion, aquaculture practices, dredging activities, harbour and urban developments has contributed immensely to the horizontal shrinkage of the Cochin backwaters (Gopalan et al. 1983). Further, the construction of two hydraulic barriers during the 1970's one at Pathalam (28 km north of Cochin inlet) and the other at Thannermukkam (43 km north of Cochin inlet) to prevent saline intrusion into the upstream agricultural fields has imposed severe flow restrictions and increased siltation which also caused shrinkage in the Cochin backwaters area considerably (Gopalan et al. 1983). Sediment accumulation rates in the estuarine and mangrove areas of the Cochin backwaters are 3–6 times higher than that in the adjacent inner shelf area (Manjunatha et al. 1998). The annual maintenance dredging volume of 10 x 10^6 m^3 from the Cochin harbour region indicates the intensity of sedimentation (Rasheed, 1997). The Vembanad Lake is wide (0.8 – 1.5 km) and deeper (4 – 13 m) towards south but becomes narrow net-worked (0.05 – 0.5 km) and shallower (0.5 – 3.0m) in its northern part (Balachandran et al. 2008). The bathymetry of the water body indicates that depth variation generally occurs between 1.5 m to 6.0 m in most parts except for the shipping channels dredged are maintained at 10 to 13 m depth (Menon et al. 2000).

The Vembanad Lake is facing serious environmental threats which include pollution due to discharge of industrial, agricultural and domestic effluents (Thomson, 2002). During the 1940's, industries were allowed to establish along the upper reaches of the Vembanad Lake without understanding its complex hydrodynamics. Inadequate technology and high cost involved for waste water treatment eventually resulted in accumulation of pollutants, especially in the northern region (Qasim, 2003). The effluents from

the industries at Eloor (260 MLD), Ambalamughal (80 MLD) and Piravam (60 MLD) are discharged into the lower parts of the Periyar, Chitrapuzha and Muvattupuzha rivers are mixed into the northern, central and southern parts of the lake by tides and freshwater flows. In addition to the release of waste oil, paints and paint scrapings from the Cochin port, the city's domestic sewage (2550 MLD) is also drained into the central part of the lake. Moreover, wastes from the agricultural lands (paddy fields) located at Periyar (160 km^2) as well as Muvattupuzha (80 km^2) and Kuttanad (660 km^2) regions is discharged into the northern and southern parts of the lake respectively. The central part of the lake is reported to be dynamic whereas the northern and southern parts showed flow restrictions and hence are more sensitive to the accumulation of pollutants (Balachandran et al. 2008). The increasing loads of industrial waste and domestic sewage have created conditions that are extremely destructive to flora and fauna of the northern and central parts of the lake respectively (Menon et al. 2000). Due to tidal activity pollutants from the northern and central lake gets dispersed towards the southern lake making the fresh water system of the lake also gets threatened (Balachandran et al. 2008). In addition agricultural waste inputs from the lands located around the lake also pollute the freshwater regions. As a result Cochin backwaters is widely regarded as one of the polluted estuaries in India which receive contaminated freshwater inputs and discharges of effluents and untreated sewage from many points throughout its tidally mixed zone. Recently, changes brought about in the Cochin backwaters like reclamation and its consequent shrinkage and discharge of pollutants has made adverse impacts on the potential of aquatic ecosystems that used to support high levels of bio-productivity and bio-diversity. Recognizing its biological productivity, bio-diversity and socio-economic importance, the Vembanad Lake has been included in the Ramsar site (No.1214) of vulnerable wetlands to be protected from human interventions (Wetlands, 2002).

Physiographically, this area can be divided into 3 distinct natural zones - the gneissic highlands (>75 m above mean sea level), midlands or lateritic plateaus (8–75 m) and the lowlands or coastal plains (<8 m). Topography of the area covers altitudes ranging from below mean sea level to above 3000 m in Western Ghats area. The head water elevation of these rivers varies between 700 and 1,830 m with respect to mean sea level. The highlands, which act as the main production zone for sediments, are generally under dense forests and/or forest plantations.

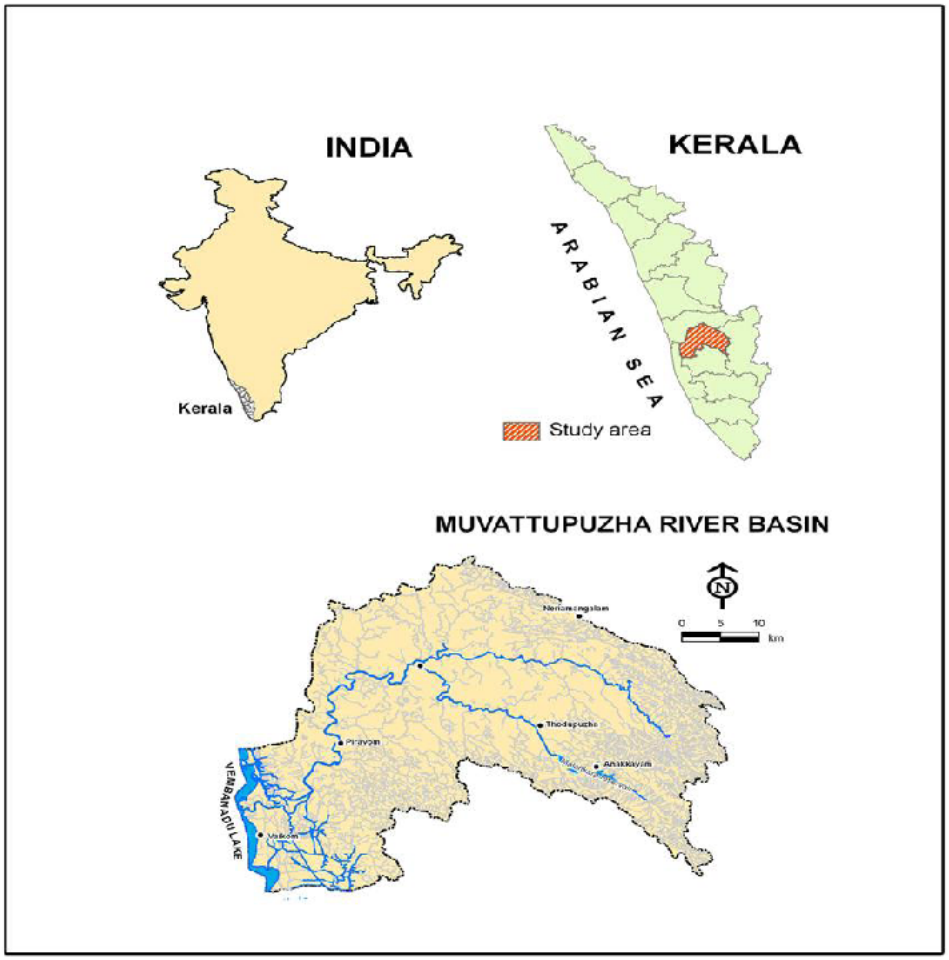

Figure 1.1.1. Map of Muvattupuzha River and northern Vembanad Lake

1.2. Geology of rocks in the rivers draining into the Vembanad Lake

The Archaean metamorphic units in southern India broadly comprise of a granite-green stone terrain in the north and a granulite terrain in the south (Omana and Santhosh, 1996). Study area occupies at the south-western part of this large southern Indian granulite terrain. The watershed areas (Periyar, Muvattupuzha, Pampa, Manimala, Meenachil & Achenkovil Rivers) of the Vembanad Lake are occupied by four major rock units (Padmalal et al., **1997**). They are (1) Precambrian crystalline, (2) Tertiary sedimentary, (3) Pleistocene lateritic and (4) Recent to sub-Recent sedimentary units. The Precambrian crystalline rocks expose all through the highland western ghats area and a considerable portion of the midlands, and they are mainly comprised of massif charnockites, garnet-biotite gneisses, khondalities and hornblende gneisses. A large part of these rocks has undergone polymetamorphic and polydeformational activities. At many places the Precambrian crystalline rocks are intruded by acidic (granite & pegmatite) and basic (gabbro & dolerite) rocks. Some rocks have undergone extensive lateralization process and this constitutes as laterites cover over the Precambrian crystalline unit and Tertiary sedimentary unit at many places, mainly in midland and coastal areas. The Tertiary sedimentary rocks, which have very few exposures in the coastal areas, are represented by Vaikkom, Quilon and Warkalli formations, which in turn are composed of sandstones, clays and lime-stones. Recent-to-sub-recent sediments are mostly alluvial which constitute only a small portion in the total watershed areas of the Vembanad Lake. The coastal terrain, river mouths, estuary and the near shore shelf areas are underlined by a thick succession of Quaternary sediments which comprised of sand, silt, clay, peat and shell beds and Tertiary sediments with the basement made up of charnockite (Nair and Rao, 1980).

1.3. A need for environmental impact assessment study of human intervention in the rivers draining into the Vembanad Lake

Rivers are the most important life supporting systems of nature. But man has changed the nature of many worlds' rivers by controlling their floods, constructing large impoundments, overexploitation of living and non-living resources and using it for disposal of wastes, all of which threatens even the existence of river ecosystem itself (Haslam, 1990; Ittekkot and Lanne, 1991). During the past three-four decades, rivers in the densely populated areas of Kerala state are subjected to immense anthropogenic pressures due to various kinds of human interventions (Padmalal et al. 2008). The natural flow regimes and hydrographic conditions of many rivers are either modified or regulated through construction of dams, barrages and embankments. Furthermore, the discharge of domestic, agricultural and industrial effluents in the catchments, flood plains as well as riverine channels has led severe environmental deterioration in the rivers of Kerala. If the current pace of disturbances continues, it will result in irreversible environmental problems and degradation in most river basins of the Kerala State. The situation is rather alarming in the rivers that draining into the Vembanad Lake catchments as the area hosts one of the fast developing urban-cum-industrial centres, the Kochi city, otherwise called the "*Queen of Arabian Sea*". For instance, since late 1976, to facilitate the hydro-electric project, the water stored in a dam across Periyar River catchment has being diverted to Muvattupuzha River after the production of electricity. A substantial proportion of the sediments derived from the uplands or uphill's are being trapped in these reservoirs constructed for irrigation and hydroelectric power generation. Although, river flows and sediment loads are variable within and among years, sediment balance and channel stability occur over long-term only. Instabilities introduced by human

activities like deforestation, sand, clay and gravel mining, and by natural processes like extreme precipitation, forest fires can cause river channel beds and banks to become net sources of sediment. The annual sedimental yield for the river basins of Vembanad lagoon is estimated to be 32 million tonnes, which is attributed to high rates of chemical weathering by human interferences in the water-sheds and its catchments at the Western Ghats (Thomson, 2002). Even though the environmental quality of the Muvattupuzha River is equally alarming due to inter-basin water transfer, discharge of agricultural and urban pollutants, indiscriminate sand and brick clay mining in the mid and low lands etc. no comprehensive works have reported to assess on its environmental impacts. These human activities are of special environmental concern in river-basins because they create localized imbalances in sedimentation and erosion processes. All these points to an immediate need for multidisciplinary studies in the riverine environments of the Vembanad Lake for assessing the extent of degradation consequent to these anthropogenic activities. This is very much important for laying down strategies for regulating the anthropogenic activities on an environment friendly basis and also for creating awareness on its impacts on the physical, chemical and biological environment of these life support systems.

1.4. Environmental pollution by heavy metals and its toxic effects

The environmental pollution is caused by a variety of pollutants in water, air and soil (Salomons and Forstner, 1980). One of the major concerned pollutants of living environment is "Hazardous Metals" also termed as "Trace Elements" (Forstner and Wittmann, 1983). This term is used in geochemical and biochemical literature to refer to a group of otherwise unrelated chemical elements which are found in nature at very low concentrations. Their concentrations in different natural environments vary widely.

"Heavy metals" are one of the most widespread inorganic contaminants in water, air and soil, and their presence of increasing levels in the environment is causing serious concern in public, owing to its toxicity as shown by most of them. Heavy metals are usually defined as metals with high atomic number, atomic weight and a density greater than 5.0g cm^{-3}, but in the literature it is find so many different definitions. Recently, International Union of Pure and Applied Chemistry (IUPAC) defined the term "heavy metal" as a confusing and misleading one. Generally speaking, metals are natural components of the Earth's crust and some of them (e.g., copper, selenium, & zinc) are essential as trace elements to maintain the metabolism of the human body even if, at higher concentrations, they may have toxic effects. Many other metals (e.g., mercury, cadmium, lead, etc.) have direct toxic effects on human health.

Owing to their chemical characteristics, metals remain in the environment, in many cases only changing from one chemical state to another one and eventually accumulating in the food chain. Environmental pollution by heavy metals in the terrestrial environment occurs through a variety of human activities such as mining, refining, ore smelting, combustion of fossil fuels, application of fertilizers and pesticides in agriculture and electroplating industries. The effluents produced by these industries contain a variety of heavy metals, such as cadmium, copper, chromium, nickel, lead, and zinc, and their release in water bodies may significantly contribute to the increased presence of toxic heavy metals in aquatic environments. Owing to their high water solubility, heavy metals can be easily absorbed by living organisms and, due to their mobility in natural water ecosystems and their toxicity to living forms, have been ranked as major inorganic contaminants in surface and ground waters. Even if they may be present in dilute, almost undetectable

quantities, their recalcitrance to degradation and consequent persistence in water bodies imply that, through natural processes such as bio-magnification, their concentration may become elevated to such an extent that they begin exhibiting toxic effects. Of the 35 metals considered dangerous for human health, 23 have been defined as heavy metals: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc. However, the main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, and arsenic (this element is a metalloid but it is usually defined as a heavy metal). Large amounts of any of these metals may cause acute or chronic toxicity (poisoning), resulting in damaged or reduced mental and central nervous functions, modify blood composition, and damage the lung, kidney, liver, and other vital organs.

Long-term exposure to the above-mentioned heavy metals may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long term contact with some metals or their compounds may even cause cancer. Heavy metals may enter the human body through food, water, and air, or may be absorbed through the skin when they enter into contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Although several adverse health effects of heavy metals have been known since a long time, exposure to these metals is continuing and even increasing in some parts of the world. Thus, the control of heavy metal dumplings and the removal of toxic heavy metals from waters has become a challenge for the twenty-first century.

1.5. Global heavy metal pollution scenarios and threats

Heavy metal pollution of the natural environment is becoming a potential global problem as metals are indestructible and most of them have toxic effect when they exceed the threshold levels. Metals are continuously released into the biosphere by natural weathering of rocks and also by numerous anthropogenic activities such as mining, combustion of fossil fuels, industrial and urban sewage and agricultural practices (Zhang and Zhang, 2007; Zhang et al. 2011; Dubey et al. 2012). Domestic sewage, agricultural and industrial effluents are discharged in the water courses universally in untreated or partially treated forms. These naturally add a variety of pollutants which include among others certain toxic heavy metals and metalloids. Pollution of the natural environment with toxic metals has increased dramatically since the onset of the industrial revolution (Nriagu, 1979). The episode which brought the attention of the world towards heavy metal pollution was the "Minimata" disease which occurred in Japan in 1953. On a global scale there is now abundant evidence that anthropogenic activities have polluted the environment with heavy metals from the poles to the tropics and from the mountains to the depths of the oceans (Pacyna and Pacyna, 2001).

Heavy metals are the most widespread pollutants that occur commonly in the drinking water globally, which give rise to public health concerns throughout the continents of Asia, Africa, North America, South America, Antarctica, Europe and Oceania. Asia, the largest continent on earth in which China, Bangladesh, Vietnam, Taiwan, Thailand, Nepal and India are located where environmental concerns arises due to the presence of large amounts of heavy metals dissolved in drinking water. In Asian countries arsenic is found at high concentrations in groundwater, drinking water and surface soil (Chen, 2006). Chatterjee et al. (1995) found that arsenic concentration in ground

water was above the maximum permissible limit of WHO guideline value in the six districts of West Bengal, India, covering an area of 34,000 km^2 with a population of 30 millions. Groundwater arsenic contamination and consequent illnesses of people have been reported in half of 18 districts in West Bengal, India (Chowdhury et al. 2001). Borah et al. (2010) found that the drinking water sources in Assam, India, are heavily polluted with lead. Additionally, Borah et al. (2010) reported that iron content in the drinking water sources of that area exceeds the WHO guideline value of 300 ppb. Chaudhary and Kumar (2009) found that iron concentrations in well waters in villages around Kali river, India exceeded the WHO limit of iron (300 ppb) and suggested the possible sources of iron pollution in drinking water are from various iron industries located close to Kali river. Sundaray et al. (2012) found that Ni, Pb and Cd concentrations in water samples of Mahanadi river is above the maximum permissible limits of WHO and BIS which would pose human health risks.

Frisbie et al. (2009) demonstrated that some tube wells from Bangladesh had U, Mn, As, Pb, Ni and Cr concentrations exceeding WHO health-based drinking water guidelines. Furthermore, Nickson et al. (2005) revealed that drinking water sampled in Muzaffargarh, Pakistan, reached up to 906 $\mu g\ l^{-1}$ As. Moreover, Maharjan et al. (2005) found that the tube wells which are the only source for drinking water in Terai, Nepal, where As concentrations ranged from 3 to 1072 $\mu g\ l^{-1}$ with a mean value of 403 $\mu g\ l^{-1}$ and therefore arsenicosis victims counts up 6.9 % of Nepalese population. Likewise, Buschmann et al. (2007) reported seasonal fluctuations in the arsenic concentrations (from 1 to 1340 $\mu g\ l^{-1}$) in drinking water from wells in Cambodia.

In Sri Lanka, cadmium is one of the most troublesome toxic heavy metals which accumulates in the water reservoirs and agricultural soil as a result of intensive use of Cd contaminated phosphate fertilizers that causes chronic renal failure (Bandera et al. 2010). Limbong et al. (2004) found concentrations of mercury in drinking water from Indonesia, very close to values established by WHO. It is known that more than 60,000,000 Bangladeshis are drinking water with unsafe concentrations of one or more elements such as As, Mn, U, Pb, Ni and Cr (Frisbie et al. 2009), notwithstanding the WHO efforts to improve their water quality. Wang et al. (2007) reported that in Bangladesh, the growth and the intelligence quotient scores of children exposed to high arsenic concentrations were affected and expressed Camacho et al. (2011) found that cognitive development in children were affected by arsenic contamination. It is known that since 1990's, a large number of people have been experiencing various health problems from drinking arsenic contaminated water (50 to 1,860 $\mu g\ l^{-1}$) in 13 countries of Inner Mongolia, China, where 4,11,000 people are currently at risk from arsenic poisoning (Guo et al. 2007).

Taiwanese population who were chronically exposed to high levels of arsenic in drinking water developed cancers in the skin, lung, urinary bladder and potentially the kidney (IARC, 2004). Additionally, blackfoot disease in Taiwanese population is attributed to intake of groundwater contaminated with arsenic from pesticides (Chen et al. 1992). Kumar et al. (2010) indicated that 23% of overall arsenic exposure in US population is from drinking water from domestic wells contaminated with arsenic. Fewtrell et al. (2002) found in England and Wales that human population exposed to elevated Cu level in drinking water that is, 3 $mg\ l^{-1}$, are likely to become ill. Chen (2007) revealed that in Taiwan gallium, indium and arsenic were introduced into groundwater

via. industrial effluents and their concentration into drinking water were Ga, 19.34 μg l^{-1}; In, 9.25 μg l^{-1} and As, 34.19 μg l^{-1}. Arsenic concentration in drinking water is approximately 3.5 times higher than the WHO guideline values, but there are no criteria or standards for Ga and In (WHO, 2008).

Africa, the second-largest of the world and second most-populous continent after Asia suffers from many environmental problems including deforestation, degradation, desertification, air and water pollution, loss of soil fertility, dramatic decline and loss of biodiversity. Asante et al. (2007) reported contamination by As, Mn, Hg and Pb in drinking water from Tarkwa, Ghana. As and Mn concentrations were above the WHO guideline values for drinking water suggesting human health risk of great concern for those metals. Dzoma et al. (2010) found that water samples from Koekemoerspruit, Africa have As and Cd levels of 12 μg l^{-1} and 10 μg l^{-1}, respectively, those levels are several magnitudes higher than the WHO maximum permissible levels for drinking water of 10 μg l^{-1} and 3 μg l^{-1}, respectively.

In North America, water pollution is becoming a bigger issue due to pollution from farms, factories which may contaminate drinking water. High arsenic concentrations (> 10 μg l^{-1}) are widespread in drinking water aquifers in the western United States, the Great Lakes region and New England (Ryker, 2003). Nevertheless, Erickson and Barnes (2005) found that in the upper midwest USA, elevated arsenic concentrations of 10 ppb, the USEPA drinking water guideline value, in public drinking water systems which were associated with the human activities that increase the heavy metal pollution. Wyatt et al. (1998) reported that drinking water samples of wells or storage tanks from Northern Mexico, that is, Sonora state, had 117 μg l^{-1} As, 50 to 120 μg l^{-1} Pb, and 1 to 25 μg l^{-1} Hg, which appears that As, Hg and Pb contamination in drinking water for this area is a major concern.

In South America water pollution studies by Marshall et al. (2007) noted that drinking water in region of Chile which is supplied mainly by rivers that contain inorganic arsenic at very high concentrations. Alonso et al. (2006) found concentrations of aluminium, arsenic, manganese and iron above the guideline values of WHO in drinking water from Bolivia. Recently, the arsenic exposure in Latin America has been reviewed by McClintock et al. (2012), they estimated that at least 4.5 million people in Latin America are chronically exposed to high level of As that is > 50 $\mu g\ l^{-1}$, and some as high as 2000 $\mu g\ l^{-1}$ As.

Even though, Antarctica is often considered as one of the last pristine regions where also metal contaminants enter the continent through air, water, bird, marine mammals and by anthropogenic activities (Hughes and Convey, 2012). Mercury is a globally dispersed toxic metal that affects even remote polar areas that subsequently deposited in the surface snows in mainly coldest climatic stages (Jitaru et al. 2009). Concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb were determined in feathers of penguin collected in the Antarctic Peninsula. The highest levels of several elements were found in samples from King George Island (8.08 $\mu g\ g^{-1}$, 20.29 $\mu g\ g^{-1}$ and 1.76 $\mu g\ g^{-1}$ dry weight for Cr, Cu and Pb, respectively) and Deception Island (203.13 $\mu g\ g^{-1}$, 3.26 $\mu g\ g^{-1}$ and 164.26 $\mu g\ g^{-1}$ dry weight for Al, Mn and Fe, respectively), were probably associated with human activities that resulting in a large-scale transport of pollutants which contribute to an increase of heavy metal levels (Runcie and Riddle, 2004; Jerez et al., 2011).

The European countries also showed heavy metal pollution events. Kelepertsis et al. (2006) found elevated concentrations of As (125 $\mu g\ l^{-1}$) and Sb (21 $\mu g\ l^{-1}$) in the drinking water of Eastern Thessaly, Greece, where more than 5,000 people drink water containing As and Sb above the USEPA guidelines, while, Jovanovic et al. (2011) found that 63 % of all water samples

exceeded Serbian and European standards for arsenic in drinking water and Cavar et al. (2005) reported that in three villages from eastern Croatia, the mean arsenic concentrations in drinking water samples were 38 μg l^{-1}, 172 μg l^{-1} and 619 μg l^{-1} respectively which could pose a serious health threat to around 3% of Croatian population.

In Oceania continent, where countries such as Australia and New Zealand are situated, the presence of heavy metals in water systems assumes local significance of both natural and anthropogenic origin. Here coal-based power stations contribute considerably to Cu, Ni, Co and Cr pollution (562, 157, 113 and 490 μg g^{-1}, respectively) in fluvial sediments (Birch et al. 2001).

During the past few decades globally riverine ecosystems are polluted with heavy metals released from anthropogenic and terrigenous sources (Alagarsamy and Zhang, 2005). In India, even though industrialization has not reached the level of the developed countries, pollution of aquatic habitats by heavy metals seems to be an inevitable problem. Kerala is one among the most thickly populated regions in the world and the population density is increasing at a rate of 14 % per decade. As a result of the measures to satisfy the needs of huge population, the rivers of Kerala have been increasingly polluted from the industrial and domestic wastes and from the pesticides and fertilizers used in agriculture. As a consequence of agricultural pollution, Nair et al. (2011) found that Fe, Pb and Cd concentrations in some water samples of Meenachil river is above the maximum permissible limits of BIS for drinking purpose which may pose human health risks.

Most of the industries (60 %) in Kerala state are situated at Kochi which includes chemical, engineering, food, drug, paper, rayon, rubber, textiles and plywood industries which is clustered at two zones-one at Eloor on the banks of river Periyar and another at Ambalamughal by the side of

Chitrapuzha which is a tributary of Periyar (Joy et al. 1990). The main polluting chemical industries located at Eloor are Fertilizers and Chemicals Travancore Limited (FACT), Indian Rare Earths Limited (IRE), Hindustan Insecticides Limited (HIL), Periyar Chemicals, United Catalysts, Merchem and Cominco Binani Zinc etc. Similar industrial units located at Ambalamughal are NPK Fertilizer Plant (FACT), Petroleum Refinery (KRL) and Hindustan Organic Chemicals Limited. Another industrial unit located at Piravam on Muvattupuzha River bank is the Hindustan News Print Factory. The effluents of these industries contain large amount of hazardous pollutants like heavy metals, phosphates, sulphides, ammonia, fluorides and insecticides which were discharged into the downstream reaches of the river. The effluents from the industries at Eloor, Ambalamughal and Piravam are discharged into the lower parts of the Periyar, Chitrapuzha and Muvattupuzha rivers are mixed into the northern, central and southern parts of the Vembanad Lake by tides and freshwater flows. Hence, even though the backwaters of Kerala, especially the Vembanad Lake, support as much biological productivity and diversity as tropical rain forests which supports the rich fisheries potential of Kerala are now vulnerable with heavy metal pollution due to the effluent discharges from urban, industrial and agricultural sectors (Nair et al. 1990; Menon et al. 2000). The aquatic life in the Cochin estuarine systems is reported to be severely affected by heavy metal pollution and its subsequent bioaccumulation (Balachandran et al. 2005).

1.6.Review of the literature relevant to the present study

Rivers constitute an important pathway for the transport of continental material to the oceans (Martin and Whitfield, 1983). Rivers are the major sources of dissolved and particulate materials to the oceans and are thereby the primary contributors to the geochemical composition of both ocean water and

marine sediments (Carey et al. 2002). Trace elements of natural and/or anthropogenic origin, including heavy metals, are transported by rivers and transferred to the coastal marine system through estuaries. Among the various contaminants, trace metals are of particular concern due to their environmental persistence, biogeochemical recycling and ecological risks. Heavy metals such as Fe, Zn, and Cu, are essential biological micronutrients required for the growth of many aquatic organisms. These micronutrients can become toxic at high concentrations. Other metals, for example Pb and Cd, are not required for growth and are highly toxic in trace amounts. Therefore, the types and levels of heavy metals that enter into the coastal systems are critically important.

Rivers and estuaries are essentially biogeochemical reactors whose heterogeneous reactions determine the fate and supply of trace metals of continental origin to oceans. Understanding the fate and effect of heavy metal contaminants in these environments is of extreme importance owing to their impact on ecosystem (Forstner and Wittmann, 1983). The conventional paradigm for the behaviour of these reactive materials in freshwater ecosystems was to identify the processes by which dissolved and particulate materials are associated with minerals settling to sediments. The key process to understand metal transport and environmental availability in aquatic systems involves identifying sources and sinks and in quantifying the metal associations within sediments and metal interactions that occur between water, sediments and biota. Because of the dynamic nature of aquatic systems, biogeochemical processes are often complex and their transformations often remain obscure. Trace metals are removed from water by settling particles and by organic matter in the settling process. Metals bound to solid particles are not fixed permanently, but recycled through biogeochemical reactions in response to changes of physical and chemical conditions in the water column

(Davis and Leckie, 1978; Sigg et al. 1987). Turbulent mixing of fresh water (river water), rain water and waste water from anthropogenic sources can generate rapid changes in Eh, pH, hardness and trace element concentrations in these environmental compartments (Forstner, 1981; Poulton and Raiswell, 2000). Since metal adsorption from aqueous solutions depends on adsorbent and adsorbate concentration and on the speciation of metals in solution metal partitioning with water and sediments can change with varying physico-chemical conditions (i.e. with changes in Eh, pH & solute concentrations) and with transport and mixing processes because of addition, dilution or removal of available substrates (Benjamin and Leckie 1981; Oakley et al. 1981; Salomons and Forstner, 1984). Hence, it is difficult to understand the origins, pathways and fates of dissolved and particulate materials in freshwater ecosystems. However the distribution and partitioning of trace metals in rivers and estuaries which are of central interest to the understanding of the global cycling and transport of metals to oceans.

Kerala's fresh water bodies and surface soil are facing gross pollution problems following the release of solid wastes and untreated liquid effluents from industries, domestic and agricultural sectors and are contaminated with trace metals because the state lacks an efficient solid as well as liquid-waste disposal system (Centre for Earth Science Studies, 2012). In 2003, Greenpeace, Germany reported high levels of trace metals deposition in water and sediment samples at the downstream industrial areas of the northern part (Periyar River) of the Cochin backwaters and concluded that Eloor industrial area as one of the most vulnerable industrially polluted "hot spots" in the world. This is as a consequence of human intervention in the Cochin backwaters which dates back from 1836 but has accelerated during the last five decades following rapid urbanization and industrialization. The unplanned

industrial development and economic activities for supporting the needs of increased population (6277 people per km^2) continues to exert an ever growing pressure on the estuarine ecosystem of northern Vembanad Lake by adding loads of contaminants. As a result, Cochin backwaters (northern Vembanad Lake) is regarded as one of the vulnerable ecosystems in India, which is presently undergoing environmental deterioration due to increased anthropogenic activities following the uncontrolled discharge of pollutants from both diffuse and point sources (Menon et al. 2000). But the real sources responsible for trace metal pollution of this region are not fully understood. Rivers, streams, land run-off, urban wastes, agricultural wastes, industrial discharges, and atmospheric wet and dry depositions can be all sources of pollutants to the Vembanad Lake. Since the real contribution of trace metal pollutants or other contaminants from the rivers discharging into Vembanad Lake catchments is seldom known, pollution monitoring studies on a regular basis across the lake and its catchments is necessary to make an accurate assessment of the status of pollution, to identify the point and non-point sources of pollutants and take remedial measures for mitigating the adverse impacts of these pollutants on the lake's ecosystem.

Geochemical assessment of trace metal enrichment in aquatic sediments is an important component in understanding environmental pollution and its impact on the ecosystem (Forstner and Wittmann, 1983). Sediments are major repositories for trace metals and besides providing the environmental status; they are also used to estimate the level of pollution in a region (Burton Jr. and Scott, 1992). Bottom sediments are recognized as long-term integrators of geochemical processes and hence information on elemental distribution pattern from sediments can establish its sources, the long-term behaviour of trace metals, anthropogenic impact and environmental status in

both rivers and coastal ecosystems (Alagarsamy and Zhang, 2005; Alagarsamy, 2006; Alagarsamy and Zhang, 2010). In the southwest coast of India, during the past few decades, there has undergone a considerable number of research efforts to identify the sources and sinks of heavy metals in downstream parts of rivers, estuaries and near shore environments (Murty et al., 1973; Murty and Veeryya, 1981; Venugopal et al., 1982; Shankar et al., 1987; Nair et al., 1990; Paropkari, 1990; Ouseph, 1992; Padmalal and Seralathan, 1993; 1995; Manjunatha and Shankar, 1997; Padmalal et al., 1997). Quite, recently research interest has gained in anthropogenic contamination issues of hydrosphere by heavy metals which magnified the urgency of elucidating the biogeochemical cycles of toxic metals in rivers, estuaries and coastal ecosystems. Although there are indications that the Vembanad Lake has become increasingly contaminated with trace metals in the past 24 years the available data are restricted to localized northern parts of the estuary which are affected by industrial discharges and hence lack spatial resolution (Balachandran et al. 2005). Similar studies also noted that the magnitude of trace metal pollution in sediments of the Cochin backwaters has been increasing over the last few decades and was regarded as a product of anthropogenic contamination from domestic, agricultural and industrial sources (Selvam et al. 2011; Martin et al. 2012). There is need to expand the spatial and temporal coverage of sediment samplings in the Vembanad Lake catchments to better understand the transport and fate of trace metal contaminants and their potential ecosystem impacts for management purposes. An integrated geochemical study incorporating trace metal composition of riverine, estuarine and nearshore shelf environments of Vembanad Lake has not been carried out so far in this area.

From the literature survey it is clear that even though some studies are available on the distribution of trace metals in sediments of the northern Vembanad Lake or Cochin backwaters, information regarding their behaviour in water, suspended particulate matter and sediments from the upper reaches of the Muvattupuzha River basin is extremely scarce. In view of this, the upstream part of Muvattupuzha River basin is selected for trace metal distribution study in water, suspended particulate matter and sediments. The aim of the present study was to evaluate the distribution, potential seasonal variations and partitioning of heavy metals in this river system, focusing on their distribution in both the dissolved and particulate phases and various sedimentary phases. In this concern, the hydrological parameters in water column (temperature, pH & dissolved oxygen), sedimentary parameters (texture & organic carbon) and the concentrations of trace metals (Cd, Cu, Ni, Zn, Pb, Cr, Co, Fe, & Mn) in water, suspended particulate matter and sediments were determined at 18 sampling stations within the upstream freshwater zone of the Muvattupuzha River during the 6 samplings (July 2005 – May 2006), at bimonthly intervals.

1.7. Scope of the present study

Muvattupuzha River is one of the major perennial rivers in Central Kerala with a length of about 121 km , catchment area of 1554 km^2, annual sediment load input of 1,57,000 tonnes and an annual run-off 4780 million m^3 of fresh water. The drainage basin of the river supports a majority of population located on its banks for serving domestic, irrigational and agricultural purposes over Idukki, Ernakulam and Kottayam districts. The hinterlands of the Muvattupuzha River are predominantly an agricultural area with the staple crops of rubber, paddy and coconut. The agricultural areas and urban township located on the upper river banks of Muvattupuzha discharge

untreated agricultural and domestic effluents into the river. In this context a thorough study on the various environmental quality parameters (water & sediment quality) of this area is of utmost concern for an accurate assessment of the environmental impact of anthropogenic activities on an otherwise pristine environment.

Heavy metals enter into the aquatic environments of the Vembanad Lake through natural sources such as weathering of rocks and soil in the catchments and anthropogenic sources like agricultural, municipal, domestic, and industrial wastes. Since Muvattupuzha River acts as a major source of fresh water (24.2 %) that debouch into the Vembanad Lake near Vaikom, it is also expected to carry a pollution load of materials enriched with trace metals from urban townships and agricultural areas. The heavy metal distribution in the Muvattupuzha River may be considerably influenced by the tropical features of the basin like high rates of chemical weathering and by various human activities like agricultural run-off, domestic waste release, irrigation, deforestation, construction of dams and reservoirs, inter-basin water transfer etc. in localized areas which may led to a disbalanced transport of metals in various phases (dissolved phase, particulate phase & various sedimentary phases). Even though several references are available on the distribution of heavy metals in the Cochin backwaters, information regarding the same from the adjoining upper reaches of Muvattupuzha River is woefully lacking. No systematic study has been conducted on the upper freshwater zone of this river to assess the distribution or reactivity of trace metals in water, suspended particulate matter and sediments. Hence the broad scope of this study includes a detailed characterisation of distribution and partitioning of trace metals in order to understand its bio-geochemical cycling and transport by assessing its concentration in the environmental compartments like water, suspended

particulate matter and sediments from the upstream areas of the Muvattupuzha River. Moreover, the assessment of trace metal fractionation in sediments in both the mobile and bound phases of the Muvattupuzha River is environmentally significant since it helps to determine the eco-toxicological potential of these metals.

1.8. Objectives of the present study

The major objectives of the present investigation were four fold:

1. To study the hydrography and sediment characteristics of the Muvattupuzha River.
2. To find the trace metal distribution in dissolved and particulate phases of the Muvattupuzha River.
3. To quantify the total trace metal enrichment in surficial sediments of the Muvattupuzha River.
4. To assess the trace metal fractionation in surficial sediments of the Muvattupuzha River.

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Chapter 2

MATERIALS AND METHODS

2.1. Description of the study area

The Muvattupuzha River lies between north latitudes 9°45' – 10°05' N and east longitudes 76°22' – 76°50' E and confluences with three major tributaries namely Thodupuzha River, Kaliyar River and Kothamangalam River near Muvattupuzha town which debouches into the northern Vembanad Lake near Vaikom. Muvattupuzha River is one of the major perennial rivers in Central Kerala with a length of about 121 km and a catchment area of 1554 km^2. The river originates from the Taragamkanam Hills of the Westen Ghats and drains mainly through highly lateritized crystalline rocks. The drainage basin of the river spreads over Idukki, Ernakulam and Kottayam districts of Central Kerala. After flowing as a single stream upto Vettukattumukku, the river branches into two distributaries namely Ittupuzha and Murinjapuzha. The river exhibits dendritic drainage pattern. The river discharge ranges from 50 m^3/sec (pre-monsoon) to 400 m^3 /sec (monsoon). Peak discharge is recorded during June to October. Considerable changes have taken place in the flow characteristics of the Muvattupuzha River after the commissioning of the Idukki hydroelectric project in 1976, across the adjoining Periyar River. The tail-race water (19.83-78.5 m^3/sec) was directed into the Thodupuzha tributary from Moolamattom power station. This tail-race water with an almost constant

flow together with surface run off even though have not only altered the morphological characteristics considerably but influenced the sediment dynamics and ecological habitat of the river basin as well. The Muvattupuzha River annually transports 1, 57,000 tonnes of sediments and 4780 million m^3 of fresh water into the Vembanad Lake (Milliman and Syvitski, 1992).

The area has a tropical humid climate with a temperature variation of 20 to 39°C and the average annual rainfall is 3000 mm (Soman, 1997). Among the various meteorological parameters, rainfall is the most difficult to predict due to its inherent variability in time and space (Guenni and Hutchinson, 1998). The rainy season here extends from the months of June to November (*Figures* 2.2.1. and 2.2.2.). Southwest monsoon sets up in June and till lasts towards September with the heaviest rainfall during the months of June to September. The northeast monsoon strikes in October and continues till November and may also extend to December. Of the total rainfall, southwest monsoon contributes about ~ 75% and the remaining by northeast monsoon and summer showers (*Table 2.1.1*). Due to its peculiar climatology the river basin supports a wide range of vegetation.

Table 2.1.1. Monthly rainfall (mm) of Idukki and Ernakulam districts during the June 2005 to May 2006

District	Jun 2005	July 2005	Aug 2005	Sep 2005	Oct 2005	Nov 2005	Dec 2005	Jan 2006	Feb 2006	Mar 2006	April 2006	May 2006	Annual
Idukki	840.5	820.2	355.3	472.8	279.0	193.1	20.4	12.7	0.0	62.0	42.9	622.5	3401.9
Ernakulam	787.0	1986.0	636.0	968.5	369.4	250.1	113.9	10.3	0.0	138.3	135.2	651.1	5707.0
Average	813.8	1403.1	495.7	720.7	324.2	221.6	67.2	11.5	0.0	100.2	89.1	636.8	4554.5

2.2. Sampling sites

The land use patterns and the location of sampling sites are depicted in *Figure*s 2.2.1. and 2.2.2. respectively. The highlands consist of agricultural land, wasteland and forest land. The forest area occupies nearly 50 % of the highlands which consists of deciduous forests, evergreen forests and degraded forests. The eastern side of the highlands is covered by the Thodupuzha reserved forests. Teak plantations are identified in the forest fringes. Arakulam reserved forest is in the uplands of the Thodupuzha River. Small patches of grasslands are seen in this area. Tenkondam reserved forest constitutes a small portion in the uplands of Kaliyar tributary. Patches of dense mixed jungle is seen in the lower part of the area. Rocky cliffs and escarpments are other features in the highlands. Nearly 40 % of the area is classified as mixed crops with settlements. Rest of the area is land with or without scrub. The midlands consists of agricultural and wastelands. The upper part of the midlands is dominated by rubber plantations, which in turn, intermingled with mixed crops and settlements. Reserved forests like Nedumala, Ezhallur and Maniyandram are seen as small pockets in areas between Thodupuzha and Kaliyar Rivers. Open scrub are also seen as patches in the upper region. The wasteland, which occupies only 2 % of the total area, is land with or without scrub. The downstream areas are characterized by valleys and floodplains and are usually flooded during monsoon season. The lowlands consist of agricultural land, wasteland, built up land and water bodies. Nearly 35% of the region is under mixed agricultural / horticultural plantations and about 15% under double cropped paddy cultivation. Built up land occupies nearly 5% in the region. Fallow land covers nearly 8% and sandy area about 2%. The rest of the area is covered by water bodies.

Considering the specific geographical features, water flow regimes and anthropogenic activities, 18 representative stations were identified in the upstream of the Muvattupuzha River after a preliminary survey for the whole study. The sampling site *(Table 2.1.2.*) starts from the downstream point at Piravam (Station 1) to the far away upstream point at Moolamattam (Station16). Station 1 is located at Piravam where sand mining is predominant. Stations 2, 3 and 4 are located nearby agricultural lands at Mamalassery, Ramangalam and Thammanimattom where sand mining is predominant. Station 5 is located at Peruvammoozhi where nearby burned bricks wastes are disposed. Station 6 is located at Ooramana which is nearby agricultural lands. Station 7 is located at Kayanadu which is nearby a check dam for Muvattupuzha Town. Station 8 is located at the Muvattupuzha-Triveni-Sangamam confluence of three rivers (Thodupuzha, Kaliar & Kothamangalam). Station 9 is located at Arakkuzhamoozhi which is nearby Arakkuzha Town. Station 10 is located at Arikkuzha which is nearby agricultural lands. Station 11 is located nearby the municipal Town Thodupuzha. Station 12 is located at Emaralla which is nearby Thodupuzha. Station 13 is located nearby Malankara dam outlet. Station 14 is located nearby Malankara dam which is used for irrigation purposes. Station 15 is located nearby Moolamattom Mini Township colony. Station 16 is located at Arakkulam which is nearby Idukki dam tunnel phase outlet. Station 17 is located at Perumattom which is at the lower reaches of Kothamangalam Puzha. Station 18 is located at Karimattom which is at the lower reaches of Kaliyar Puzha. Both the stations 17 and 18 are adjacent to Thrivani Sangamam and surrounded by agricultural lands.

Table 2.1.2. Latitude and Longitude of sampling stations

Station Number	Sampling Stations	Longitude	Latitude
S1	Piravam	76° 28' 52.448" E	9° 52' 9.493" N
S2	Mamalassery	76° 28' 19.242" E	9° 54' 48.162" N
S3	Ramangalam	76° 28' 20.316" E	9° 56' 11.558" N
S4	Thammanimattom	76° 29' 13.835" E	9° 57' 5.177" N
S5	Peruvammoozhi	76° 30' 29.893" E	9° 58' 14.745" N
S6	Ooramana	76° 31' 45.978" E	9° 57' 36.079" N
S7	Kayanadu	76° 32' 39.146" E	9° 57' 12.532" N
S8	Movattupuzha Triveni Sangamam	76° 35' 2.787" E	9° 59' 1.120" N
S9	Arakkuzha Moozhi	76° 36' 1.426" E	9° 55' 54.426" N
S10	Arikkuzha	76° 38' 24.765" E	9° 54' 56.773" N
S11	Thodupuzha	76° 42' 20.545" E	9° 54' 4.336" N
S12	Emaralla	76° 43' 37.119" E	9° 51' 47.767" N
S13	Malankara Dam outlet	76° 44' 29.666" E	9° 51' 11.769" N
S14	Malankara Dam	76° 46' 54.838" E	9° 49' 38.848" N
S15	Moolamattom	76° 48' 29.674" E	9° 49' 5.725" N
S16	Arakkulam	76° 49' 9.732" E	9° 48' 40.140" N
S17	Perumattom	76° 35' 58.809" E	9° 59' 37.130" N
S18	Karimattom	76° 36' 21.726" E	9° 59' 34.948" N

2.3. Sampling and Method of Analysis

Surface water and surficial sediment samples were collected at bimonthly intervals from the Muvattupuzha River at eighteen stations during the period of July 2005 to May 2006. Water samples were collected using a 5-litre Niskin water sampler and transferred to 5-litre acid cleaned polythene carboys (Grasshoff et al. 1999). Water samples meant for metal analysis were filtered through pre-weighed and acid washed 0.45 µm membrane (Millipore) filters to separate them into dissolved and particulate fractions. The filtered water samples were stored in 2.5 litre acid cleaned polythene carboys after

acidifying with pure 6N HCl (Merck) to pH 3-4. Filters containing suspended particulate matter were placed in a plastic petridish, dried, weighed and stored in a vacuum dessicator.

Sediment samples were collected using a stainless steel, plastic lined Van Veen Grab. At each station, 2 to 3 grabs of sediments were sampled and the top 5 cm layer was carefully skimmed from all the grabs using a plastic scoop, homogenised, and collected in polyethylene bags. The sediment samples were stored in a deep freezer at -20°C till analyses were performed.

2.3.1. Dissolved trace metals

Owing to extremely low concentrations of trace elements, particularly transition metals in river water, it is often necessary to pre-concentrate them prior to their determination by Atomic Absorption Spectrophotometer. Dissolved metals were pre-concentrated using solvent extraction of the chelates formed with a mixture of complexones (Ammonium Pyrrolidine Dithiocarbamate (APDC) and Diethylammonium Diethyl Dithio Carbamate (DDDC) into chloroform, followed by back-extraction into nitric acid (Danielsson et al. 1978, 1982). Metal estimations were carried out on the concentrates by an Atomic Absorption Spectrophotometer after calibration using E-Merck standard solutions. Analytical blanks were prepared using the same procedures and reagents.

2.3.2. Particulate trace metals

Filters containing suspended particulate matter and blank filters were treated with a mixture of (1ml each) concentrated perchloric acid and concentrated nitric acid (Merck, suprapure) and evaporated to dryness. The residue after cooling was dissolved and diluted to 25 ml with 1N HNO_3 and transferred to 60ml screw capped polythene bottle. This solution containing

the particulate trace metals was stored in a refrigerator until their analysis in an Atomic Absorption Spectrophotometer.

2.3.3. Total trace metals in sediments

The total metals in sediments were extracted from the air dried and finely powdered sediment samples using an acid digestion technique in a Teflon beaker (Loring and Rantala, 1977, 1992). 1.0 g of sediment samples was treated with 5ml HF and 2ml $HClO_4$ and heated on a hot plate to almost dryness. The residue obtained was further treated with 5 ml $HClO_4$ and then with 5ml HNO_3 and heated upto dryness. The clear residue obtained was finally cooled and made to 25 ml using 1:1 HCl solution and were transferred to 60ml screw capped polythene bottles. This solution was kept in a refrigerator until their trace metal analysis in an Atomic Absorption Spectrophotometer.

2.3.4. Trace metal speciation in sediments

The air dried sediment samples were sieved to obtain 75 µm sediment fractions. The sequential extraction technique proposed by Tessier et al. (1979) was followed for the partitioning of trace metals into the following five fractions:

2.3.4.1. Exchangeable

1g sediment sample was extracted at room temperature for 1 hour with 10 ml of 1M $MgCl_2$ (pH 7.0) with continuous agitation.

2.3.4.2. Bound to carbonates

The residue obtained from the above step was leached at room temperature with 10 ml of 1M sodium acetate adjusted to pH 5.0 with acetic acid. The mixture was agitated for 5 hours.

2.3.4.3. Bound to Fe-Mn oxides

The residue obtained from the above step was refluxed at 100°C with 20ml of 0.04M hydroxylamine hydrochloride in 25% acetic acid for 6 hours.

2.3.4.4. Bound to organic matter

To the residue obtained from the above step, 3 ml of 0.02M nitric acid and 5ml of 30% hydrogen peroxide were added and pH was adjusted to 2.0 with nitric acid. The mixture was refluxed at 100°C for 2 hours. Again a second 3ml of 30% hydrogen peroxide were added and pH was adjusted to 2.0 with nitric acid. The mixture was again refluxed at 100°C for 3 hours. After cooling, 5ml of 3.2M ammonium acetate in 20% nitric acid was added. The sample was diluted to 100ml and agitated continuously for 30 minutes.

2.3.4.5. Residual

The residue obtained from the above step was digested with a HF-$HClO_4$-HNO_3 mixture in a Teflon beaker (Loring and Rantala, 1977, 1992).

Total metal concentrations in sediments and metal ion concentrations in different extracts of sediments were determined using a Perkin–Elmer Flame Atomic Absorption Spectrophotometer (Model 3110) using an air-acetylene flame. Quantification of metals was based upon calibration curves of standard solutions of respective metals.

2.3.5. Temperature, pH, dissolved oxygen and chlorinity

Temperature of water was measured *insitu* using a sensitive centigrade thermometer with a graduation of 0 – 50 ^{o}C.

pH of water was measured *insitu* using a portable pH meter (*Systronics*) with an accuracy of ± 0.1 pH units after calibration with standard pH buffers of pH 7.0 and 9.2.

The dissolved oxygen was estimated by Winkler's method as described in Grasshoff et al. (1999). In the dissolved oxygen estimation, the water sample (60ml) is allowed to react with (0.5 ml each) Winkler A (manganese chloride) and Winkler B (alkaline potassium iodide) respectively. The precipitated manganese hydroxide is acidified (with 50% HCl) and the liberated iodine is titrated against standard sodium thiosulfate solution using starch as the indicator.

Chloride content in water is estimated by titrating with standard silver nitrate solution using potassium chromate as indicator (Mohr-Knudsen method). The end point is the appearance of a permanent reddish tinge.

2.3.6. Chemical Oxygen Demand

Chemical Oxygen Demand (COD) in water samples is determined by heating with excess potassium dichromate solution in concentrated sulphuric acid solution for two hours and titrating with standard ferrous ammonium sulphate using ferroin as an indicator. At the end point when all the excess potassium dichromate has been reduced the colour of indicator changes from blue-green to reddish-brown. The amount of dichromate consumed is calculated and the oxidisable organic matter is reported in terms of oxygen equivalents.

2.3.7. Sediment texture

Sediment texture was analysed by the method of pipette analysis (Krumbein and Pettijohn, 1938). 10 g of dried sediment was taken in a beaker and is added with 7.5 g of sodium hexametaphosphate and 200 ml of distilled

water which is kept overnight. Next day the sample was stirred up using a glass rod and sieved through 63 µm-mesh sized sieve into a 1000 ml measuring cylinder. The residue retrieved in the sieve will be sand. It is transferred into a glass petridish of known weight to find the weight of the sand portion. From this the percentage of sand in sediments can be determined.

The filtered portion collected in the measuring cylinder was made up to 1000 ml by adding distilled water and is stirred well using a hand stirrer for two hours and two minutes. Now 20 ml of the sample from 10 cm depth of the cylinder was taken using a pipette and is poured into a small glass beaker of known weight. Dry the beaker in an oven and weigh it to find out the weight of the material in the beaker. From this the percentage of clay can be determined. From the percentage amounts of sand and clay, the percentage amount of silt can be determined.

2.3.8. Organic Carbon

Sediment organic carbon was estimated on dried sediments by the procedure of El Wakeel and Riley (1957) modified by Gaudette et at. (1974). In a test tube 0.2 g of the cleaned powdered sediment sample was taken and 10 ml of chromic acid was added. The test tubes were shaken well and heated in a water bath for 2 hrs until the sample was digested and then poured the content into a conical flask containing 200 ml of distilled water. To this 2 drops of Ferrous phenanthroline indicator was added and titrated against 0.2 N ferrous ammonium sulphate. The end point was the appearance of a brick red colour. A blank determination was carried out in the same manner using 10 ml of chromic acid.

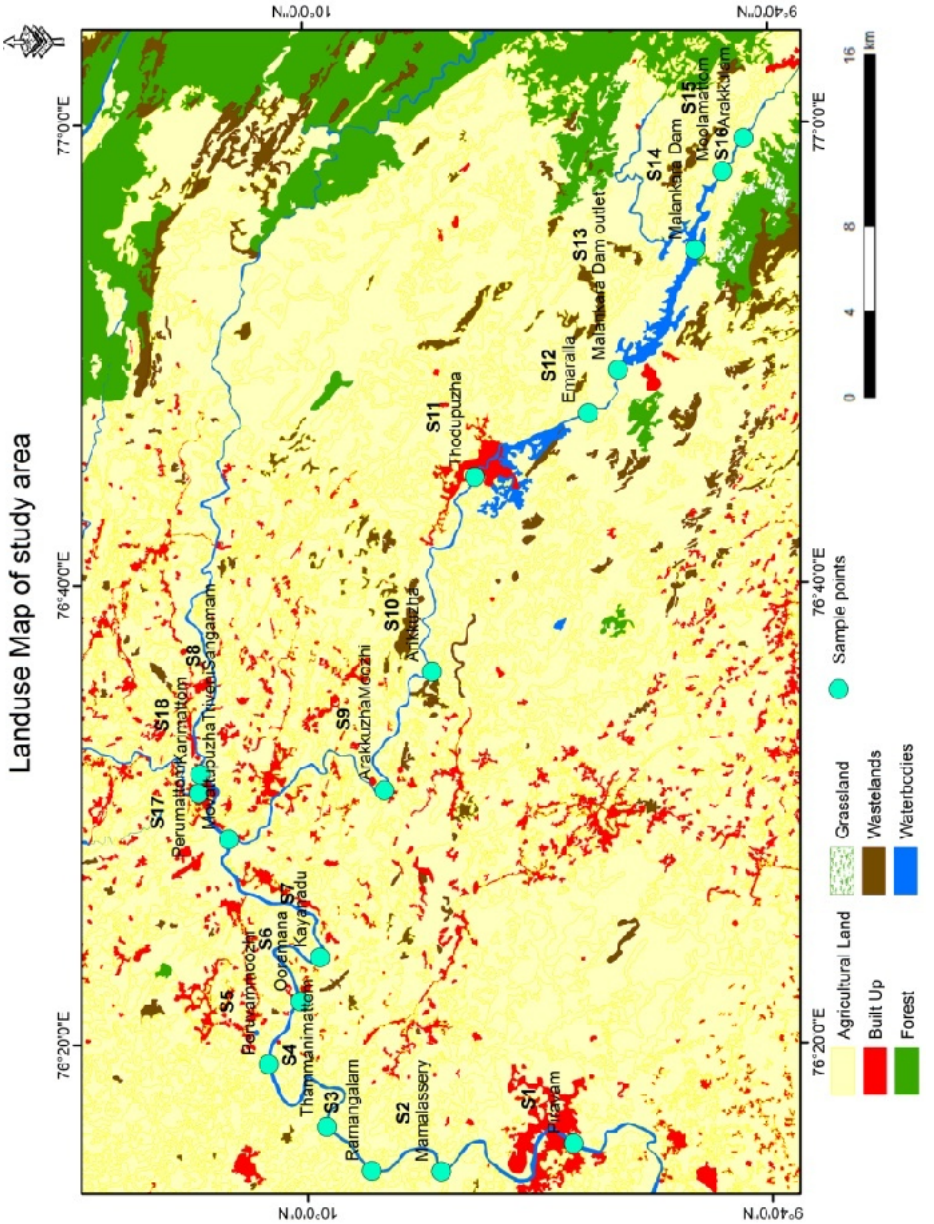

Figure 2.2.1. Land use patterns near Muvattupuzha River Basin

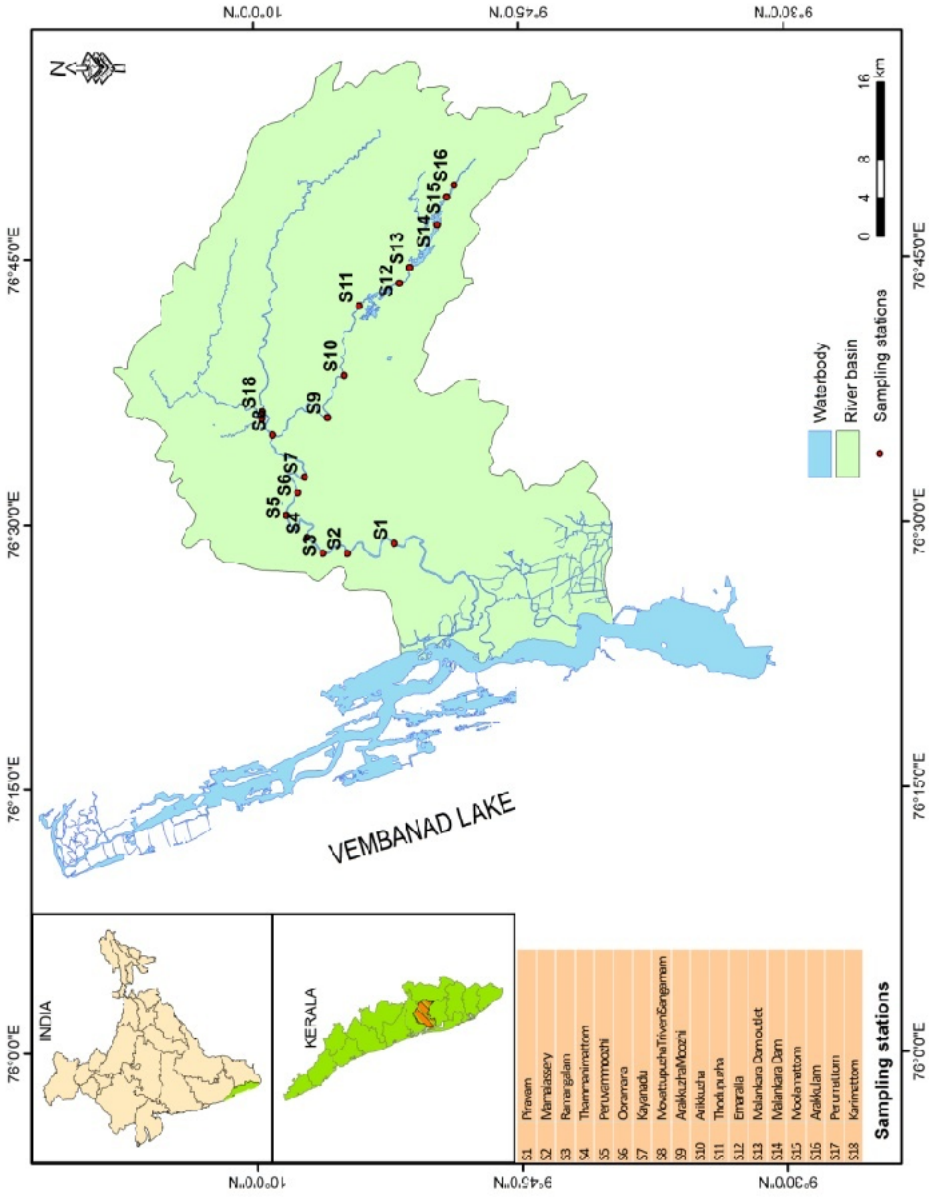

Figure 2.2.2. Map of the study area with station locations

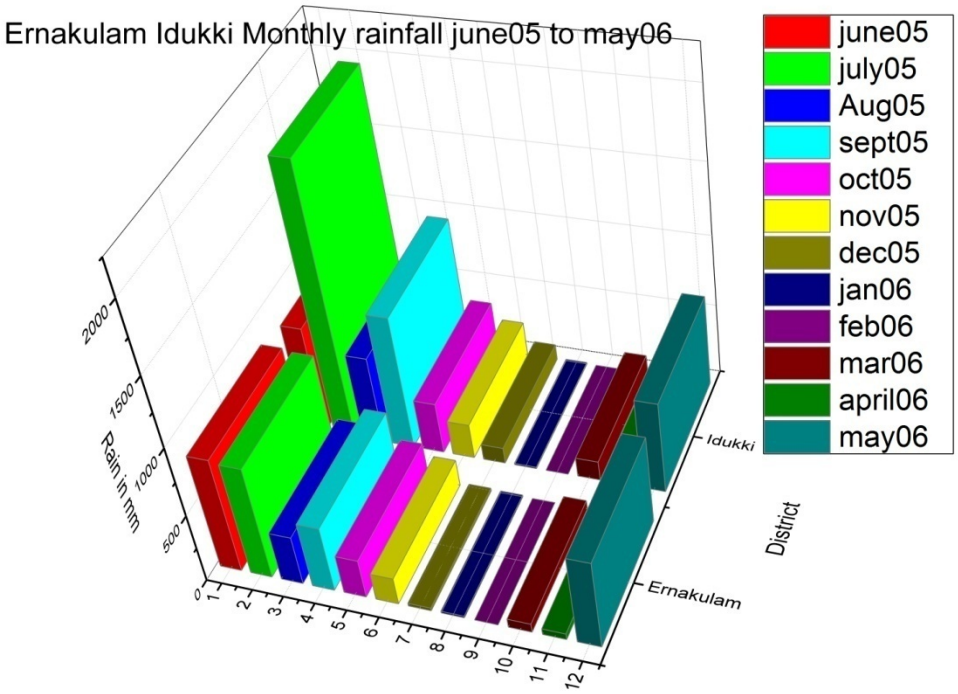

Figure 2.2.3. Monthly rainfall (mm) in Idukki and Ernakulam districts during June 2005 to May 2006

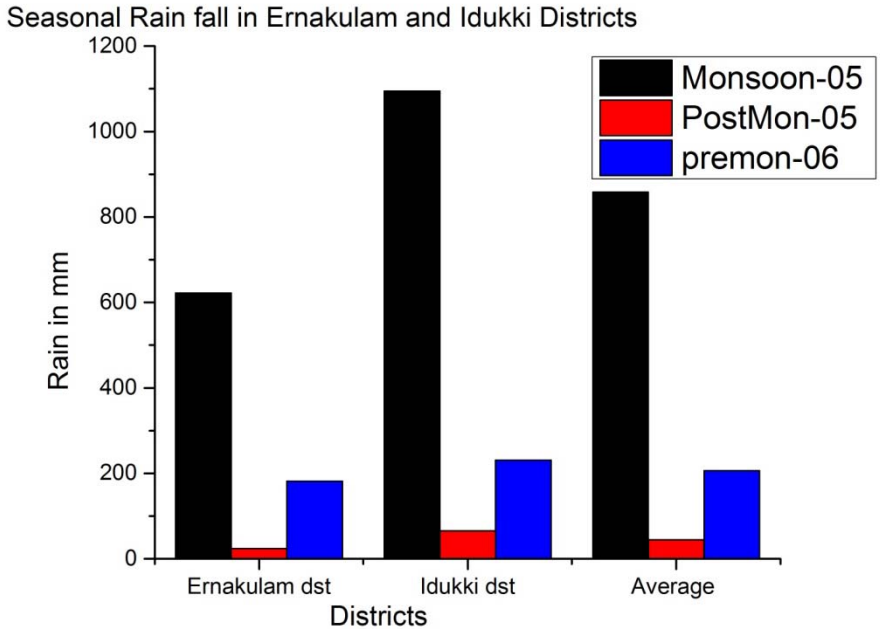

Figure 2.2.4. Seasonal rainfall (mm) in Idukki and Ernakulam districts during June 2005 to May 2006

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Chapter 3

HYDROGRAPHY AND SEDIMENT CHARACTERISTICS OF THE MUVATTUPUZHA RIVER

3.1. Introduction

Fresh water resources are an essential component of earth's hydrosphere and of all ecosystems. Rivers are an important part of earth's water cycle. They play an efficient and prominent role in sculpting earth's topography by carrying huge quantities of water and sediments from land to the sea. The influence of hydrographical parameters on the chemistry of heavy metal speciation in water and sediments of rivers, estuaries and oceans has been of a major environmental concern during the last few decades (Bardarudeen et al. 1996; Salomons and Forstner, 1984; Sankar et al. 2010). The hydrographic conditions of the Muvattupuzha River depend on the influx of fresh water, precipitation/evaporation processes, weathering etc. Sediment characteristics in this river are influenced by pH, redox potential, grain size and also by hydrography of the overlying waters (Purandara, 2008). The Muvattupuzha River discharges into the southern-central part of the Cochin backwater system and hence plays an active role on the prevailing hydrography and particle sedimentation of the northern Vembanad Lake (Balchand and Nair, 1994; Priju and Narayana, 2007).

Trace metals are transported to oceans through estuaries in dissolved and particulate forms by rivers (Salomons and Forstner, 1984). Rivers carry trace metals in dissolved and particulate forms from their source and deposit them sequentially based on their physico-chemical nature at different locations (Kim et al. 1996; Hunter et al. 1999). Thus, the variations in hydrographical parameters like pH, alkalinity, temperature, dissolved oxygen etc. affect the nature of suspended particulate matter and particle concentration in rivers and will determine the transport mechanisms of dissolved and particulate components of trace metals (Bourg et al. 2000).

Sediments are heterogeneous mixtures of dissimilar particles with varying size, composition and origin where each particle has a complex assemblage of inorganic and organic components such as silicates, amorphous oxides, carbonates, organic matter etc. Sediments are thus an integral part of biogeochemical cycle of trace metal contaminants which acting as source, sink and transformation centre (Salomons and Forstner, 1984). Sediments serve as natural buffers and form an important habitat as well as a main nutrient source for aquatic life which have an influence on the overall status of a water body with impact on ecological quality and of well being of living resources (Abhilash et al. 2012). Since sediments act as a reservoir for contaminants in aquatic systems they are a primary source of contaminant exposure for sediment-dwelling organisms and animals that feed on the bottom (Martin et al. 2011). This exposure can produce deleterious impacts on benthic communities which lead to indirect effects due to bioaccumulation.

Estimation of anthropogenic impact on sedimentary composition is pivotal for environmental monitoring studies as sediments are sensitive and reliable recorders of both natural and anthropogenic interferences. The textural characteristics of sediments play a significant role in the chemical and

biological characteristics of an aquatic environment (Hakanson and Jansson, 1983; Nair et al. 1993). Sediments act as a sink and play a vital role in determining the quality of the overlying water column and hence are useful in the assessment of environmental pollution (Remani et al. 1980; Saraladevi et al. 1992). Sediment quality monitoring is thus considered as vital to evaluate the extent of contamination and pollution histories within riverine, estuarine, coastal and shelf regions globally (Hakanson and Jansson, 1983).

Knowledge on the textural characteristics in sediments is of great importance in identifying various depositional micro environments for organic and inorganic contaminants like trace metals in rivers (Sobha et al. 2008). Environmental studies related to erosion and organic pollution assessment in rivers involves a measurement of grain size and organic carbon accumulation in sediments (Sharma and Kaur, 1997). Trace metal concentrations in sediments vary largely with grain-size, organic carbon content and sources of anthropogenic inputs (Padmalal et al. 1997).

The quality and quantity of surface water in rivers are influenced by natural factors such as rainfall, temperature and weathering of rocks and anthropogenic changes that curtail the natural flow or alter its hydrochemistry. During the last few decades, rapid industrialization, agricultural practices, urbanization, population growth and change in land use pattern have directly influenced the riverine ecosystems of Kerala in general and contributed to deterioration in water quality. In central Kerala, most of the industrial conglomerates and urban areas are being located along the river basins discharge their wastes into the river streams. In addition, application of pesticides and chemical fertilizers in agricultural fields, urban runoffs and atmospheric depositions also contribute to the pollution of water bodies. Anthropogenic activities such as mining of sand, discharge of domestic,

industrial and agricultural effluents have caused environmental pollution problems and affected water quality and sediment characteristics of the Muvattupuzha River (Padmalal et al. 2008; Joseph and Shanthi, 2009). Since sedimentary environment directly influences the physico-chemical and ecological characteristics of aquatic resources a deteriorated sediment quality may severely impact the supports that sustain aquatic life and the surrounding ecosystem which also includes human beings dependent on it (Kavitha and Kumar, 2013). Situated in a hydrographically and physiographically unique locality, monitoring of the water quality and sediment characteristics of this area provides ample scope to create a threshold data base since how anthropogenic activities affects the water quality or sediment texture from the upstream parts of this riverine ecosystem is seldom known. This chapter presents the results of the bimonthly investigations on hydrography (pH, temperature, dissolved oxygen, chemical oxygen demand (COD) & chloride contents) of the water column and sediment characteristics (sand, slit, clay & organic carbon contents) at 18 stations from the upstream regions of the Muvattupuzha River.

RESULTS AND DISCUSSION

3.2. Hydrography of the water column

The spatial and bimonthly variations of pH, Temperature, Dissolved Oxygen, Chemical Oxygen Demand (COD) and Chloride content in the water column at 18 stations from the upstream regions of the Muvattupuzha River are given in Annexure as *Tables A3.1.0. to A3.1.5*. The bimonthly mean values and standard deviations of pH, Temperature, Dissolved Oxygen, Chemical Oxygen Demand (COD) and Chloride content in the water column at 18 stations from the upstream regions of the Muvattupuzha River is given in

Table 3.2.2. In order to describe seasonal variations of pH, Temperature, Dissolved Oxygen, Chemical Oxygen Demand (COD) and Chloride content in the water column, mean values calculated for the respective two months of monsoon (July/September), post-monsoon (November/January) and pre-monsoon (March/May) periods were plotted and are shown in *Figures 3.1.1.* to *3.1.5.* respectively.

Table 3.2.2. Bimonthly mean values and standard deviations of pH, Temperature, Dissolved Oxygen, Chloride and Chemical Oxygen Demand in the water column of the Muvattupuzha River

Month	pH	Temperature (°C)	Dissolved Oxygen (mg/l)	Chloride (mg/l)	COD (mg/l)
July 2005	7.00 ± 0.21	26.0 ± 1.3	9.53 ± 0.87	10.16 ± 2.25	33.17 ± 13.59
September 2005	7.36 ± 0.18	25.4 ± 1.3	9.54 ± 1.14	7.36 ± 1.40	123.49 ± 65.90
November 2005	6.96 ± 0.20	26.2 ± 1.6	8.18 ± 0.76	11.46 ± 2.10	15.71 ± 8.40
January 2006	7.11 ± 0.24	28.5 ± 1.6	6.52 ± 0.36	12.82 ± 8.99	8.82 ± 5.22
March 2006	7.00 ± 0.09	30.5 ± 2.0	5.76 ± 0.34	14.32 ± 5.91	60.22 ± 25.90
May 2006	7.05 ± 0.19	31.4 ± 1.3	6.33 ± 0.36	25.33 ± 14.30	32.85 ± 20.60

3.2.1. pH

In natural aquatic systems most of the metabolic activities of organisms are pH dependent. The pH value measurement of freshwater systems is an important index of water quality which enables to identify the zones of pollution regarding the acidic or alkaline discharges in watershed areas (Chang, 2008). pH values in rivers are affected by the nature of dissolved material and by the chemical and biochemical processes.

Various factors like photosynthetic activity of phytoplankton, discharge of fresh water from Idukki dam, discharge of effluents from domestic, agricultural and industrial sources, salt-water intrusion from Cochin backwaters and presence of high amount of laterite soils in the river catchments can alter the pH of the Muvattupuzha River waters (Gopinath, 2003). pH value in the water

column varies from 6.52 to 7.56 during the July 2005 to May 2006. pH in the water column averages to 7.00 ± 0.21, 7.36 ± 0.18, 6.96 ± 0.20, 7.11 ± 0.24, 7.00 ± 0.09 and 7.05 ± 0.19 respectively during the July, September, November, January, March and May months. The average pH value in the Muvattupuzha River does not exhibit considerable seasonal trends (*Figure 3.1.1.*). The bimonthly variation of pH values at most sites exceed 7.00 which are slightly higher than the pure water probably due the discharge of terrestrial runoff. Balachand (1983) also reported the similar alkaline nature of the Muvattupuzha River waters from the downstream areas which were affected by industrial pollution. The pH value ranges of 6.52 to 7.56 obtained during the present study is within the pH value ranges of 6.5 to 8.5 reported for drinking water quality guidelines as per suggested by BIS (1991) and WHO (1993).

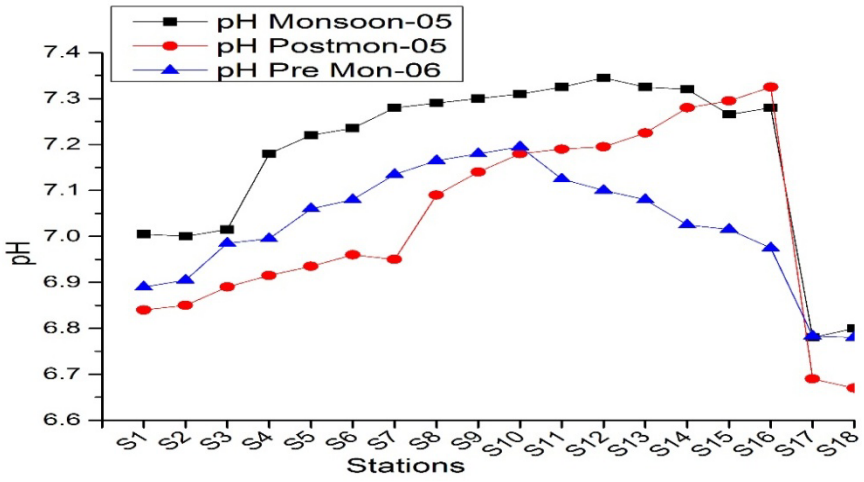


Figure 3.1.1. Seasonal variations of pH in the water column of the Muvattupuzha River

3.2.2. Temperature

The temperature variation in the hydrosphere depends on the changing climatic conditions which results in characteristic patterns of water column circulation that greatly influences the aquatic life because of wide range of temperature tolerances for various organisms (Pauly and Christensen, 1995).

Water temperature fluctuations affect the biological productivity of ecosystems through its influence upon metabolic processes, physiological functions in organisms and are considered as an ecologically significant factor on which the spawning in fishes depends (Petchey et al. 1999; Rose, 2000).

Temperature in the water column varies from 23.9 to 33.2°C during the July 2005 to May 2006. Temperature in the water column averages to 26.0 ± 1.3°C, 25.4 ± 1.3°C, 26.2 ± 1.6°C, 28.5 ± 1.6 °C, 30.5 ± 2.0°C and 31.4 ± 1.3°C respectively during the July, September, November, January, March and May months. The seasonal average temperature values showed relatively colder waters persist during monsoon months and post-monsoon months whereas relatively warmer waters persist during pre-monsoon months in the Muvattupuzha River (*Figure 3.1.2.*). The persistence of relatively colder waters during the monsoon and post-monsoon months is attributed to relatively colder atmosphere and high rainfall in the study region. Balachand (1983) also reported a similar strong seasonality in temperature with low values in monsoon than post-monsoon or pre-monsoon periods of the Muvattupuzha River waters from the downstream areas which were affected by industrial pollution.

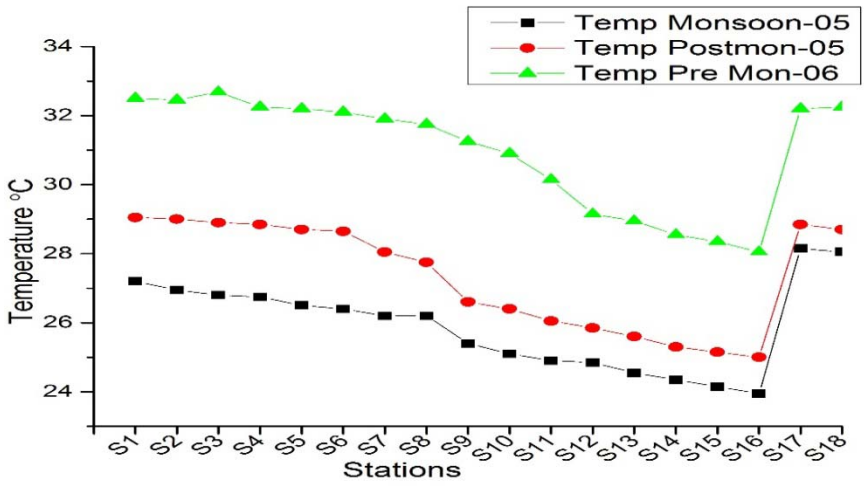


Figure 3.1.2. Seasonal variations of Temperature (°C) in the water column of the Muvattupuzha River

3.2.3. Dissolved Oxygen

Dissolved oxygen analysis measures the amount of gaseous oxygen dissolved in water which acts as an indicator of the ecological health of the stream (Chang, 2005). The dissolved oxygen content in rivers is a remarkable parameter in determining the water quality criteria which is crucial for the survival of fish and many other aquatic organisms (Cox, 2003). Oxygen gets into river water by diffusion from air, by aeration and as a waste product of photosynthesis (Chambers, 2001). The localized biological production, temperature variations and biochemical degradation of organic matter are the controlling factors determining the dissolved oxygen concentration levels in rivers.

Dissolved oxygen content in the water column varies from 5.07 to 11.57 mg l^{-1} during the July 2005 to May 2006. Dissolved oxygen in the water column averages to 9.53 ± 0.87 mg l^{-1}, 9.54 ± 1.14 mg l^{-1}, 8.18 ± 0.76 mg l^{-1}, 6.52 ± 0.36 mg l^{-1}, 5.76 ± 0.34 mg l^{-1} and 6.33 ± 0.36 mg l^{-1} respectively during the July, September, November, January, March and May months. The dissolved oxygen concentrations at stations 1 to 18 indicate that the Muvattupuzha River water contains high amount of dissolved oxygen (5.07 to 11.57 mg l^{-1}) mainly due to photosynthetic activities of phytoplanktons and water circulation. Dissolved oxygen content in the water column showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 3.1.3.*). Balachand (1983) also reported a similar strong seasonality in the dissolved oxygen levels with higher values during the monsoon months when compared to post-monsoon or pre-monsoon months of the Muvattupuzha River waters.

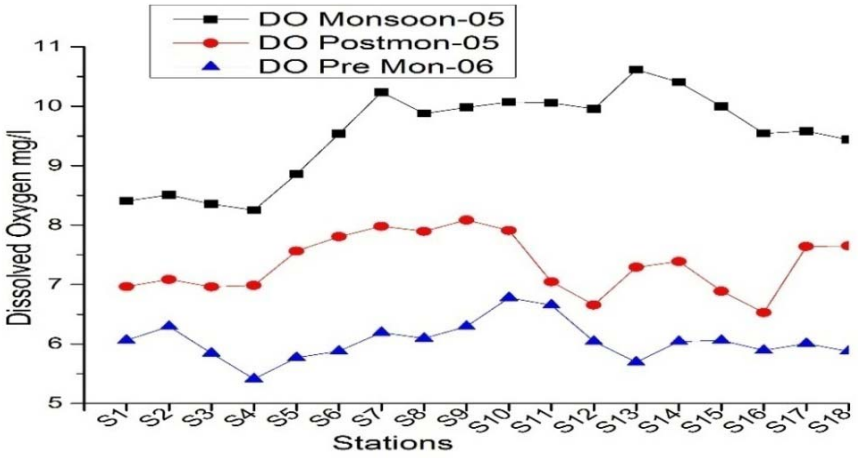


Figure 3.1.3. Seasonal variations of Dissolved Oxygen (mg l^{-1}) in the water column of the Muvattupuzha River

The higher dissolved oxygen values obtained during the monsoon period is due to the more amounts of oxygen readily dissolved in the water column associated with the lowering of temperature and turbulence produced by heavy rains and high local precipitation. This is supported by a highly significant and strong negative correlation ($r = -0.719$, significant at $p < 0.001$) of dissolved oxygen with temperature which indicates that an increase in temperature leads to the reduced dissolution of ambient oxygen into the river water. Dissolved oxygen content in the Muvattupuzha River at most sampling sites exceed the permissible limit (5 to 6 mg l^{-1}) of water quality criteria proposed by BIS (1991).

3.2.4. Chemical Oxygen Demand

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent to the oxidisable organic matter content of water or it measures the oxygen demand of organic compounds present in water or it estimates the carbonaceous fraction of organic matter in water (Joseph and Shanthi, 2009). COD in the water column varies from 1.61 to 240.26 mg l^{-1} during the July 2005 to May 2006. COD in the water column averages to

33.17 ± 13.59 mg l^{-1}, 123.49 ± 65.90 mg l^{-1}, 15.71 ± 8.40 mg l^{-1}, 8.82 ± 5.22 mg l^{-1}, 60.22 ± 25.90 mg l^{-1} and 32.85 ± 20.60 mg l^{-1} respectively during the July, September, November, January, March and May months. COD in the water column showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 3.1.4.*). Average values of COD showed a very higher value of 123.49 mg l^{-1} during the September month which is followed by higher value of 60.22 mg l^{-1} during the March month. Similarly, average values of COD showed moderate values of 33.17 mg l^{-1} and 32.85 mg l^{-1} during the July and May months respectively. Average values of COD showed a lower value of 15.71mg l^{-1} during the March month which is followed by lower value of 8.82 mg l^{-1} during the January month.

According to BIS (1991), the maximum permissible limit of COD for discharge of effluents into surface waters of rivers is 250 mg l^{-1}. The higher COD values (> 100 mg/l) encountered at stations S_2 to S_6 (COD, 104.23 to 240.26 mg l^{-1}) and at stations S_{16} to S_{18} (COD, 102.48 to 231.52 mg l^{-1}) during the monsoon month of September 2005 may be due to the presence of high amount of oxidisable organic matter in the Muvattupuzha River derived from by land drainage. The higher COD values (> 100 mg l^{-1}) encountered at stations S_2 to S_6 (COD, 104.23 to 240.26 mg l^{-1}) during the monsoon month of September 2005 can be due to discharge from laterite soils that containing agricultural wastes rich in organic chemicals into the Muvattupuzha River associated with the heavy rainfall from the adjoining rubber plantations (Gopinath, 2003). Similarly, the higher COD values (> 100 mg l^{-1}) encountered at stations S_{16} to S_{18} (COD, 102.48 to 231.52 mg l^{-1}) during the monsoon month of September 2005 is due to drainage of organic rich domestic effluents from Moolamattom and Kothamangalam townships (Karthikeyan et al. 2002; Joseph and Shanthi, 2009).

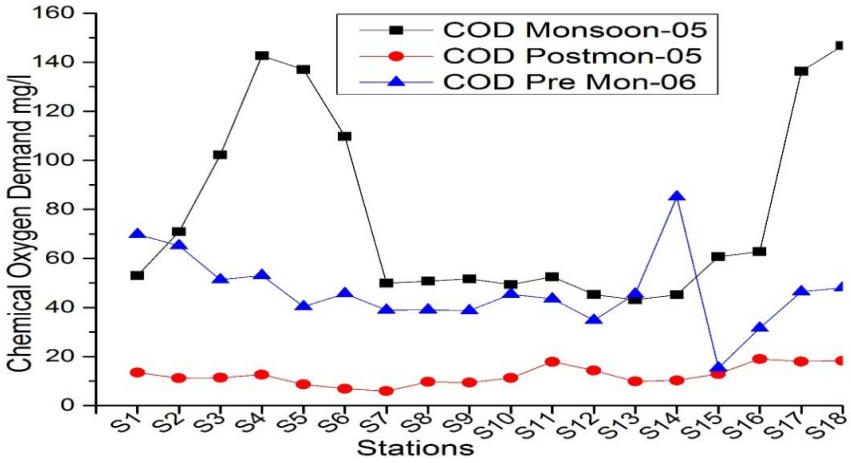


Figure 3.1.4. Seasonal variations of Chemical Oxygen Demand (mg l^{-1}) in the water column of the Muvattupuzha River

3.2.5. Chloride

The chloride ion is highly mobile and is eventually transported to rivers by the dissolution of salt deposits, discharge of effluents from chemical industries, oil-well operations, domestic sewage, agricultural runoff, irrigation drainage and seawater intrusion in coastal areas (Johnston, 1987). Each of these sources may result in local contamination of surface water bodies.

Chloride content in the water column varies from 6.12 to 56.48 mg l^{-1} during the July 2005 to May 2006. Chloride content in the water column averages to 10.16 ± 2.25 mg l^{-1}, 7.36 ± 1.40 mg l^{-1}, 11.46 ± 2.10 mg l^{-1}, 12.82 ± 8.99 mg l^{-1}, 14.32 ± 5.91 mg l^{-1} and 25.33 ± 14.30 mg l^{-1} respectively during the July, September, November, January, March and May months.

Average chloride ion in water column of the Muvattupuzha River is accumulated seasonally (*Figure 3.1.5.*) in the following pattern: pre-monsoon months > post-monsoon months > monsoon months. The relative increase in chloride content during pre-monsoon is attributed to agricultural runoff and

the high rate of evaporation caused by high air temperature (Gopinath, 2003). The monsoonal decrease in chloride ion content is due to heavy fresh water influx, its consequent dilution and strong flushing. However, all the water samples showed chloride values below the desirable limit of 250 mg l^{-1} proposed by BIS (1991) for the drinking water suggesting a low amount of chloride in the Muvattupuzha River from the surrounding agricultural land masses.

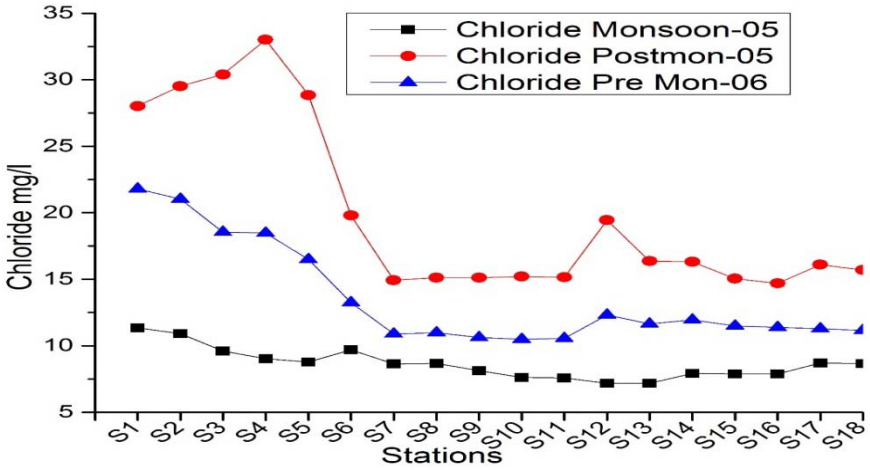


Figure 3.1.5. Seasonal variations of Chloride (mg l^{-1}) in the water column of the Muvattupuzha River

3.3. Sediment characteristics

3.3.1. Textural classification of sediments

The nature and extent of fluctuation in the composition of sediments can indicate the extent of stress on shallow aquatic environments (Sudhanandh et al. 2011; Nair and Sujatha, 2012; 2013). The sediments derived in rivers are in a balance between the erosional and depositional forces of the ecosystem (Seralathan and Padmalal, 1994). Grain size analysis is a fundamental procedure in sedimentology and limnology and it gives basic information on

the sediment composition in a depositional environment. Natural sediments consist of particles of different sizes and for deciding the size groups, several class intervals based on average diameter have been suggested. One such system includes the grading of particles into sand (> 63 μm), silt (4 - 63 μm) and clay (< 4 μm) sizes (Krumbein and Pettijohn, 1938).

Tables A3.1.6 to A3.2.1 (given in Annexure) summarises the bimonthly weight percentages of sand, silt and clay in sediments of the Muvattupuzha River. The bimonthly mean values and standard deviations of sand, silt and clay content in sediments at 18 stations from the upstream regions of the Muvattupuzha River is given in *Table 3.2.3.* In order to describe seasonal variations of sediment texture, mean values calculated for the respective two months of monsoon (July/September), post-monsoon (November/January) and pre-monsoon (March/May) periods were plotted and is shown in *Figure 3.1.6.*

Table 3.2.3. Bimonthly mean values and standard deviations of Sand, Silt, Clay and Organic Carbon in sediments of the Muvattupuzha River

Month	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Nature of Sediment
July 2005	48.56 ± 22.11	46.42 ± 21.25	5.02 ± 1.95	3.49 ± 1.54	Sandy-Silt
September 2005	50.65 ± 21.72	44.10 ± 20.87	5.26 ± 1.97	4.36 ± 2.02	Sandy-Silt
November 2005	47.00 ± 22.08	48.68 ± 21.55	4.33 ± 1.73	2.80 ± 1.45	Silty-Sand
January 2006	41.58 ± 21.49	54.95 ± 21.37	3.47 ± 1.46	3.10 ± 1.87	Silty-sand
March 2006	33.56 ± 20.80	63.79 ± 20.87	2.65 ± 1.03	1.40 ± 0.95	Silty-sand
May 2006	36.96 ± 22.21	59.21 ± 22.20	3.84 ± 1.54	0.76 ± 0.28	Silty-sand

Sand content in the sediments varies between 9.95 to 93.55 % during the July 2005 to May 2006. Sand content in the sediments averages to 48.56 ±

22.11 %, 50.65 ± 21.72 %, 47.00 ± 22.08 %, 41.58 ± 21.49 %, 33.56 ± 20.80 % and 36.96 ± 22.21 % respectively during the July, September, November, January, March and May months. Average sand was observed to be accumulated seasonally in the Muvattupuzha River sediments in the following pattern: monsoon months > post-monsoon months > pre-monsoon months (*Figure 3.1.6.).*

Silt content in the sediments varies between 3.65 to 87.81 % during the July 2005 to May 2006. Silt content in the sediments averages to 46.42 ± 21.25 %, 44.10 ± 20.87 %, 48.68 ± 21.55 %, 54.95 ± 21.37 %, 63.79 ± 20.87 % and 59.21 ± 22.20 % respectively during the July, September, November, January, March and May months. Average silt was shown to be accumulated seasonally in the Muvattupuzha River sediments in the following pattern: pre-monsoon months > post-monsoon months > monsoon months (*Figure 3.1.6.).*

Clay content in the sediments varies between 1.32 to 8.12 % during the July 2005 to May 2006. Clay content in the sediments averages to 5.02 ± 1.95 %, 5.26 ± 1.97 %, 4.33 ± 1.73 %, 3.47 ± 1.46 %, 2.65 ± 1.03 % and 3.84 ± 1.54 % respectively during the July, September, November, January, March and May months. Average clay was found to be accumulated seasonally in the Muvattupuzha River sediments in the following pattern: monsoon months > post-monsoon months > pre-monsoon months (*Figure 3.1.6.).*

From the tables A3.1.6 to A3.2.1, it is evident that Muvattupuzha River sediments showed a wide range of sediment texture. Sandy-silt and silty-sand are the dominant sediment types in the upstream regions of the Muvattupuzha River bed. Sandy-silt predominates towards top upstream stations whereas silty-sand is progressively enriched towards down upstream stations. The

particle size analysis of the sediments from the Muvattupuzha River bed during all seasons reveals that upstream sediments are medium to coarse grained which indicates that the fluvial fluxes of sediments are transported in association with the water currents (Ganesh et al. 2013). Laterite soil sedimented in the Muvattupuzha River basin as a result of weathering transportation from the adjoining hill rocks and its deposition from neighbouring agricultural lands either as alluvium or colluviums are generally coarse in nature (Gopinath, 2003). Thus, the coarseness of sediments (sandy nature) in the top upstream stations is due to the relative proximity of the weathering sources, high energy conditions existing by water currents and influx of sediments from the neighbouring three tributaries viz. Kothamangalam, Kaliyar and Thodupuzha rivers (Padmalal, 1992). The progressive increase of medium and fine sands towards down upstream stations from top upstream stations indicates a low energy regime in the down upstream stations of the Muvattupuzha River (Padmalal, 1992). The increase in the average clay content of sediments during the heavy run-off monsoon period indicates the relative contribution and transportation of bed-load sediments as fine particles to the Vembanad Lake (Priju and Narayana, 2007; Purandara et al. 2011).

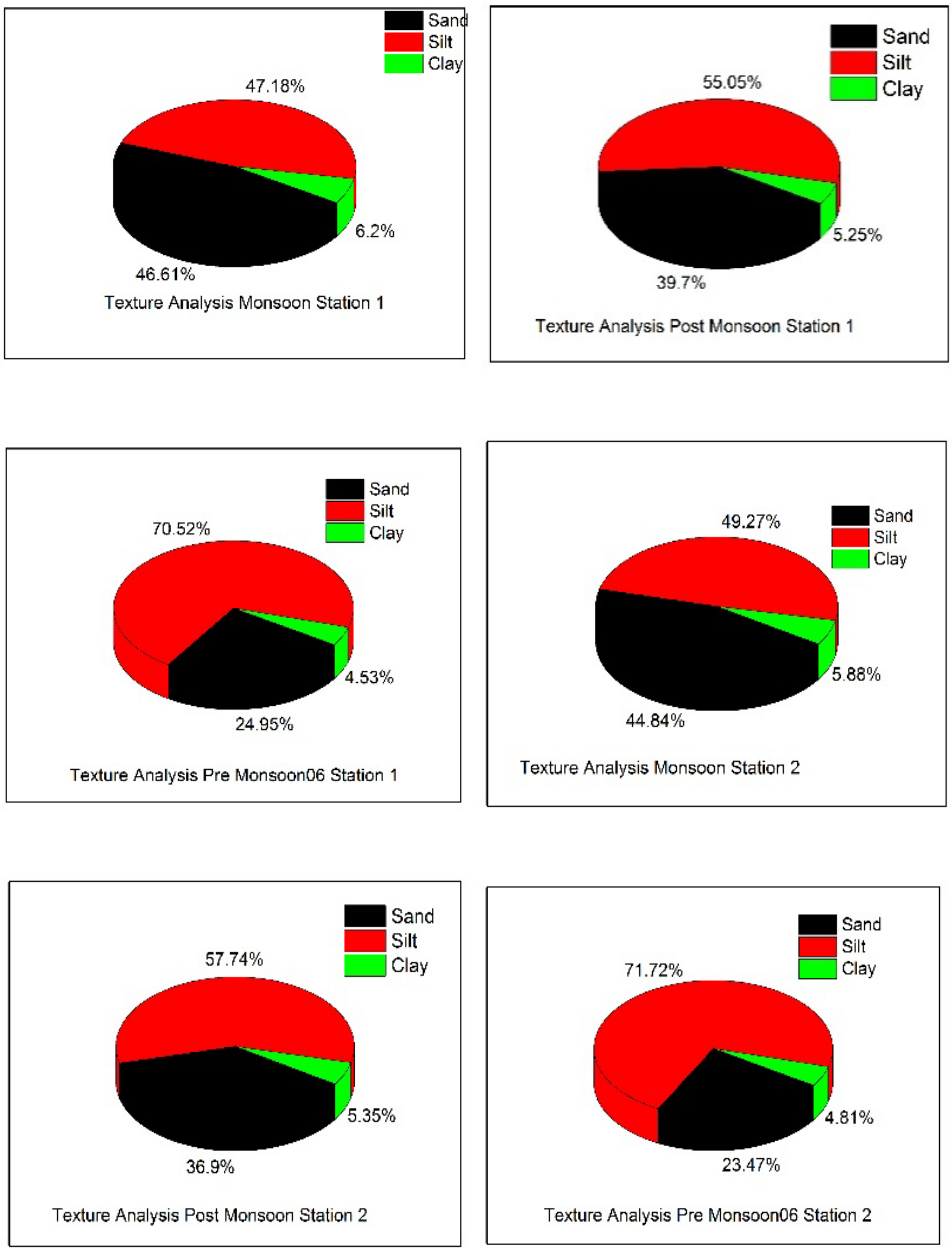


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*

* Monsoon = Monsoon05 = Monsoon 2005 *Post Monsoon = Post Monsoon05 = Post Monsoon 2015
* Pre Monsoon = Pre Monsoon06 = Pre Monsoon 2006

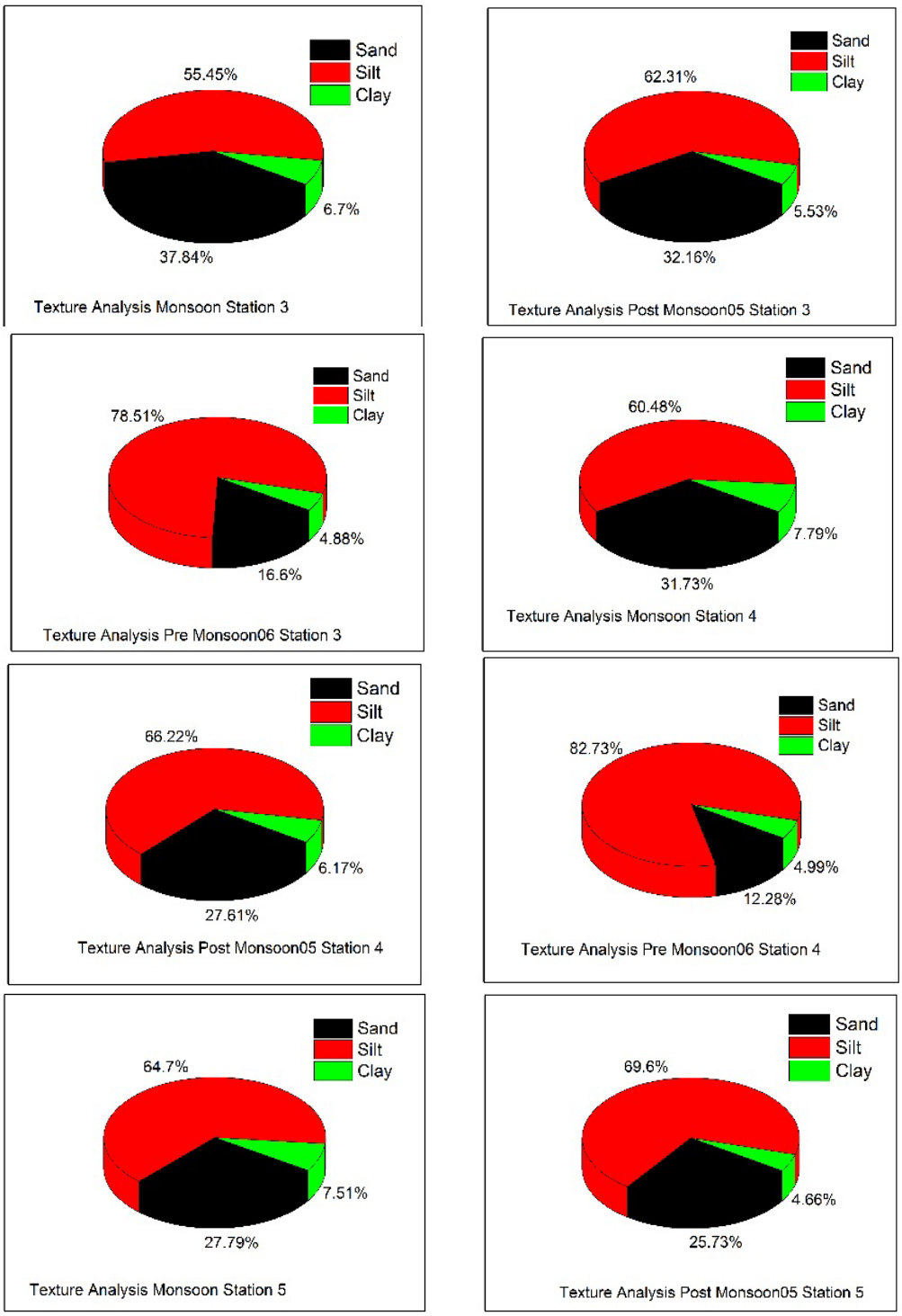


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*

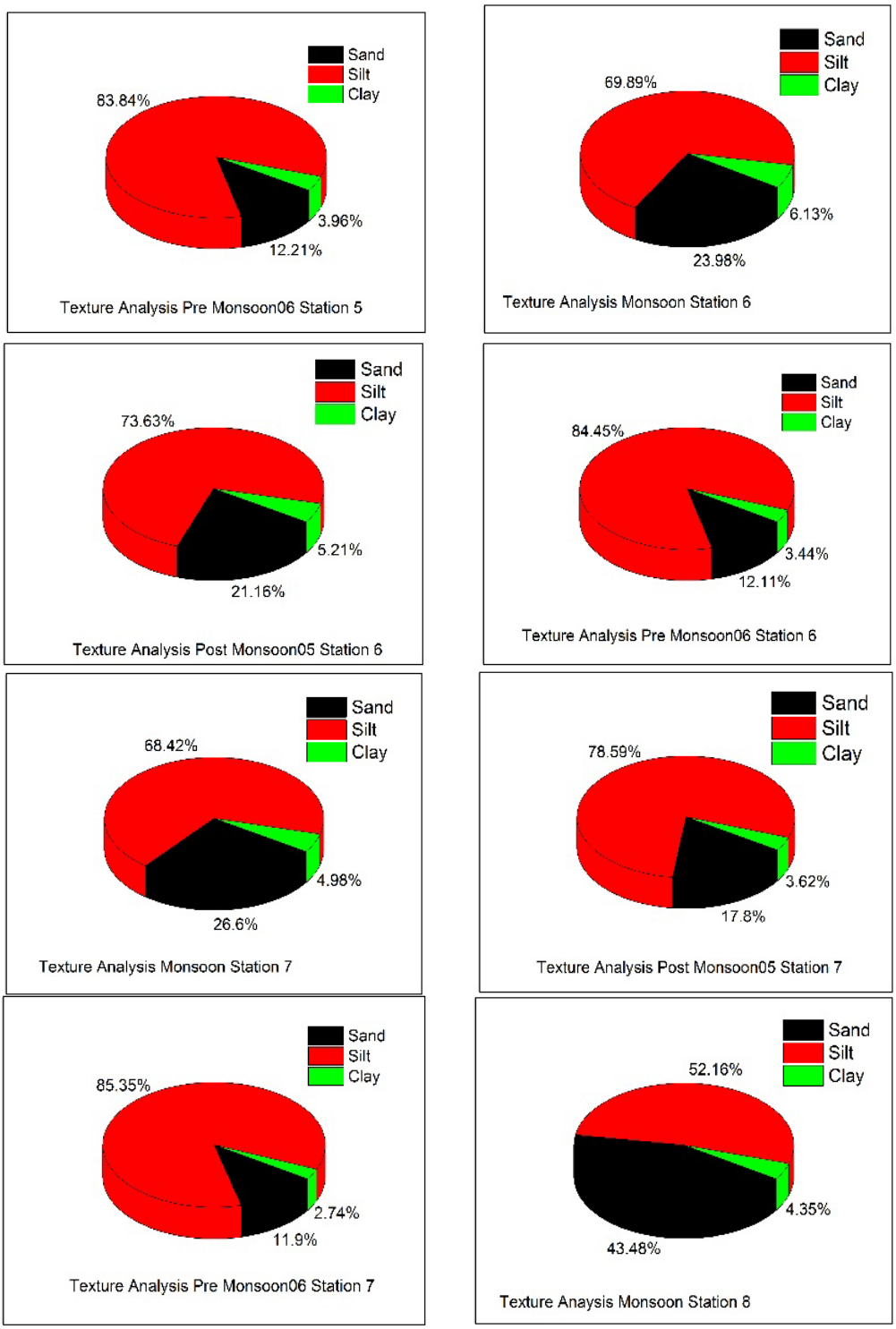
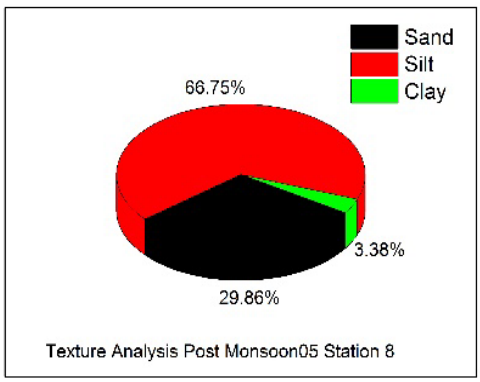
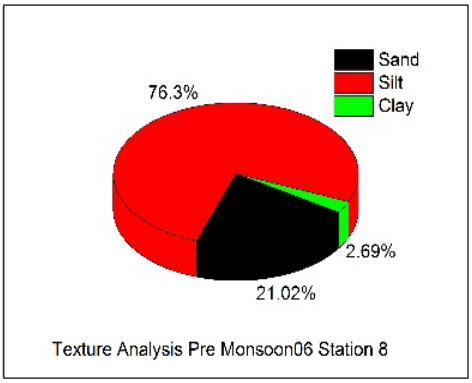
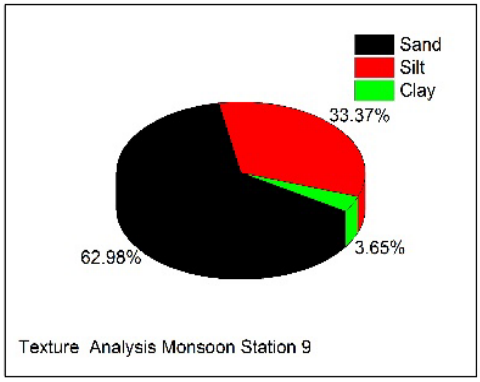
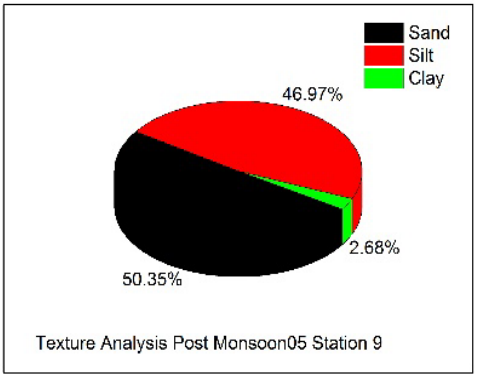


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*









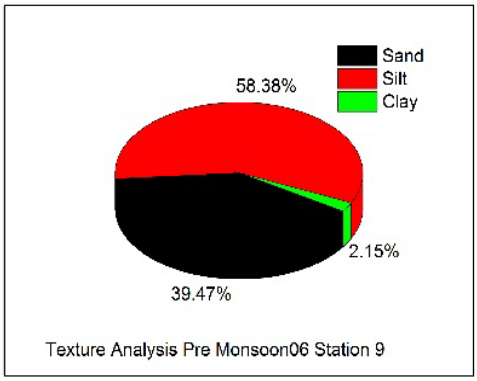


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*

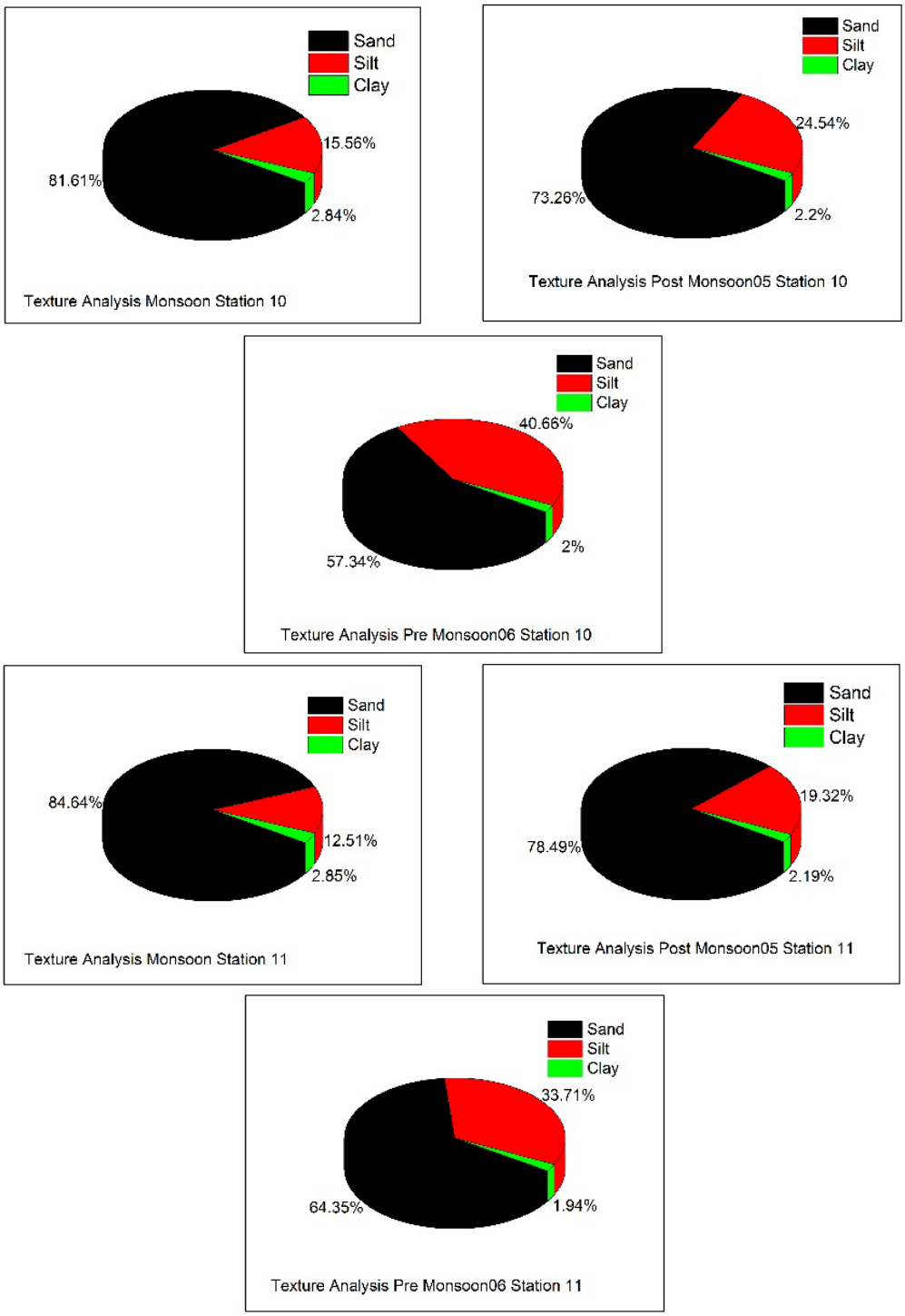


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*

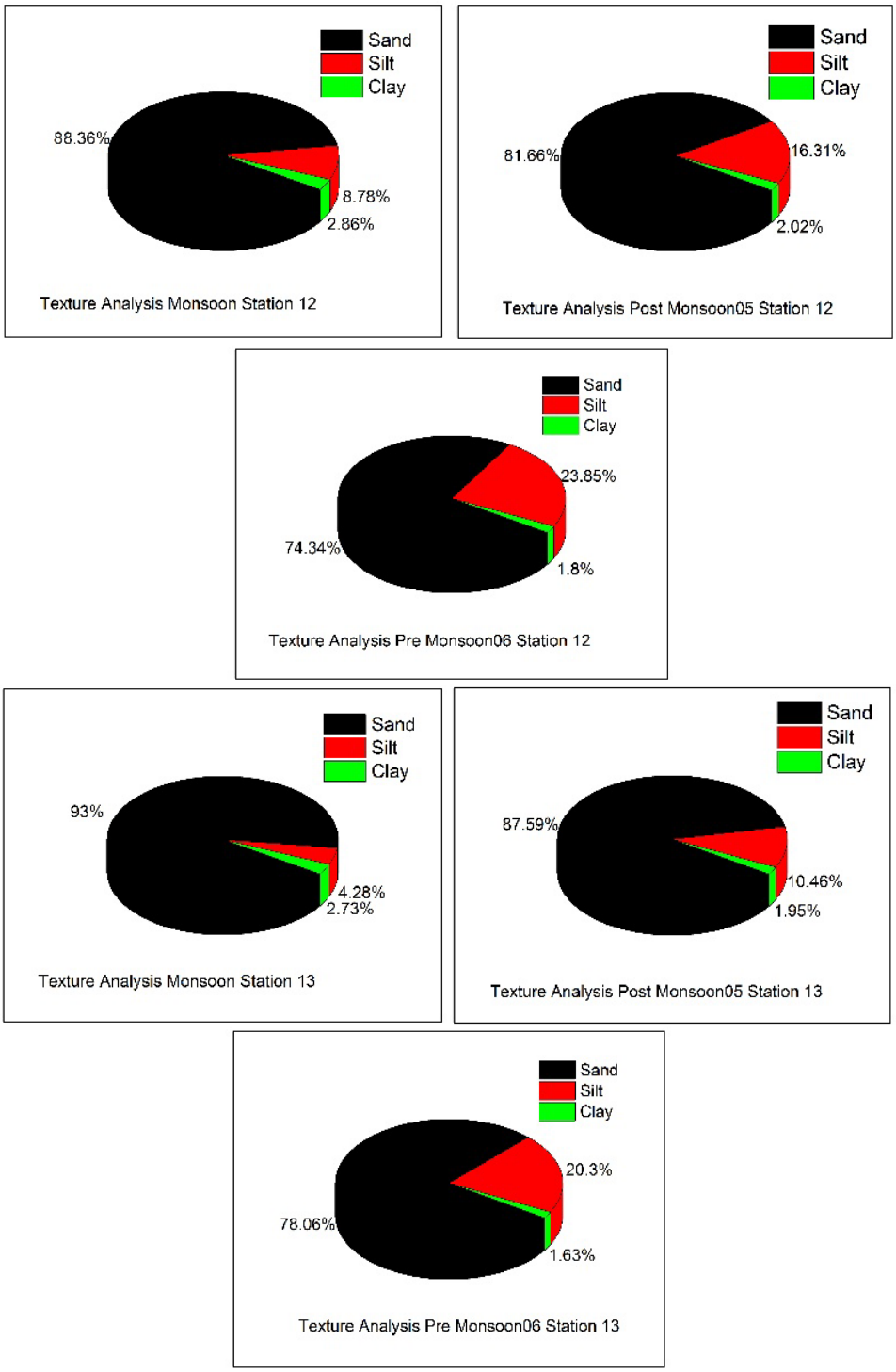


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*

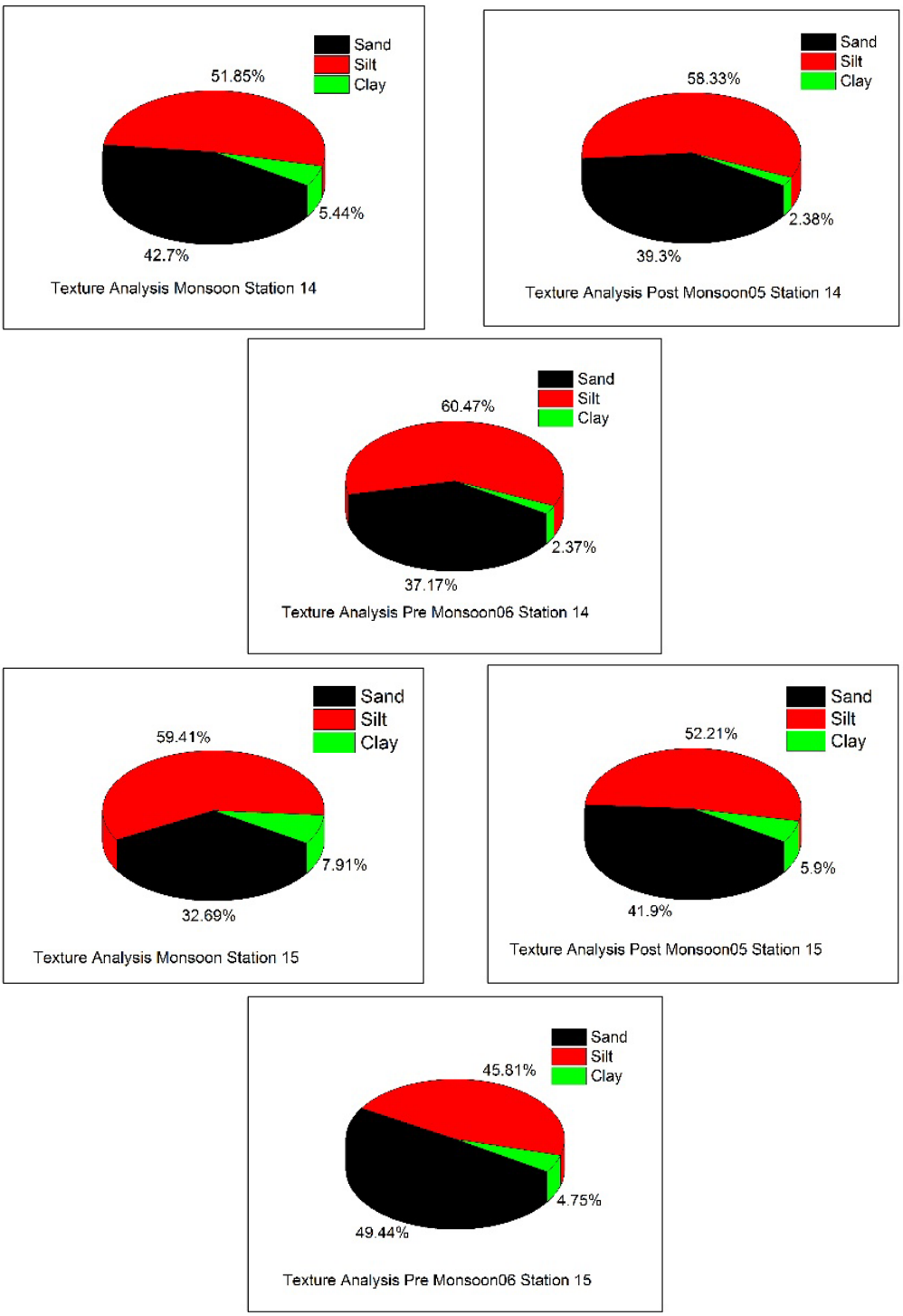


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*

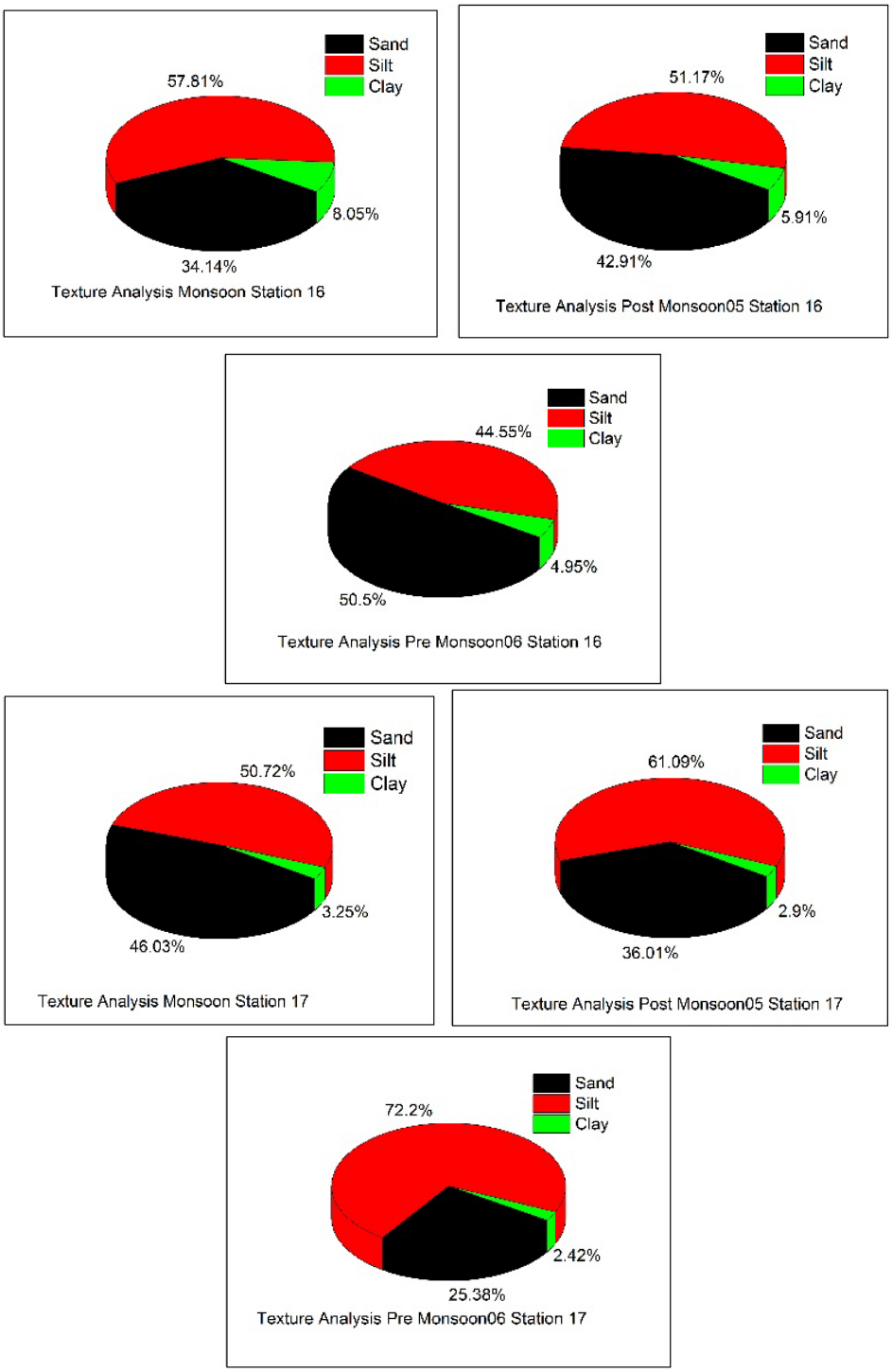


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River……*Continued*

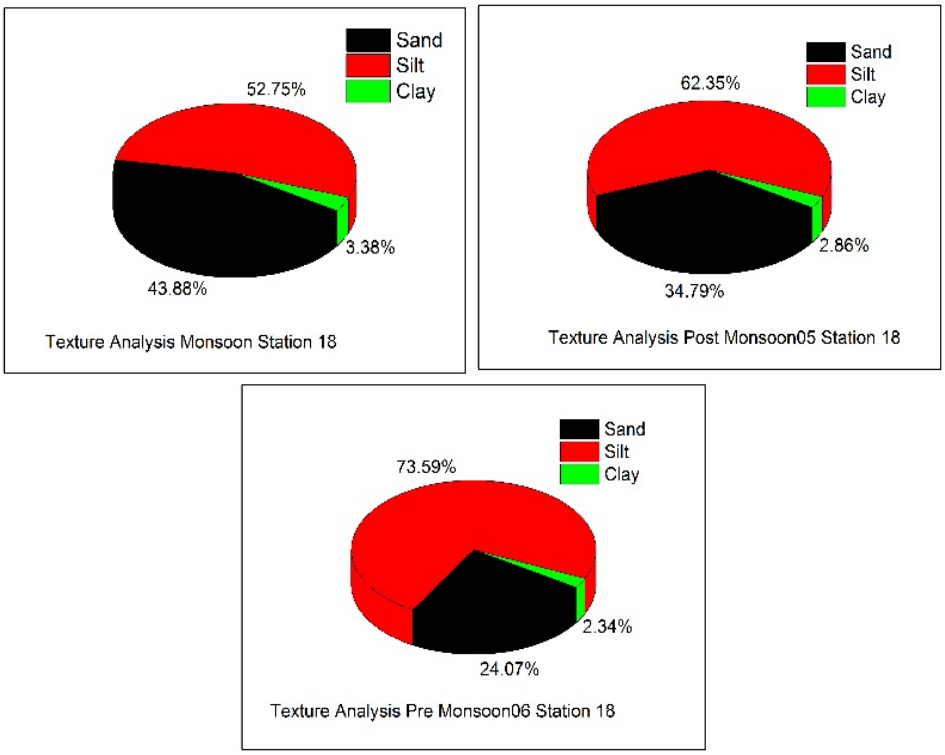


Figure 3.1.6. Seasonal variations of sediment texture in the Muvattupuzha River

3.4. Sediment Organic Carbon

Investigations on organic carbon content in sediments indicate the extent of biological activity and indirectly the fertility of the overlying river water as well as the status of organic pollution in the river (Unnithan, 1975; Vijayan et al. 1976). In most unpolluted rivers organic carbon content of the bottom sediments is < 5 % whereas in areas where organic pollutants are high, organic carbon level often exceeds 5 % (Alagarsamy, 1991). *Tables A3.1.6 to A3.2.1* (given in Annexure) summarises the bimonthly organic carbon levels in sediments of the Muvattupuzha River. Organic carbon content in sediments varies between 0.32 to 6.99 % during July 2005 to May 2006. Organic carbon content (*Table 3.2.2.)* in the sediments averages to 3.49 ± 1.54 %, 4.36 ± 2.02 %, 2.80 ± 1.45 %, 3.10

± 1.87 %, 1.40 ± 0.95 % and 0.76 ± 0.28 % respectively during the July, September, November, January, March and May months.

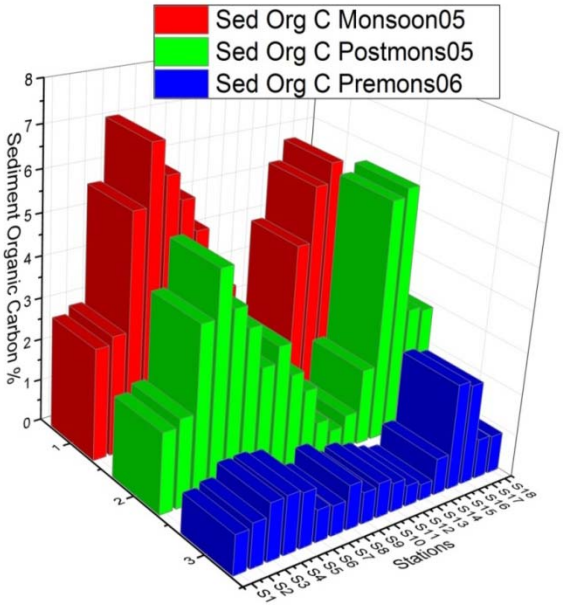


Figure 3.1.7. Seasonal variations of sediment organic carbon in the Muvattupuzha River

In order to describe seasonal variations of sediment organic carbon, mean values calculated for monsoon (July/September), post-monsoon (November/January) and pre-monsoon (March/May) periods were plotted and is shown in *Figure 3.1.7.* The factors that contribute to organic matter enrichment in sediments are the supply of organic matter, the rate of deposition, the movement of the water body and the texture of sediments. Average organic carbon is accumulated seasonally in the Muvattupuzha River sediments in the following pattern: monsoon months > post-monsoon months > pre-monsoon months (*Figure 3.1.7.*). It is likely that land run-off and terrigenous organic detrital sources settling in river mainly contributed to the organic carbon content in bed sediments (Saraladevi et al. 1992; Madhu et al. 2010). Consistent with a higher COD load in water column, a higher sediment

organic carbon values (> 5 %) are also encountered at stations S_3 to S_6 and at stations S_{15} to S_{16} during the monsoon months of 2005 which indicated the presence of organic rich pollutants in sedimented soils that discharged into the Muvattupuzha River from agricultural and domestic wastes by land run-off (Alagarsamy, 1991; Abhilash et al. 2012). Higher sediment organic carbon values were reported during the monsoon period (0.3–6.6%) than pre-monsoon period (0.8–4.3%) for the Cochin backwaters which is also is attributed to land drainage (Saraladevi et al. 1992; Martin et al. 2012). The progressive decrease of organic carbon accumulation in bed sediments from monsoon to post-monsoon and to pre-monsoon periods is due to the existing high energy non-depositional conditions such as the incessant stirring up of bottom sediments by water currents for the settlement of fine particles, high dissolved oxygen in the overlying waters and sandy texture of the sediments in the Muvattupuzha River. These factors are detrimental to the ample supply and accumulation of organic matter in sediments which leads to low organic carbon content in sediments during the post-monsoon and pre-monsoon periods.

3.5. Concluding remarks

Muvattupuzha River with its drainage basin exhibiting a tropical humid climate is one of the major perennial rivers in Central Kerala which supporting a majority of human population located on its banks for serving domestic, irrigational and agricultural purposes over Idukki, Ernakulam and Kottayam districts. The hydrodynamics of the Muvattupuzha River were strongly dependent on the influx of natural fresh water runoff from its neighbouring three tributaries namely Thodupuzha, Kaliyar and Kothamangalam rivers which becomes very heavy during the monsoon season when compared to non-monsoon season and the regular steady availability of tail-race water from the Moolamattom hydro-electric power station throughout the year. In the

context of immense anthropogenic pressures due to various human interventions like inter-basin water transfer, discharge of agricultural and urban pollutants, indiscriminate sand and brick clay mining, water and sediment quality parameters, were studied during the bimonthly intervals of July 2005 to May 2006 from the upstream stretch of the Muvattupuzha River at stations of Moolamattam to Piravam which is flowing through municipal townships and agricultural lands. The effluent discharges from domestic and agricultural sources affects the water quality of the river as evidenced from its hydrographic parameters and high carbonaceous load of organic matter. Temperature and dissolved oxygen showed pronounced seasonal variations which were brought about by the effect of turbulence and heavy local precipitation from the prevailing monsoonal rains. A major type of pollutant load in the river is organic and several stations experienced high organic loads as evidenced from the high organic carbon levels in sediments during the monsoon period. However due to strong flushing a relative dominance of coarse fractions (sand) over fine grained particles (slit & clay) is noted at all stations which prevents an effective organic carbon accumulation in sediments. Thus, monsoonal floods and large influx of water from Idukki dam provide an adequate dilution effect to mask the impact of any pollutant loads from domestic and agricultural sources in the Muvattupuzha River.

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Chapter 4

PARTITIONING OF TRACE METALS IN DISSOLVED AND PARTICULATE PHASES OF THE MUVATTUPUZHA RIVER

4.1. Introduction

Rivers are the major sources of dissolved and particulate materials to the oceans and are thereby the primary contributors to the geochemical composition of both ocean water and marine sediments (Radakovitch et al. 2008; Fang et al. 2009). Trace metals are added to the riverine environment from both natural and anthropogenic sources (Gundersen et al. 2001; Hatje et al. 2001; Nimick et al. 2005; Leung and Jiao, 2006; Ouyang et al. 2006). Runoff from land is a major source of addition of trace elements to the rivers. Rivers bring in trace metals both as dissolved species and as adsorbed onto suspended matter, the concentration of which may vary with the nature of rocks in the catchment areas (Sarin et al. 1985; Subramanian et al. 1987). Geologic weathering of rocks ultimately produces clay and other minerals that make up the bulk of detrital sediments as well as dissolved metals in rivers (Jackson, 1998). Many of the human activities can add metals to the riverine environment, like mining, metal-ore processing and transportation, domestic and agricultural waste disposal etc. However from the numerous sources of

trace metals to the riverine environment, it is difficult to determine which possible source is most important.

Environmental impact of a metal depends on its behaviour rather than its source (Korfali and Davies, 2003, 2005). It is well known that trace metals are present in aquatic environments in different forms (species) and the distribution between these species is a critical factor in understanding the role of trace metals in aquatic systems. The bio-availability, toxicity, reactivity, and ultimate fate of trace metals depend on their speciation. The behaviours including mobility, transport, transfer and biological uptake, depend on the chemical and physical form of the metal. The size of the metal species or the particle with which it is associated is critical, as this will control its transport and settling. A given metal will behave differently as physically, chemically and biologically in each of its forms and it will partition itself among the various possible forms in response to environmental conditions (Shiller and Boyle, 1991). In this respect, it is important to note that many trace metals are reactive and will quickly get partitioned between the water and particles if added to the riverine environment in a dissolved form. Although free metal ions in the dissolved phase are considered to be the most bioavailable species, trace metals adsorbed or complexed to suspended solids are also important, as they become mobilized under changed physico-chemical conditions either in the water column or upon settling as bottom sediment (Campbell, 1995).

An understanding of trace metal behaviour requires a quantitative description of water/particle interactions which appear to govern the fate of trace metals in the riverine environment (Stumm, 1992). The interactions of dissolved metals with suspended particles (SPM) in river/estuaries exert a

major control on the concentrations and distribution of trace metals in oceans (Goldberg, 1954; Turekian, 1977; Whitfield and Turner, 1987). The net riverine flux of trace elements transported to oceans depends on the weathering features of the drainage basin. Rather than natural ones, due to higher anthropogenic influences in the Indian continent the average particulate trace metal concentrations of Indian rivers is higher than that of Chinese rivers and the global average values (Alagarsamy and Zhang, 2005). However, data on trace metal partitioning between dissolved and suspended particulate phases are scarce because only a few such measurements have been made in Indian riverine environments. Data on dissolved and particulate trace metals are very scanty for the upper fresh water region of the Muvattupuzha River. The present work is hence the first of its kind focusing on to understand the partition dynamics of the metals between the dissolved and particulate phases from this region. This chapter presents the results of the bimonthly investigations on dissolved and particulate trace metals in the water column at 18 stations from the upstream regions of the Muvattupuzha River.

RESULTS AND DISCUSSION

4.2. Spatial and bimonthly variations of dissolved trace metals

The spatial and bimonthly variations of dissolved trace metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in water at 18 stations from the upstream regions of the Muvattupuzha River are given in Annexure as *Tables A4.1.0 to A4.1.5*. The bimonthly mean values and standard deviations of dissolved trace metals in the water column at 18 stations from the upstream regions of the Muvattupuzha River are given in *Table 4.4.0.*

Table 4.4.0. Bimonthly mean values and standard deviations of dissolved trace metals in the water column of the Muvattupuzha River

Month	dFe (ppb)	dMn (ppb)	dCo (ppb)	dNi (ppb)	dCu (ppb)	dZn (ppb)	dCd (ppb)	dCr (ppb)	dPb (ppb)
July 2005	47.26 ±8.53	29.71 ± 2.95	0.302±0.090	0.595±0.129	1.502±0.203	16.43±1.18	1.015±0.084	0.650±0.073	0.769±0.113
Sept 2005	49.84 ±10.73	29.27 ± 2.91	0.302±0.090	0.587±0.113	1.470±0.144	18.32±0.99	1.001±0.106	0.649±0.066	0.736±0.105
Nov 2005	36.99 ±2.04	23.34±2.18	0.210±0.052	0.516±0.105	1.030±0.115	13.93±1.13	0.899±0.091	0.542±0.030	0.489±0.076
Jan 2006	35.45 ±6.39	22.35±2.18	0.219±0.086	0.518±0.103	0.990±0.112	15.12±0.87	0.864±0.058	0.542±0.065	0.495±0.075
March 2006	24.11 ± 3.44	16.17±1.58	0.132±0.031	0.461±0.039	0.959±0.127	9.27±0.80	0.776±0.060	0.468±0.048	0.351±0.050
May 2006	23.82 ± 2.48	15.85±1.55	0.153±0.042	0.440±0.038	0.929±0.124	9.73±0.54	0.725±0.077	0.470±0.034	0.342±0.054

In order to describe seasonal variations of dissolved metals, mean values calculated for the respective two months of monsoon (July/September), post-monsoon (November/January) and pre-monsoon (March/May) periods were plotted and are shown in *Figures 4.1.1.* to *4.1.9.* respectively.

4.2a. Dissolved iron

Dissolved iron content in water column varies between 16.24 to 69.70 ppb during the months of July 2005 to May 2006. Dissolved iron content in water column averages to 47.26 ± 8.53 ppb, 49.84 ± 10.73 ppb, 36.99 ± 2.04 ppb, 35.45 ± 6.39 ppb, 24.11 ± 3.44 ppb and 23.82 ± 2.48 ppb respectively during the July, September, November, January, March and May months. Comparatively, a higher dissolved Fe concentration is recorded during the monsoon than other seasons (*Figure 4.1.1*). The dissolved Fe averages (36.25 ppb) of the Muvattupuzha River is much higher than the dissolved Fe averages (*Table 4.4.1.*) reported for some other Indian rivers like Cauvery (9.90 ppb) and Godavari (7.50 ppb) respectively (Jameel, 2001; Patil and Shrivastava, 2003). However, the dissolved Fe averages (36.25 ppb) of the Muvattupuzha River is considerably lower than the dissolved Fe averages (*Table 4.4.1.*) reported for the Kuttanad backwaters (73.10 ppb) and Chitrapuzha River (62.33 ppb) respectively (Unnikrishnan, 2000; Joseph, 2002). The concentration of dissolved Fe during the present study does not exceed the maximum permissible limit of Fe (1000 ppb) for drinking water quality standards (WHO, 1993; BIS, 1991; ICMR, 1986). The dissolved Fe concentrations at stations S_{15} to S_{16} during July 2005, and at stations S_1 to S_2, S_5 to S_7 during September 2005 exceeds the world river average of 55 ppb (Salomons and Forstner, 1984).

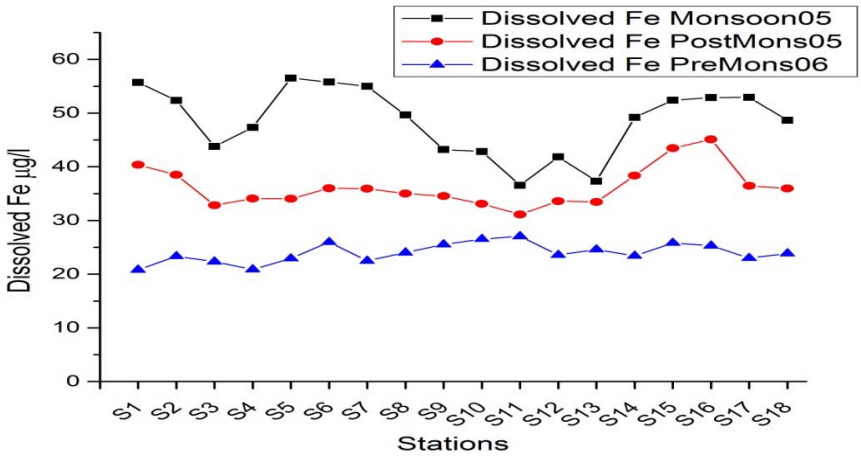

Figure 4.1.1. Seasonal variations of dissolved iron (ppb) in the water column of the Muvattupuzha River

4.2a. Dissolved manganese

Dissolved manganese content in water column varies between 13.18 to 33.85 ppb during the months of July 2005 to May 2006. Dissolved manganese content in water column averages to 29.71 ± 2.95 ppb, 29.27 ± 2.91 ppb, 23.34 ± 2.18 ppb, 22.35 ± 2.18 ppb, 16.17 ± 1.58 ppb and 15.85 ± 1.55 ppb respectively during the July, September, November, January, March and May months. Comparatively, a higher dissolved Mn concentration is recorded during the monsoon than other seasons (*Figure 4.1.2.*). The dissolved Mn averages (22.78 ppb) of the Muvattupuzha River is very higher than the dissolved Mn averages reported (*Table 4.4.1.*) for some other Indian rivers like Cauvery (2.60 ppb) and Kali (3.95 ppb) respectively (Jameel, 2001; Manjunatha et al. 2001). The dissolved Mn averages (22.78 ppb) of the Muvattupuzha River is also very higher than the dissolved Mn averages (2.41 ppb) reported (*Table 4.4.1.*) for the Kuttanad backwaters (Unnikrishnan, 2000). The dissolved Mn averages (22.78 ppb) of the Muvattupuzha River is also higher than the dissolved Mn averages (13.66 ppb) reported (*Table 4.4.1.*) for the Chitrapuzha River (Joseph, 2002). The maximum permissible limit of

Mn in drinking water is 500 ppb as per WHO (1993) and ICMR (1986) where as it is 300 ppb as per BIS (1991) standard. It is found that the dissolved Mn concentration averages obtained during the present study is much lower than the maximum permissible limit for drinking water standards. The dissolved Mn concentrations at all stations of the Muvattupuzha River during all months exceed the world river average of 6.0 ppb (Salomons and Forstner, 1984).

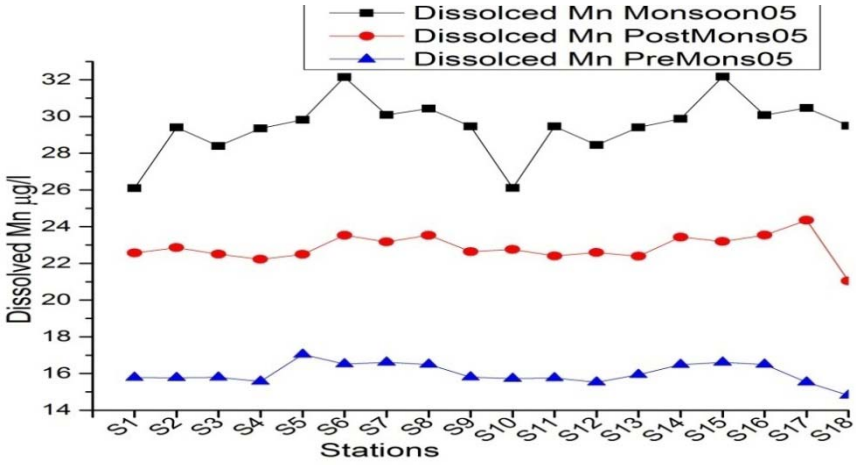

Figure 4.1.2. Seasonal variations of dissolved manganese (ppb) in the water column of the Muvattupuzha River

4.2c. Dissolved cobalt

Dissolved cobalt content in water column varies between 0.104 to 0.557 ppb during the months of July 2005 to May 2006. Dissolved cobalt content in water column averages to 0.302 ± 0.090 ppb, 0.302 ± 0.090 ppb, 0.210 ± 0.052 ppb, 0.219 ± 0.086 ppb, 0.132 ± 0.031 ppb and 0.153 ± 0.042 ppb respectively during the July, September, November, January, March and May months. Comparatively, a higher dissolved Co concentration is recorded during the monsoon than other seasons (*Figure 4.1.3.*). The dissolved Co averages (0.22 ppb) of the Muvattupuzha River are lower than the dissolved Co averages reported (*Table 4.4.1.*) for the Indian River Kali (0.70 ppb)

(Manjunatha et al. 2001). Similarly, the dissolved Co averages (0.22 ppb) of the Muvattupuzha River are lower than the dissolved Co averages reported (*Table 4.4.1.*) for the Kuttanad backwaters (0.75 ppb) (Unnikrishnan, 2000). However, the dissolved Co averages (0.22 ppb) of the Muvattupuzha River are very much lower than the dissolved Co averages (1.84 ppb) reported (*Table 4.4.1.*) for the Chitrapuzha River (Joseph, 2002). The average Co concentrations in the Muvattupuzha River are very much comparable with the world river averages of 0.2 ppb reported by several authors (Martin and Whitfield, 1983; Salomons and Forstner, 1984). The dissolved Co concentrations at stations S_1 to S_{12}, S_{15} to S_{18} during July/September 2005, S_1 to S_8, S_{17} to S_{18} during November 2005, S_1 to S_5 during January 2006, and at stations S_1 to S_4 during May 2006 exceeds the world river average of 0.2 ppb (Salomons and Forstner, 1984).

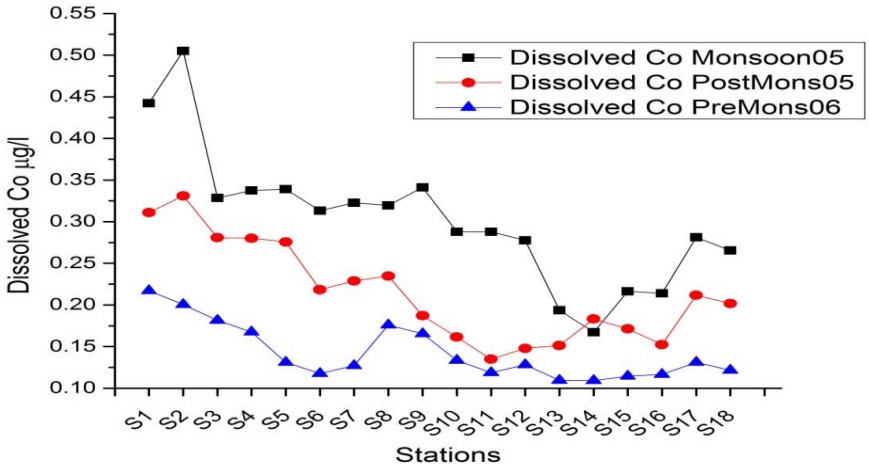

Figure 4.1.3. Seasonal variations of dissolved cobalt (ppb) in the water column of the Muvattupuzha River

4.2d. Dissolved nickel

Dissolved nickel content in water column varies between 0.364 to 0.828 ppb during the months of July 2005 to May 2006. Dissolved nickel content in

water column averages to 0.595 ± 0.129 ppb, 0.587 ± 0.113 ppb, 0.516 ± 0.105 ppb, 0.518 ± 0.103 ppb, 0.461 ± 0.039 ppb and 0.440 ± 0.038 ppb respectively during the July, September, November, January, March and May months. Higher dissolved Ni concentrations are recorded during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.1.4.*). The dissolved Ni averages (0.52 ppb) of the Muvattupuzha River are slightly lower than the dissolved Ni averages reported (*Table 4.4.1.*) for the Indian River Kali (0.80 ppb) (Manjunatha et al. 2001). The dissolved Ni averages (0.52 ppb) of the Muvattupuzha River are very much lower than the dissolved Ni averages reported (*Table 4.4.1.*) for the Kuttanad backwaters (4.13 ppb) and Chitrapuzha River (13.32 ppb) respectively (Unnikrishnan, 2000; Joseph, 2002). It is found that the dissolved Ni concentrations obtained in the present study is lower than the maximum permissible limit of 20 ppb for human consumption (WHO, 1993), whereas it is higher than the world river average (0.3 ppb; Salomons and Forstner, 1984) at all stations during all months.

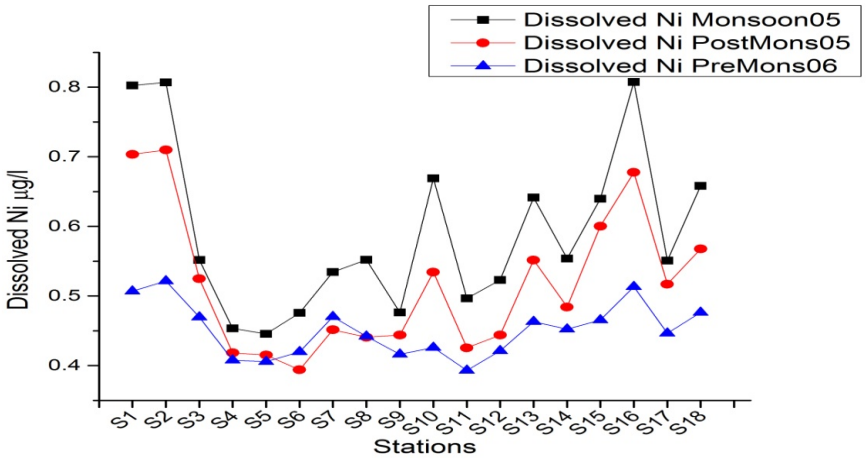

Figure 4.1.4. Seasonal variations of dissolved nickel (ppb) in the water column of the Muvattupuzha River

4.2e. Dissolved copper

Dissolved copper content in water column varies between 0.685 to 1.857 ppb during the months of July 2005 to May 2006. Dissolved copper content in water column averages to 1.502 ± 0.203 ppb, 1.470 ± 0.144 ppb, 1.030 ± 0.115 ppb, 0.990 ± 0.112 ppb, 0.959 ± 0.127 ppb and 0.929 ± 0.124 ppb respectively during the July, September, November, January, March and May months. Higher dissolved Cu concentrations are recorded during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.1.5.*).

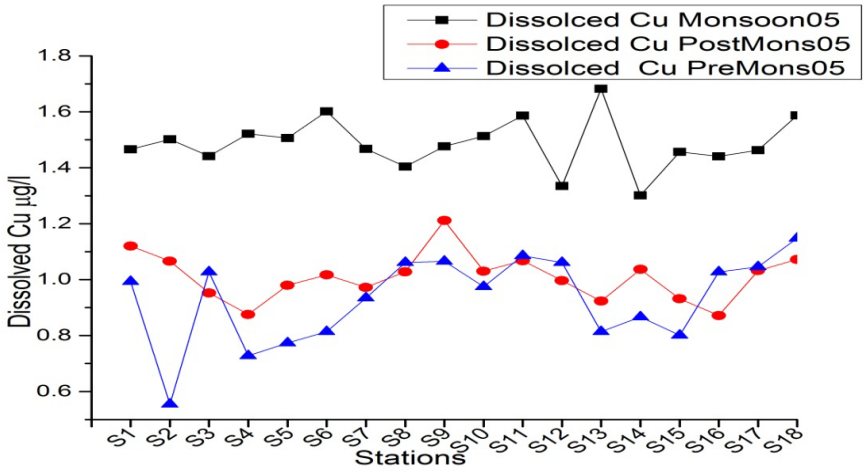

Figure 4.1.5. Seasonal variations of dissolved copper (ppb) in the water column of the Muvattupuzha River

The dissolved Cu averages (1.15 ppb) of the Muvattupuzha River is well comparable with the dissolved Cu averages reported (*Table 4.4.1.*) for the Indian rivers like Godavari (0.92 ppb) and Kali (1.34 ppb) respectively (Patil and Shrivastava, 2003; Manjunatha et al. 2001). However, the dissolved Cu averages (1.15 ppb) of the Muvattupuzha River is lower than the dissolved Cu averages (2.19 ppb) reported (*Table 4.4.1.*) for the Kuttanad backwaters (Unnikrishnan, 2000). Similarly, the dissolved Cu averages (1.15 ppb) of the

Muvattupuzha River is very much lower than the dissolved Cu averages (5.94 ppb) reported (*Table 4.4.1.*) for the Chitrapuzha River (Joseph, 2002). The values of dissolved copper obtained during the present study are very much lower than the maximum permissible limits for human consumption (2000 ppb; WHO, 1993; 1500 ppb; BIS, 1991; 1500 ppb; ICMR, 1986). The dissolved Cu concentrations at stations S_1 to S_{18} during July/September 2005, S_1 and S_7 to S_{11} during November 2005, S_1 to S_3, S_9 and S_{17} to S_{18} during January 2006, and at stations S_8 to S_9, S_{11} to S_{12} and S_{16} to S_{18} during March 2006, S_8 to S_9 and S_{17} to S_{18} during May 2006 exceeds the world river average of 1.0 ppb (Salomons and Forstner, 1984).

4.2f. Dissolved chromium

Dissolved chromium content in water column varies between 0.378 to 0.777 ppb during the months of July 2005 to May 2006. Dissolved chromium content in water column averages to 0.650 ± 0.073 ppb, 0.649 ± 0.066 ppb, 0.542 ± 0.030 ppb, 0.542 ± 0.065 ppb, 0.468 ± 0.048 ppb and 0.470 ± 0.034 ppb respectively during the July, September, November, January, March and May months. Higher dissolved chromium concentrations are observed during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.1.6.*). The dissolved Cr averages (0.55 ppb) of the Muvattupuzha River is considerably lower than the dissolved Cr averages (*Table 4.4.1.*) reported for the Kuttanad backwaters (2.71 ppb) and Chitrapuzha River (4.70 ppb) respectively (Unnikrishnan, 2000; Joseph, 2002). Dissolved Cr concentrations obtained during the present study are very lower than the maximum permissible limit of 50 ppb for human consumption (WHO, 1993; BIS, 1991; ICMR, 1986). However dissolved Cr concentrations at all stations during July/September/November 2005 and January 2006 exceeds (*Table 4.4.1.*) the world river average of 0.5 ppb (Salomons and Forstner, 1984).

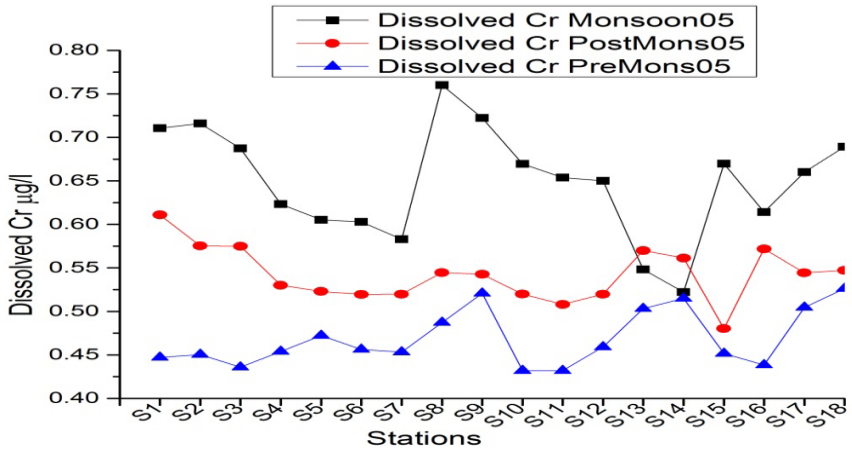

Figure 4.1.6. Seasonal variations of dissolved chromium (ppb) in the water column of the Muvattupuzha River

4.2g. Dissolved zinc

Dissolved zinc content in water column varies between 7.89 to 19.85 ppb during the months of July 2005 to May 2006. Dissolved zinc content in water column averages to 16.43 ± 1.18 ppb, 18.32 ± 0.99 ppb, 13.93 ± 1.13 ppb, 15.12 ± 0.87 ppb, 9.27 ± 0.80 ppb and 9.73 ± 0.54 ppb respectively during the July, September, November, January, March and May months. Higher dissolved zinc concentrations are noted during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.1.7.*). The dissolved Zn averages (13.8 ppb) of the Muvattupuzha River are well comparable with the dissolved Zn average value of 10.03 ppb reported (*Table 4.4.1.*) for the Kali River (Manjunatha et al. 2001). Similarly, the dissolved Zn averages (13.8 ppb) of the Muvattupuzha River are also well comparable with the dissolved Zn average value of 10.87 ppb reported (*Table 4.4.1.*) for the Kuttanad backwaters (Unnikrishnan, 2000). However, the dissolved Zn averages (13.8 ppb) of the Muvattupuzha River are very much lower than the dissolved Zn average value of 27.92 ppb reported (*Table 4.4.1.*) for the Chitrapuzha River (Joseph, 2002). Dissolved Zn concentrations obtained

during the present study is much lower than with respect to drinking water standards (5000 ppb; WHO, 1993; 15000 ppb; BIS, 1991; 15000 ppb; ICMR, 1986). The dissolved Zn concentrations at all stations during July/September/ November 2005 and at all stations during January 2006 exceeds the world river average value of 10.0 ppb (Salomons and Forstner, 1984).

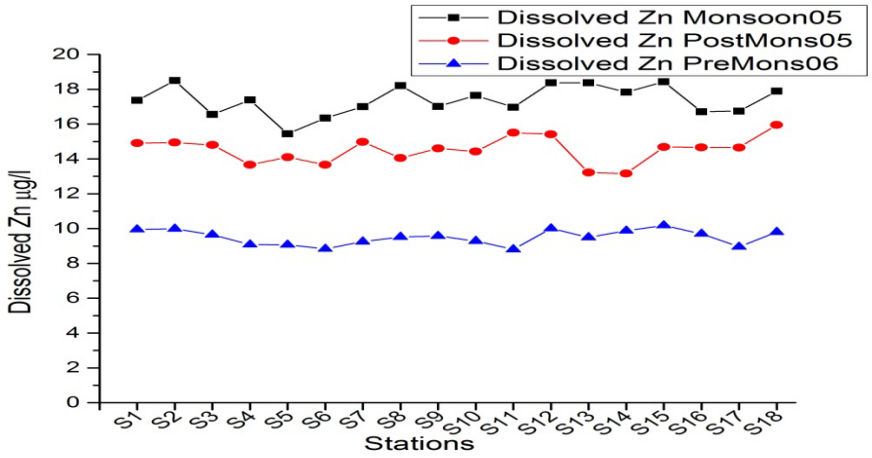

Figure 4.1.7. Seasonal variations of dissolved zinc (ppb) in the water column of the Muvattupuzha River

4.2h. Dissolved cadmium

Dissolved cadmium content in water column varies between 0.623 to 1.244 ppb during the months of July 2005 to May 2006. Dissolved cadmium content in water column averages to 1.015 ± 0.084 ppb, 1.001 ± 0.106 ppb, 0.899 ± 0.091 ppb, 0.864 ± 0.058 ppb, 0.776 ± 0.060 ppb and 0.725 ± 0.077 ppb respectively during the July, September, November, January, March and May months. Dissolved cadmium concentrations are higher during monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.1.8.*). The dissolved Cd averages (0.88 ppb) of the Muvattupuzha River are well comparable (*Table 4.4.1.*) with dissolved Cd averages of 0.81 ppb reported for the Devi River (Sundaray et al. 2012). However, the dissolved Cd

averages (0.88 ppb) of the Muvattupuzha River is considerably lower than the dissolved Cd averages (*Table 4.4.1.*) reported for the Kuttanad backwaters (2.68 ppb) and Chitrapuzha River (2.59 ppb) respectively (Unnikrishnan, 2000; Joseph, 2002). Average dissolved Cd concentrations obtained during the July/September 2005 is approximately equal to the limit of 1.0 ppb drinking water standard (ICMR, 1986). However dissolved Cd concentrations at all stations during all months exceed the world river average value of 0.020 ppb (Salomons and Forstner, 1984).

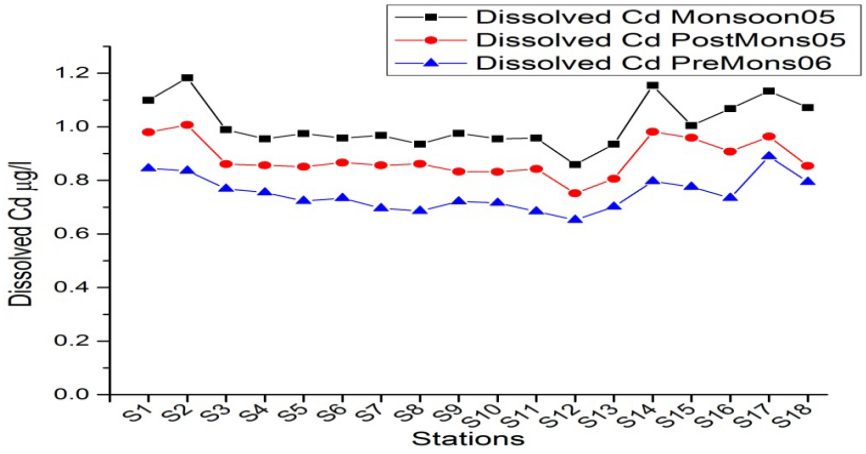

Figure 4.1.8. Seasonal variations of dissolved cadmium (ppb) in the water column of the Muvattupuzha River

4.2i. Dissolved lead

Dissolved lead content in water column varies between 0.254 to 0.945 ppb during the months of July 2005 to May 2006. Dissolved lead content in water column averages to 0.769 ± 0.113 ppb, 0.736 ± 0.105 ppb, 0.489 ± 0.076 ppb, 0.495 ± 0.075 ppb, 0.351 ± 0.050 ppb and 0.342 ± 0.054 ppb respectively during the July, September, November, January, March and May months. Higher dissolved Pb concentrations are noted during the monsoon period than post-monsoon or pre-monsoon periods (*Figure 4.1.9.*).

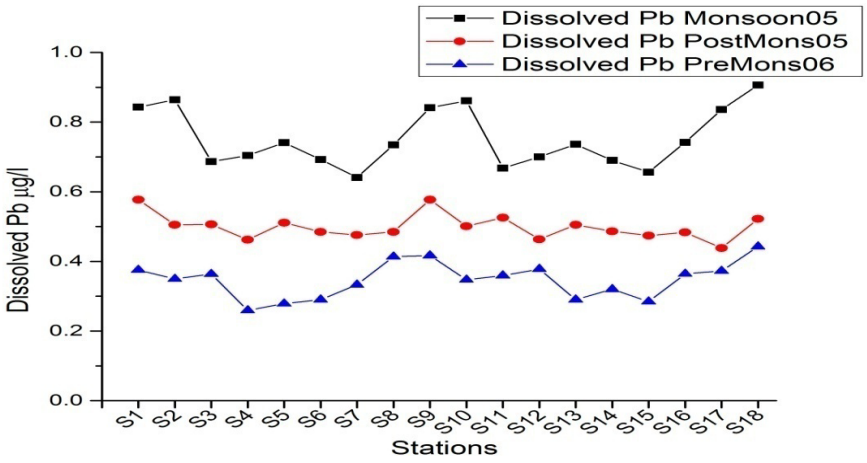

Figure 4.1.9. Seasonal variations of dissolved lead (ppb) in the water column of the Muvattupuzha River

The dissolved Pb averages (0.53 ppb) of the Muvattupuzha River broadly agree with the dissolved Pb averages of 0.70 ppb reported (*Table 4.4.1.*) for the Kali River (Manjunatha et al. 2001). However, the dissolved Pb averages (0.53 ppb) of the Muvattupuzha River is very much lower than the dissolved Pb averages (*Table 4.4.1.*) reported for the Kuttanad backwaters (10.63 ppb) and Chitrapuzha River (8.47 ppb) respectively (Unnikrishnan, 2000; Joseph, 2002). Dissolved Pb concentrations obtained during the present study are much lower than with respect to drinking water standards (10 ppb; WHO, 1993; 50 ppb; BIS, 1991; 100 ppb; ICMR, 1986). However dissolved Pb concentrations at all stations during all months exceed the world river average value of 0.2 ppb (Salomons and Forstner, 1984).

Table 4.4.1. Comparison of average dissolved metal concentrations of the Muvattupuzha River with other Indian riverine/estuarine systems as well as world river average

Rivers/Estuaries	Fe (ppb)	Mn (ppb)	Cr (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Pb (ppb	References
Cauvery river	9.90	2.60	48.8	-	38.3	6.0	81.6	0.43	136	Jameel (2001)
Godavari river	7.50	-	-	-	0.14	0.92	0.66	0.07	5.60	Patil and Shrivastava (2003)
Kali river	51000	3.95	-	0.70	0.80	1.34	10.03	0.13	0.70	Manjunatha et al. (2001)
Devi estuary	98.18	7.19	2.51	3.80	9.39	5.61	15.45	0.81	5.57	Sundaray et al. (2012)
Chitrapuzha river	62.33	13.66	4.70	1.84	13.32	5.94	27.92	2.59	8.47	Joseph (2002)
Kuttanad backwaters	73.1	2.41	2.71	0.75	4.13	2.19	10.87	2.68	10.63	Unnikrishnan (2000)
World river average	40000	8.2	-	0.20	0.50	1.50	30.0	0.02	0.10	Martin and Whitfield (1983)
World river average	55	6.0	0.50	0.20	0.30	1.00	10.0	-	0.20	Salomons and Forstner (1984)
Muvattupuzha river	36.25	22.78	0.55	0.22	0.52	1.15	13.8	0.88	0.53	Present study

The order of abundance of bimonthly average concentration of dissolved metals in water of the Muvattupuzha River is:

Fe > Mn > Zn > Cu > Cd > Pb > Cr > Ni > Co (for July and September 2005)
Fe > Mn > Zn > Cu > Cd > Cr > Ni > Pb > Co (for November 2005 and January, March and May 2006)

The order of abundance of dissolved metals during different seasons showed that Fe was the most abundant metal in the dissolved form which was followed by Mn and the least abundant metal in the dissolved form was Co. Of the 9 metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) studied the average concentrations of Cr, Ni, and Pb vary considerably between monsoon months and non-monsoon months.

4.2.1. Correlations between dissolved trace metals

To investigate the behaviour of dissolved trace metals in water column of the Muvattupuzha River, Pearson correlation coefficient (r) between metals are calculated. In the dissolved phase (n = 108), strong correlations existed (*Table 4.4.4.*) between nine trace metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb). In the dissolved phase of trace metals, the best correlations were for Fe and metals like Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb ($r = 0.538$ to 0.836) significant at $p < 0.001$, Mn and metals like Co, Ni, Cu, Cr, Zn, Cd & Pb ($r = 0.440$ to 0.843) significant at $p < 0.001$, Co and metals like Ni, Cu, Cr, Zn, Cd & Pb ($r = 0.459$ to 0.713) significant at $p < 0.001$, Cu and metals like Ni, Cr, Zn, Cd & Pb ($r = 0.446$ to 0.828) significant at $p < 0.001$, Cr and metals like Ni, Zn, Cd & Pb ($r = 0.543$ to 0.831) significant at $p < 0.001$, Ni and metals like Zn, Cd & Pb ($r = 0.543$ to 0.673) significant at $p < 0.001$, Zn and metals

like Cd & Pb ($r = 0.727$ to 0.817) significant at $p < 0.001$, Cd and metal Pb ($r = 0.748$) significant at $p < 0.001$, were observed suggesting that the cycling of these metals was firmly linked in the water column of the Muvattupuzha River. The high degree of correlations between dissolved metals indicating that they are coming from similar sources and behave similarly.

4.2.2. Spatial trends of dissolved trace metals

Dissolved Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb concentrations during all months showed considerable regional variations possibly due to varying inputs from natural or anthropogenic sources of the hinterlands. The minimum and maximum values observed for these metals also vary from one month to another. The spatial distribution pattern of dissolved metals thus indicates that trace metal inputs in dissolved form are possibly derived from land sources like municipal effluents as well as agricultural runoff.

4.2.3. Seasonal trends of dissolved trace metals

The seasonal trend of dissolved metal (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) concentrations is observed as follows: monsoon > post-monsoon > pre-monsoon. The increase in concentration of various dissolved metals in water during the monsoon months (July/September) when compared to post-monsoon months (November/January) or pre-monsoon months (March/May) indicates the influence of freshwater as a major source of trace metal input in the river. The temporal variations may be due to either natural sources or anthropogenic sources. Anthropogenic sources enhancing trace metal levels are agricultural chemicals like fertilizers and biocides or municipal sewage. Similarly, natural causes like change in pH, redox conditions or water currents

can also increases the trace metal levels in the water column of the Muvattupuzha River. The observed higher values for dissolved trace metals during monsoon season than other seasons suggests significant inputs of agro-chemical residues from agricultural lands and municipal wastes through the runoff washing process and partly from remobilisation of metals from the sedimentary phases due to strong water currents. The observed low concentrations of dissolved metals during post-monsoon and pre-monsoon periods are possibly due to dilution effect and reduced resuspension of sediments by weak water currents.

4.3. Spatial and bimonthly variations of particulate trace metals

The spatial and bimonthly variations of trace metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in suspended particulate matter (SPM) at 18 stations from the upstream regions of the Muvattupuzha River are given in Annexure as *Tables A 4.2.2. to A4.2.7.* The bimonthly mean values and standard deviations of particulate trace metals in the water column at 18 stations from the upstream regions of the Muvattupuzha River are given in *Table 4.4.2.*

In order to describe seasonal variations of particulate metals, mean values calculated for the respective two months of monsoon (July/September), post-monsoon (November/January) and pre-monsoon (March/May) periods were plotted and are shown in *Figures 4.2.0* to *4.2.8.* respectively.

Table 4.4.2. Bimonthly mean values and standard deviations of particulate trace metals in the water column of the Muvattupuzha River

Month	pFe (ppb)	pMn (ppb)	pCo (ppb)	pNi (ppb)	pCu (ppb)	pZn (ppb)	pCd (ppb)	pCr (ppb)	pPb (ppb)
July 2005	301.29±81.99	131.09±14.86	0.419±0.154	1.117±0.195	1.291±0.172	35.09±2.76	0.765±0.048	0.860±0.091	2.130±0.356
Sept 2005	295.27±80.35	124.86±12.80	0.434±0.201	1.019±0.190	1.410±0.123	36.84±3.18	0.755±0.055	0.850±0.081	2.194±0.367
Nov 2005	230.01±35.65	107.75±11.48	0.330±0.157	0.981±0.172	0.984±0.106	29.97±2.39	0.653±0.070	0.720±0.042	1.504±0.208
Jan 2006	220.83±34.20	108.83±11.59	0.354±0.179	0.887±0.179	0.978±0.111	30.08±2.60	0.626±0.061	0.710±0.074	1.424±0.215
March 2006	149.50±23.17	81.83±9.70	0.251±0.116	0.800±0.088	0.947±0.126	22.49±1.79	0.533±0.042	0.627±0.056	0.765±0.114
May 2006	152.40±32.31	85.57±9.60	0.248±0.076	0.756±0.061	0.889±0.120	21.56±1.17	0.497±0.046	0.620±0.041	0.783±0.118

4.3a. Particulate iron

Particulate iron content in river varies between 106.18 to 474.67 ppb during the months of July 2005 to May 2006. Particulate iron content in river averages to 301.29 ± 81.99 ppb, 295.27 ± 80.35 ppb, 230.01 ± 35.65 ppb, 220.83 ± 34.20 ppb, 149.50 ± 23.17 ppb and 152.40 ± 32.31 ppb respectively during the July, September, November, January, March and May months. Particulate Fe showed a higher concentration values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.0.*). The particulate Fe averages (225 ppb) of the Muvattupuzha River broadly agree with the particulate Fe averages of 321 ppb reported (*Table 4.4.3.*) for the Kakinada Bay (Ray et al. 2006). However, the particulate Fe averages (225 ppb) of the Muvattupuzha River is considerably lower than the particulate Fe averages of 321 ppb reported (*Table 4.4.3.*) for the Gautami-Godavari estuary (Ray et al. 2006). Similarly, the particulate Fe averages (225 ppb) of the Muvattupuzha River is very much lower than the particulate Fe averages of 1150 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

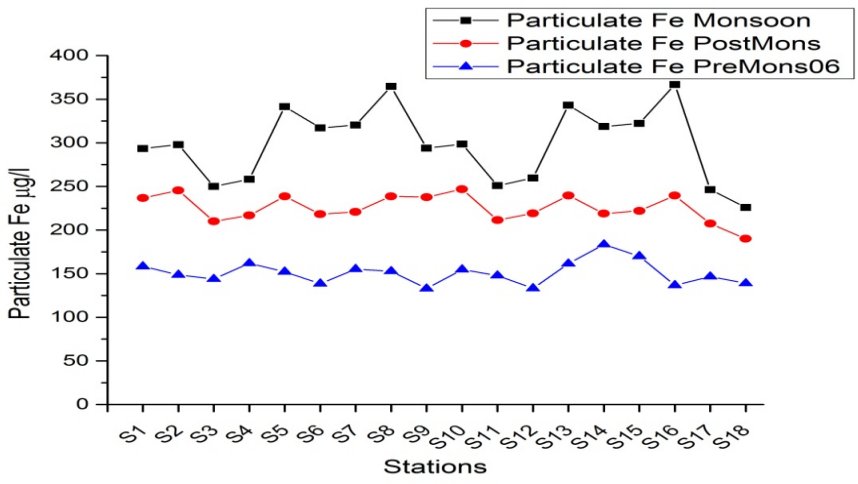

Figure 4.2.0. Seasonal variations of particulate iron (ppb) in the water column of the Muvattupuzha River

4.3b. Particulate manganese

Particulate manganese content in river varies between 65.67 to 149.25 ppb during the months of July 2005 to May 2006. Particulate manganese content in river averages to 131.09 ± 14.86 ppb, 124.86 ± 12.80 ppb, 107.75 ± 11.48 ppb, 108.83 ± 11.59 ppb, 81.83 ± 9.70 ppb and 85.57 ± 9.60 ppb respectively during the July, September, November, January, March and May months. Particulate Mn showed higher concentrations during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.1.*). The particulate Mn averages (106 ppb) of the Muvattupuzha River is very much higher than the particulate Mn averages of 13.6 ppb and 15.8 ppb reported (*Table 4.4.3.*) for the Kakinada Bay and Gautami-Godavari estuary respectively (Ray et al. 2006). However, the particulate Mn averages (106 ppb) of the Muvattupuzha River is lower than the particulate Mn averages of 190 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

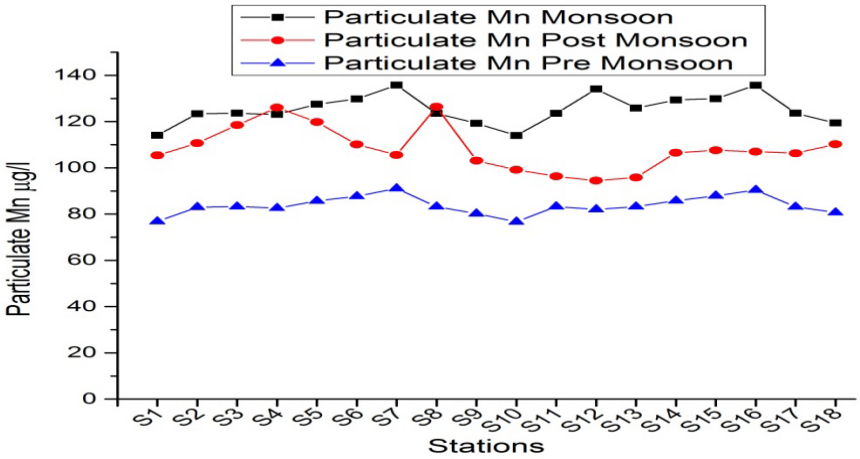

Figure 4.2.1. Seasonal variations of particulate manganese (ppb) in the water column of the Muvattupuzha River

4.3c. Particulate cobalt

Particulate cobalt content in river varies between 0.124 to 0.905 ppb during the months of July 2005 to May 2006. Particulate cobalt content in

river averages to 0.419 ± 0.154 ppb, 0.434 ± 0.201 ppb, 0.330 ± 0.157 ppb, 0.354 ± 0.179 ppb, 0.251 ± 0.116 ppb and 0.248 ± 0.076 ppb respectively during the July, September, November, January, March and May months. Particulate Co showed higher concentration values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.2.*). The particulate Co averages (0.34 ppb) of the Muvattupuzha River is very lower than the particulate Co averages of 2.50 ppb and 5.68 ppb reported (*Table 4.4.3.*) for the Kakinada Bay and Gautami-Godavari estuary respectively (Ray et al. 2006). Similarly, the particulate Co averages (0.34 ppb) of the Muvattupuzha River is also lower than the particulate Co averages of 1.40 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

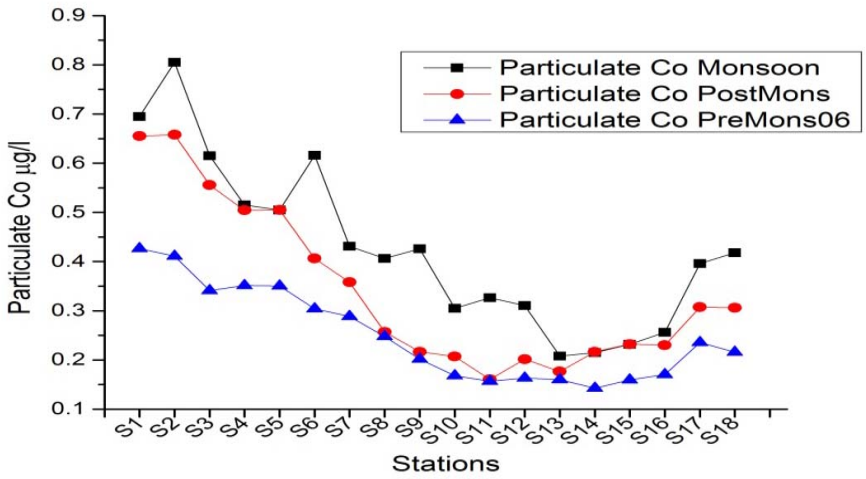

Figure 4.2.2. Seasonal variations of particulate cobalt (ppb) in the water column of the Muvattupuzha River

4.3d. Particulate nickel

Particulate nickel content in river varies between 0.665 to 1.490 ppb during the months of July 2005 to May 2006. Particulate nickel content in river averages to 1.117 ± 0.195 ppb, 1.019 ± 0.190 ppb, 0.981 ± 0.172 ppb, 0.887 ± 0.179 ppb, 0.800 ± 0.088 ppb and 0.756 ± 0.061 ppb respectively

during the July, September, November, January, March and May months. Particulate Ni showed higher concentrations during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.3.*). The particulate Ni averages (0.93 ppb) of the Muvattupuzha River is very lower than the particulate Ni averages of 21.50 ppb and 31.90 ppb reported (*Table 4.4.3.*) for the Kakinada Bay and Gautami-Godavari estuary respectively (Ray et al. 2006). Similarly, the particulate Ni averages (0.93 ppb) of the Muvattupuzha River is also lower than the particulate Ni averages of 1.38 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

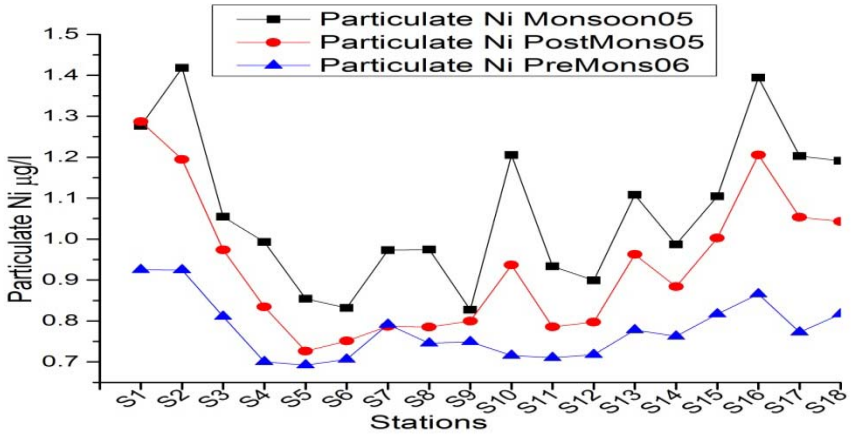

Figure 4.2.3. Seasonal variations of particulate nickel (ppb) in the water column of the Muvattupuzha River

4.3e. Particulate copper

Particulate copper content in river varies 0.655 to 1.625 ppb between during the months of July 2005 to May 2006. Particulate copper content in river averages to 1.291 ± 0.172 ppb, 1.410 ± 0.123 ppb, 0.984 ± 0.106 ppb, 0.978 ± 0.111 ppb, 0.947 ± 0.126 ppb and 0.889 ± 0.120 ppb respectively during the July, September, November, January, March and May months. Particulate Cu showed higher concentration values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure*

4.2.4.). The particulate Cu averages (1.08 ppb) of the Muvattupuzha River is very lower than the particulate Cu averages of 30.1 ppb and 30.1 ppb reported (*Table 4.4.3.*) for the Kakinada Bay and Gautami-Godavari estuary respectively (Ray et al. 2006). However, the particulate Cu averages (1.08 ppb) of the Muvattupuzha River broadly agrees with the particulate Cu averages of 1.50 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

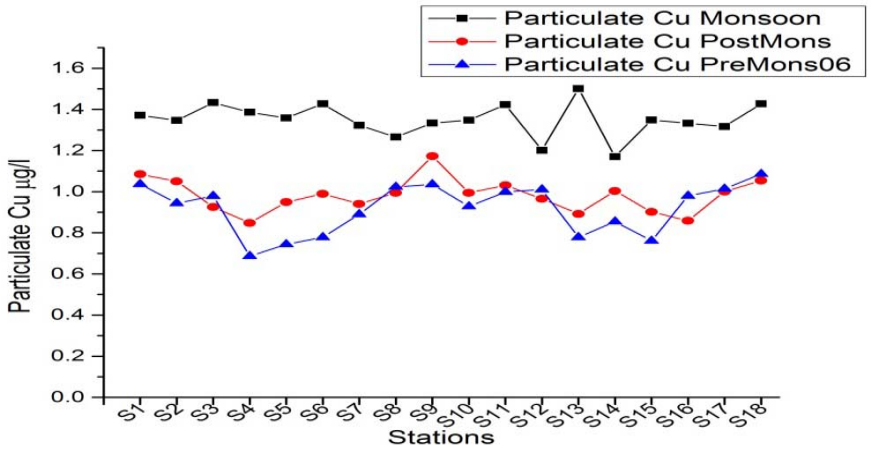

Figure 4.2.4. Seasonal variations of particulate copper (ppb) in the water column of the Muvattupuzha River

4.3f. Particulate chromium

Particulate chromium content in river varies between 0.518 to 0.985 ppb during the months of July 2005 to May 2006. Particulate chromium content in river averages to 0.860 ± 0.091 ppb, 0.850 ± 0.081 ppb, 0.720 ± 0.042 ppb, 0.710 ± 0.074 ppb, 0.627 ± 0.056 ppb and 0.620 ± 0.041 ppb respectively during the July, September, November, January, March and May months. Particulate Cr showed higher concentrations during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.5.*). The particulate Cr averages (0.73 ppb) of the Muvattupuzha River is

very lower than the particulate Cr averages of 2.38 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

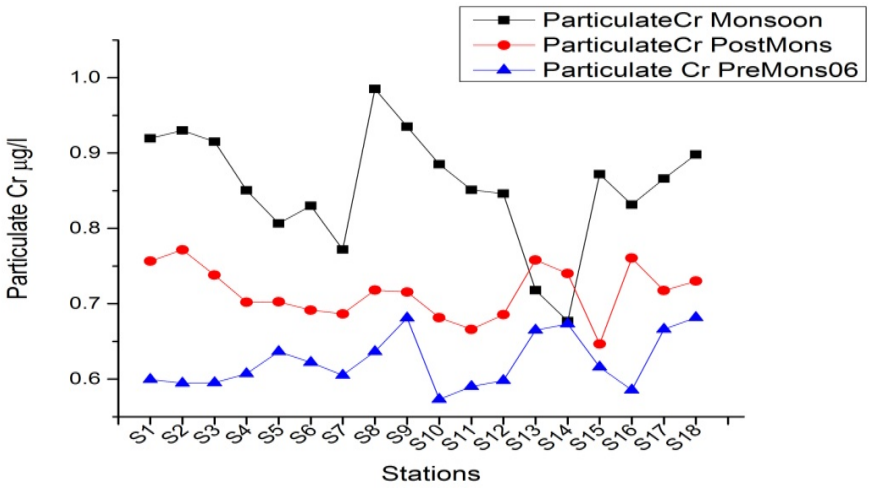

Figure 4.2.5. Seasonal variations of particulate chromium (ppb) in the water column of the Muvattupuzha River

4.3g. Particulate zinc

Particulate zinc content in river varies between 18.91 to 41.69 ppb during the months of July 2005 to May 2006. Particulate zinc content in river averages to 35.09 ± 2.76 ppb, 36.84 ± 3.18 ppb, 29.97 ± 2.39 ppb, 30.08 ± 2.60 ppb, 22.49 ± 1.79 ppb and 21.56 ± 1.17 ppb respectively during the July, September, November, January, March and May months. Particulate Zn showed higher concentration values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.6.*). The particulate Zn averages (29.37 ppb) of the Muvattupuzha River is higher than the particulate Zn averages of 9.50 ppb and 16.30 ppb reported (*Table 4.4.3.*) for the Gautami-Godavari estuary and Kakinada Bay respectively (Ray et al. 2006). Similarly, the particulate Zn averages (29.37 ppb) of the Muvattupuzha River is very higher than the particulate Zn averages of 6.71 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

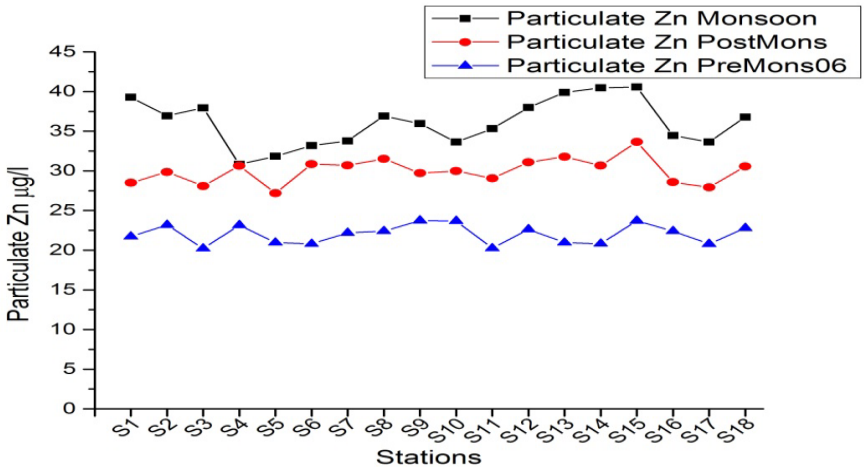

Figure 4.2.6. Seasonal variations of particulate zinc (ppb) in the water column of the Muvattupuzha River

4.3h. Particulate cadmium

Particulate cadmium content in river varies between 0.426 to 0.878 ppb during the months of July 2005 to May 2006. Particulate cadmium content in river averages to 0.765 ± 0.048 ppb, 0.755 ± 0.055 ppb, 0.653 ± 0.070 ppb, 0.626 ± 0.061 ppb, 0.533 ± 0.042 ppb and 0.497 ± 0.046 ppb respectively during the July, September, November, January, March and May months. Particulate Cd showed higher concentrations during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.7.*). The particulate Cd averages (0.64 ppb) of the Muvattupuzha River is very lower than the particulate Cd averages of 6.00 ppb and 6.75 ppb reported (*Table 4.4.3.*) for the Kakinada Bay and Gautami-Godavari estuary respectively (Ray et al. 2006). However, the particulate Cd averages (0.64 ppb) of the Muvattupuzha River is very higher than the particulate Cd averages of 0.13 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

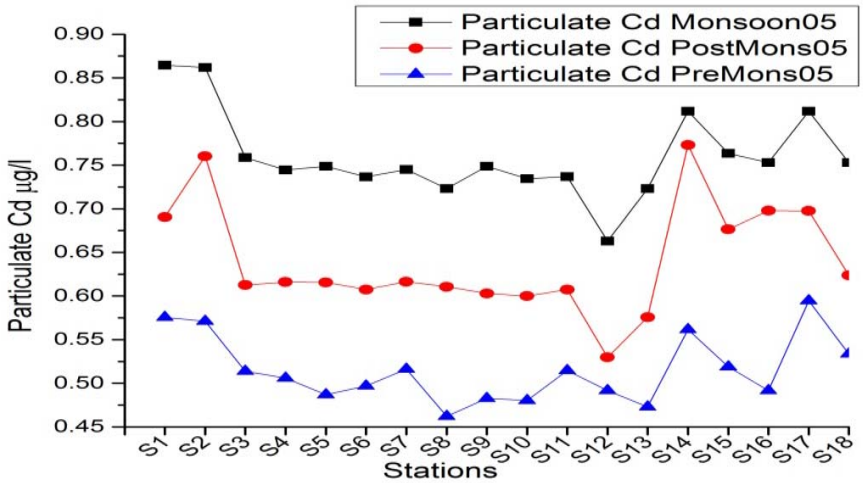

Figure 4.2.7. Seasonal variations of particulate cadmium (ppb) in the water column of the Muvattupuzha River

4.3i. Particulate lead

Particulate lead content in river varies between 0.585 to 2.766 ppb during the months of July 2005 to May 2006. Particulate lead content in river averages to 2.130 ± 0.356 ppb, 2.194 ± 0.367 ppb, 1.504 ± 0.208 ppb, 1.424 ± 0.215 ppb, 0.765 ± 0.114 ppb and 0.783 ± 0.118 ppb respectively during the July, September, November, January, March and May months. Particulate Pb showed higher concentration values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 4.2.8.*). The particulate Pb averages (1.47 ppb) of the Muvattupuzha River is lower than the particulate Pb averages of 2.06 ppb and 3.44 ppb reported (*Table 4.4.3.*) for the Kakinada Bay and Gautami-Godavari estuary respectively (Ray et al. 2006). Similarly, the particulate Pb averages (1.47 ppb) of the Muvattupuzha River is also lower than the particulate Pb averages of 2.84 ppb reported (*Table 4.4.3.*) for the Kuttanad backwaters (Unnikrishnan, 2000).

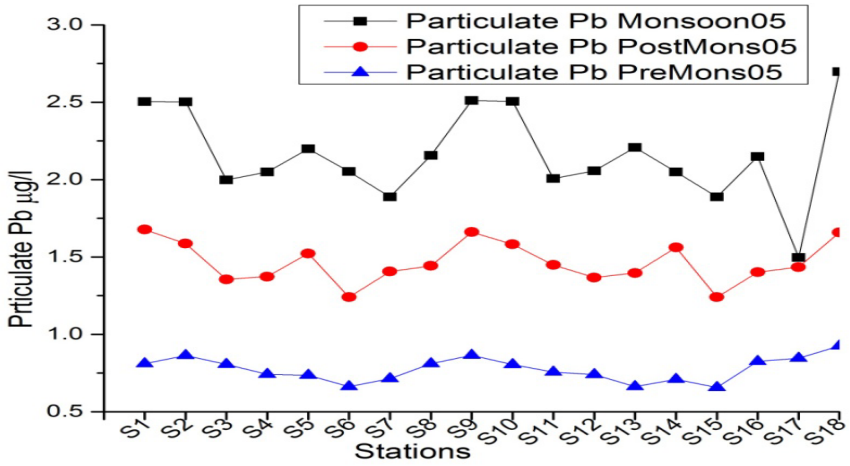

Figure 4.2.8. Seasonal variations of particulate lead (ppb) in the water column of the Muvattupuzha River

Table 4.4.3. Comparison of average particulate metal concentrations of the Muvattupuzha River with other Indian riverine/estuarine systems

Rivers/ Estuaries	Fe (ppb)	Mn (ppb)	Cr (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Pb (ppb	References
Kakinada Bay	321	13.6	-	2.50	21.5	30.1	16.30	6.00	2.06	Ray et al. (2006)
Gautami-Godavari estuary	659	15.8	-	5.68	31.9	30.1	9.50	6.75	3.44	Ray et al. (2006)
Kuttanad backwaters	1150	190	2.38	1.40	1.38	1.50	6.71	0.13	2.84	Unnikrishnan (2000)
Muvattupuzha River	225	106	0.73	0.34	0.93	1.08	29.37	0.64	1.47	Present study

The order of abundance of bimonthly average concentration of particulate metals in water of the Muvattupuzha River is:

Fe > Mn > Zn > Pb > Cu > Ni > Cr > Cd > Co (for July, September and November, 2005 and January 2006)
Fe > Mn > Zn > Cu > Ni > Pb > Cr > Cd > Co (for March 2006)
Fe > Mn > Zn > Cu > Pb > Ni > Cr > Cd > Co (for May 2006)

The order of abundance of particulate metals during different seasons showed that Fe was the most abundant metal in the particulate form which was followed by Mn and the least abundant metal in the particulate form was Co.

Of the 9 metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) studied the average concentrations of Fe, Mn, Zn, Cr, Cd and Co showed the same order of abundance between monsoon months and non-monsoon months.

4.3.1. Correlations between particulate trace metals

To investigate the behaviour of particulate trace metals in water column of the Muvattupuzha River, Pearson correlation coefficient (r) between metals are calculated. In the particulate phase (n = 108), strong correlations existed (*Table 4.4.5.*) between nine trace metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb). In the particulate phase of trace metals, the best correlations were for Fe and metals like Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb ($r = 0.383$ to 0.796) significant at $p < 0.001$, Mn and metals like Co, Ni, Cu, Cr, Zn, Cd & Pb ($r = 0.421$ to 0.733) significant at $p < 0.001$, Co and metals like Ni, Cu, Cr, Zn, Cd & Pb ($r = 0.381$ to 0.525) significant at $p < 0.001$, Cu and metals like Ni, Cr, Zn, Cd & Pb ($r = 0.467$ to 0.761) significant at $p < 0.001$, Cr and metals like Ni, Zn, Cd & Pb ($r = 0.586$ to 0.825) significant at $p < 0.001$, Ni and metals like Zn, Cd & Pb ($r = 0.564$ to 0.734) significant at $p < 0.001$, Zn and metals like Cd & Pb ($r = 0.810$ to 0.849) significant at $p < 0.001$, Cd and metal Pb ($r = 0.829$) significant at $p < 0.001$, were observed suggesting that the cycling of these metals was firmly linked in the water column of the Muvattupuzha River. The high degree of correlations between particulate metals indicating that they are coming from similar sources and behave similarly.

4.3.2. Spatial trends of particulate trace metals

Particulate Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb concentrations during all months showed considerable regional variations due to varying inputs from natural or anthropogenic sources of the hinterlands. The minimum and maximum values observed for these metals also vary from one month to

another due to variation in partition dynamics between dissolved and particulate phases. The spatial distribution pattern of particulate metals thus indicates increased inputs of trace metals in river from suspended particles which are possibly derived from land sources like municipal effluents as well as agricultural runoff.

4.3.3. Seasonal trends of particulate trace metals

The seasonal trend in concentration of particulate metals is observed as follows: monsoon > post-monsoon > pre-monsoon. The increase in concentration of various particulate metals in water during the monsoon months (July/September) when compared to post-monsoon months (November/January) or pre-monsoon months (March/May) indicates the influence of freshwater as a major source of trace metal input in the river. The observed higher values for particulate trace metals during monsoon season than other seasons is due to significant inputs of agro-chemical residues from agricultural lands and municipal wastes through the runoff process and resuspension of metal rich sediments due to strong water currents. The strong adsorption of metal rich fine particles onto suspended particulate matter resulted in an increase in concentration of particulate metals during monsoon when compared to post-monsoon or pre-monsoon periods. The observed low concentrations of particulate metals during post-monsoon and pre-monsoon periods are possibly due to reduced resuspension of sediments by weak water currents.

4.4. Partitioning of trace metals in the water column of the Muvattupuzha River

In order to find out the interrelationships between trace metals in dissolved and particulate phases with environmental parameters like pH,

temperature and dissolved oxygen, Pearson correlation coefficient (r) among these parameters were determined.

4.4.1. Correlations of dissolved and particulate trace metals with environmental parameters

All metals (n = 108) do not show any significant correlations with pH in the dissolved and particulate phases. A high degree of negative correlation ($r = -0.388$ to -0.732, significant at $p < 0.001$) was observed between the nine dissolved trace metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) and temperature. Similarly, a high degree of negative correlation ($r = -0.385$ to -0.768, significant at $p < 0.001$) was observed between the nine particulate trace metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) and temperature.

In the dissolved phase (n = 108), strong correlations ($r = 0.384$ to 0.805, significant at $p < 0.001$) exists (*Table 4.4.4.*) between nine trace metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) and dissolved oxygen. Similarly, in the particulate phase (n = 108), strong correlations ($r = 0.386$ to 0.809, significant at $p < 0.001$), exists (*Table 4.4.5.*) between nine trace metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) and dissolved oxygen.

Trace metal transport in rivers is linked to scavenging mechanisms involving hydrous oxides (Forstner and Wittmann, 1983). Fe and Mn being the abundant elements in the dissolved and particulate phases of the river, exert a major control on the distribution of other elements. The oxides and hydrous oxides of Fe and Mn constitute significant sink to trace metals in rivers through adsorption of other trace metals since metal oxide surfaces provide attractive sites for metal ion binding (Balls, 1986, 1990; Hall et al. 1996; Jenne, 1968). Thus the highly significant ($p < 0.001$) dissolved inter-elemental Fe-Mn correlation, Fe-dissolved oxygen correlation, Mn-dissolved oxygen

correlation revealed the formation of stable Fe–Mn oxyhydroxides, while the significant correlation of particulate Fe with all other metals indicated their adsorption into the suspended particulate matter which then gets incorporated into the bottom sediments by scavenging reactions in the water column. The results of the correlation matrix thus indicated that a substantial fraction of the trace metal in dissolved phase were adsorbed onto Fe and Mn geochemical phases of the suspended particulate matter which can contaminate the bottom sediments by sinking. The adsorption of trace metals into SPM revealed that the Muvattupuzha River acts as a sink for trace metals discharged from anthropogenic sources.

Table 4.4.4. Pearson product-moment correlation coefficients (r) between dissolved trace metals, pH, temperature and dissolved oxygen in the Muvattupuzha River (n= 108)

Dissolved metal	dFe	dMn	dCo	dCr	dCu	dNi	dZn	dCd	dPb	p H	Temp	D.O
dFe	**1.000**											
dMn	0.836	**1.000**										
dCo	0.641	0.609	**1.000**									
dCr	0.697	0.732	0.613	**1.000**								
dCu	0.649	0.710	0.713	0.693	**1.000**							
dNi	0.538	0.440	0.459	0.446	0.543	**1.000**						
dZn	0.792	0.843	0.642	0.689	0.729	0.543	**1.000**					
dCd	0.742	0.743	0.682	0.828	0.831	0.578	0.817	**1.000**				
dPb	0.717	0.745	0.645	0.635	0.684	0.673	0.727	0.748	**1.000**			
p H	0.004	-0.027	-0.102	-0.054	-0.038	-0.018	0.079	-0.005	-0.072	**1.000**		
Temp	-0.665	-0.732	-0.388	-0.521	-0.533	-0.426	-0.731	-0.611	-0.556	-0.104	**1.000**	
D.O	0.736	0.805	0.502	0.778	0.639	0.384	0.763	0.798	0.635	-0.019	-0.717	**1.000**

Table 4.4.5. Pearson product-moment correlation coefficients (r) between particulate trace metals, pH, temperature and dissolved oxygen in the Muvattupuzha River (n= 108)

Particulate metal	pFe	pMn	pCo	pCr	pCu	pNi	pZn	pCd	pPb	p H	Temp	D.O
pFe	**1.000**											
pMn	0.796	**1.000**										
pCo	0.383	0.421	**1.000**									
pCr	0.597	0.605	0.381	**1.000**								
pCu	0.612	0.636	0.485	0.686	**1.000**							
pNi	0.462	0.421	0.423	0.467	0.586	**1.000**						
pZn	0.695	0.733	0.385	0.691	0.725	0.564	**1.000**					
pCd	0.697	0.709	0.462	0.761	0.825	0.635	0.849	**1.000**				
pPb	0.678	0.717	0.525	0.687	0.765	0.734	0.810	0.829	**1.000**			
p H	0.115	-0.012	-0.133	0.003	-0.046	-0.068	0.071	0.026	-0.059	**1.000**		
Temp	-0.635	-0.603	-0.385	-0.494	-0.551	-0.478	-0.768	-0.686	-0.649	-0.104	**1.000**	
D.O	0.687	0.724	0.386	0.725	0.643	0.488	0.781	0.809	0.717	-0.019	-0.717	**1.000**

4.4.2. Distribution Coefficient (Kd) of trace metals

The distribution of a metal between the dissolved and particulate phases can be expressed by a partition coefficient or distribution coefficient (Kd) which is defined as the ratio of the particulate metal concentration (µg l^{-1}) over the dissolved metal concentration (µg l^{-1}). Kd values represents the relative affinity of trace metals for dissolved phase or particulate phases and is of fundamental significance in the description of the geochemical properties of elements in an aquatic system and in pollution impact assessments (Martin and Whitfield, 1983; Wood et al. 1995). An elevated Kd value indicates affinity for the particulate phase.

The bimonthly spatial and bimonthly variations of partition coefficients for the metals Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb in water at 18 stations from the upstream regions of the Muvattupuzha River are given in Annexure as *Tables A4.2.8. to A4.3.3*. The bimonthly average partition coefficient values do not exhibit considerable seasonal variations. However the bimonthly ranges

of partition coefficient values (Kd) for various metals are as follows: Fe (3.76 to 10.87), Mn (3.28 to 6.74), Co (1.02 to 3.16), Ni (1.53 to 2.49), Cu (0.850 to 1.027), Cr (1.16 to 1.43), Zn (1.62 to 3.00), Cd (0.61 to 0.91), Pb (1.60 to 3.73). These ranges or spatial variations of partition coefficient values for various metals are a consequence of variations in the relative spatial enrichment of these metal in the particulates when compared with the total metals concentration in the water column (*Tables A4.3.4. to A4.3.9.*) which are as follows: Fe (83.3 to 91.1 %), Mn (79.0 to 91.6 %), Co (50.3 to 75.4 %), Ni (60.5 to 71.3 %), Cu (45.9 to 50.7 %), Cr (53.6 to 58.9 %), Zn (61.8 to 75.0 %), Cd (38.4 to 45.5 %), Pb (61.5 to 78.9 %).

The adsorption of a metal on the suspended matter is governed by the pH of the river water and also by the nature of the suspended particles. Thus K_d can be influenced by pH, changes in suspended particle concentration, particle size and the nature of particles (Bourg, 1983; 1987). SPM may consist of biogenous and lithogeous particles with organic and mineral phases respectively that will contain different co-ordination sites to bind metals (Olsen et al. 1982; Stumm, 1992). Even though pH is assumed to be the most important factor in explaining the trace metal partitioning in dissolved and particulate phases, in systems which are highly buffered and relatively stable with respect to pH, such as the Muvattupuzha River, the influence of other environmental variables may be more important in explaining the variation in trace metal partitioning. Thus the moderate ranges or spatial variations of partition coefficient values for various metals are a consequence of the variations in proportions of lithogenous and biogenous particles binded with metals in suspended particulate matter and variations in dissolved metal concentrations occurring independently from anthropogenic sources in the water column of the Muvattupuzha River (Unnikrishnan et al. 2006).

The averaged partition coefficient values for the metals Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb in the water column during all seasons demonstrate a ranking for the metals which were as follows: Fe > Mn > Pb > Zn > Ni > Co > Cr > Cu > Cd. This ranking may be attributed to the different bio-geochemical behaviour of these elements in the Muvattupuzha River. Of all the metal investigated, cadmium and iron showed the lowest and highest Kd values respectively. Values of Kd for the particle-reactive and biologically required Fe are much higher than those organically strong bound trace metal like Cu. A high value of Kd indicates a strong affinity between the trace metal and particle. Fe showed the strongest affinity for particulate phase with a mean Kd value of ~ 6 during all seasons. Mn showed a similar strongest affinity for the particulate phase with a mean Kd value of ~ 5 during all seasons. For Fe, the particulate percentages of the total load were 83.3 to 91.1 % whereas for Mn, the particulate percentages of the total load were 79.0 to 91.6 %.

Lead showed a moderate affinity (mean Kd value ~ 3 during monsoon and post-monsoon periods) to the particulate phase. In view of high affinity of lead to particles especially of terrigenous origin it is assumed that lead is adsorbed by organic particulates which are further supported by the 61.5 to 78.9 % of the total metal load existing in the particulate form (Muller, 1996). Zinc showed a moderate affinity (mean Kd value ~ 2 during all seasons) to the particulate phase which is supported by the 61.8 to 75.0 % of the total zinc existing in the particulate form. Nickel also shows some affinity (mean Kd value ~ 1.7 during all seasons) to the particulate phase due to some fractional association with suspended particles probably in the form of fine-grained terrigenous matter which is supported by the 60.5 to 71.3 % of the total Ni existing in the particulate form. Similarly, Co followed by Cr also showed some affinity for particulate phase than the dissolved phase. Copper showed

an equal affinity (mean Kd value ~ 0.9 during all seasons) towards particulate and dissolved phases which is supported by 45.9 to 50.7 % of the total copper existing in the particulate form. Due to its inertness to adsorption on solid surfaces the metal Cd during all seasons was leastly associated with particles with a mean value of Kd ~ 0.7 which is further supported by > 60 % of the total Cd existing in the dissolved phase.

4.5. Quantification of dissolved trace metals by enrichment ratio

Trace metal inputs to rivers can be from both natural and anthropogenic sources. In the present study, an enrichment ratio for trace metals is used as a tool for quantification of contamination of the Muvattupuzha River waters with respect to global background values reported for world river metal averages (Martin and Whitfield, 1983; Salomons and Forstner, 1984). World river metal averages reported for Fe (55 ppb), Mn (6 ppb), Zn (10 ppb), Cr (0.5 ppb),Cu (1.0 ppb), Co (0.2 ppb), Ni (0.3 ppb) and Pb (0.2 ppb) were taken as background values (Salomons and Forstner, 1984). For Pb the world river average reported value of 0.02 ppb is taken as a background value (Martin and Whitfield, 1983).

The enrichment ratio (ER) for dissolved trace metals was calculated as the ratio of the concentration of dissolved constituents to the background concentration of dissolved constituents. An ER > 1 has been termed as enrichment whereas ER < 1 was taken as no enrichment with respect to background value.

The ER for the dissolved metals of the Muvattupuzha River waters with respect to global background values are presented in Annexure as *Tables* A*4.1.6. to* A*4.2.1.*, respectively. The enrichment ratio for various metals lies in the following ranges: Cd (31.13 to 62.19), Mn (2.20 to 5.64), Pb (1.270 to

4.725), Ni (1.28 to 2.76), Zn (0.85 to 1.98), Co (0.60 to 2.79), Cu (0.76 to 1.86), Cr (0.85 to 1.50), Fe (0.30 to 1.27). The enrichment ratio of these metals during all seasons follows the decreasing order: Cd > Mn > Pb > Ni > Zn > Co > Cu > Cr > Fe. Cd showed the highest enrichment ratio whereas Fe showed the lowest enrichment ratio. The order of enrichment ratio of various metals indicates that Cd, Mn, Pb and Ni are sufficiently enriched in the Muvattupuzha River waters from anthropogenic sources at a higher rate than the other metals.

All the metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) occasionally showed ER > 1 in the Muvattupuzha River suggesting its enrichment and contribution from anthropogenic sources. For instance, Fe showed ER values slightly > 1 at stations S_{15} to S_{16} during July 2005, and at stations S_1 to S_2, S_5 to S_7 during September 2005 suggesting some contaminant sources for iron enrichment. Mn showed ER values ~ 4.2 to 5.5, ~3.5 to 4.0 and ~ 2.0 to 2.8 at almost all stations during monsoon months, post-monsoon months and pre-monsoon months respectively suggesting some contaminant sources for manganese enrichment.

Co showed ER values ~ 1.2 to 2.5 at stations S_1 to S_{12}, S_{15} to S_{18} during July/September 2005, at stations S_1 to S_8, S_{17} to S_{18} during November 2005, S_1 to S_5 during January 2006, and at stations S_1 to S_4 during May 2006 respectively suggesting some contaminant sources for cobalt enrichment. Ni showed ER values ~ 1.5 to 2.7, ER values ~1.2 to 2.4 and ER values ~ 1.3 to 1.7 at almost all stations during monsoon months, post-monsoon months and pre-monsoon months respectively suggesting some contaminant sources for nickel enrichment.

Cu showed, ER values ~ 1.2 to 1.9 at stations S_1 to S_{18} during July/September 2005, ER values ~ 1.1 to 1.2 at stations S_1 and S_7 to S_{11} during

November 2005, ER values ~ 1.1 to 1.2 at stations S_1 to S_3, S_9 and S_{17} to S_{18} during January 2006, and ER value ~ 1.1 at stations S_8 to S_9, S_{11} to S_{12} and S_{16} to S_{18} during March 2006, ER value ~ 1.1 at stations S_8 to S_9 and S_{17} to S_{18} during May 2006 suggesting some contaminant sources for copper enrichment. Cr showed ER values ~ 1.0 to 1.5 at all stations during July/September/November 2005 and January 2006 suggesting some contaminant sources for chromium enrichment.

Zn showed ER values ~ 1.5 to 1.9 at all stations during July/September/ November 2005 and at all stations during January 2006 suggesting some contaminant sources for zinc enrichment. Cd showed, very high ER values ~ 45 to 60, ER values ~40 to 50 and ER values ~ 30 to 40 at almost all stations during monsoon months, post-monsoon months and pre-monsoon months respectively suggesting some strong contaminant sources for cadmium enrichment. Pb showed ER values ~ 3.2 to 4.7, ER values ~2.1 to 3.1 and ER values ~ 1.3 to 2.1 at almost all stations during monsoon months, post-monsoon months and pre-monsoon months respectively suggesting some contaminant sources for lead enrichment.

All the metals showed higher enrichment ratio during monsoon months when compared to post-monsoon or pre-monsoon months suggesting the contribution from land runoff materials in the trace metal enrichment of the Muvattupuzha River waters. The anthropogenic sources that likely enhancing the metal levels in the area is agricultural runoff (stations S_1, S_2, S_3, S_4, S_6, S_{10} & S_{18} are surrounded by agricultural lands) and domestic waste water discharges (stations S_9, S_{11} & S_{15} are situated nearby by municipal townships). Thus enrichment ratio data suggest that agricultural wastes and municipal wastes contribute to most of the metals enrichment in the Muvattupuzha River waters.

4.6. Concluding remarks

Dissolved and Particulate trace metals were studied during the bimonthly intervals of July 2005 to May 2006 from the upstream stretch of the Muvattupuzha River at stations of Moolamattam to Piravam which is flowing through municipal townships and agricultural lands. The order of abundance of dissolved and particulate metals during different seasons showed that Fe was the most abundant metal which was followed by Mn and the least abundant metal was Co. A high degree of metal-metal correlations in dissolved and particulate forms indicate that they are coming from similar anthropogenic sources and behave similarly. All the dissolved metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) occasionally showed ER > 1 in the Muvattupuzha River suggesting its enrichment and contribution from anthropogenic sources like agricultural and municipal wastes.

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Chapter 5

TOTAL TRACE METAL CONTENTS IN SURFICIAL SEDIMENTS OF THE MUVATTUPUZHA RIVER

5.1. Introduction

Pollution of the aquatic environment by heavy metals is of wide environmental concern due to its persistence, toxicity and bio-accumulative nature (Birch and Taylor, 2002; Mathew et al. 2013). Metal pollution in the riverine environment is usually caused by land run-off, mining, dredging, agricultural activities, industrial activities and domestic inputs (Macklin et al. 2006; Nouri et al. 2008; Reza and Singh, 2010). Trace metals entering the rivers become bound to suspended particulate matter which after settling down becomes an integral part of the bottom sediments (Sutherland, 2000; Suthar et al. 2009). Bottom sediments are widely used as sensitive indicators of environmental contamination by trace metals in the rivers, estuaries and oceans and monitoring of trace metal enrichment in bottom sediments might be an important component of understanding environmental pollution (Harikumar et al. 2009; Nasir and Harikumar, 2011; Song et al. 2011; Varol and Sen, 2012). Sediments usually act as sink of the heavy metals but however under changing environmental conditions of the river, sediment bound metals can turn into a source by remobilization and enter the water column (Olsen et

al. 1993; Feng et al. 1998; Manoj and Padhy, 2014). These metals in the dissolved form can become bio-available to the free floating organisms of the river like fishes and can ultimately enter into the human beings via, food chain (Ip et al. 2007). Hence, monitoring and assessment of trace metal levels in water and sediments of natural streams has gained importance in river conservation plans (Begum et al. 2009; Mohiuddin et al. 2010; Sekabira et al. 2010; Sun et al. 2012). Even though data on trace metal concentrations in sediments from the downstream regions affected by industrial pollution of the Muvattupuzha River are available to a limited extent (Padmalal and Seralathan, 1995; Padmalal et al. 1997), information on the same from the upstream regions affected by urban and agricultural pollution of the Muvattupuzha River are not available.

RESULTS AND DISCUSSION

5.2. Spatial and bi-monthly variations of total trace metals in sediments

The spatial and bimonthly variations of total trace metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in sediments at 18 stations from the upstream regions of the Muvattupuzha River are given in Annexure as *Tables A5.1.0 to A5.1.5*. The bimonthly mean values and standard deviations of total metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in sediments at 18 stations from the upstream regions of the Muvattupuzha River is also given in *Table 5.1.6.* In order to describe seasonal variations of total metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in sediments, mean values of each elements calculated for the respective two months of monsoon (July/September), post-monsoon (November/January) and pre-monsoon (March/May) periods were plotted and are shown in *Figures 5.1.1.* to *5.1.9.* respectively.

Table 5.1.6. Bimonthly mean concentrations and standard deviations of total trace metals in the sediments of the Muvattupuzha River

Month	Fe (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)
July 2005	35999±12599	205.78±126.58	8.17±2.36	19.69±7.68	13.03±3.97	44.87±15.61	0.36±0.07	36.28±6.93	10.13±3.05
Sept 2005	29467±12199	273.80±116.58	10.04±4.12	51.89±9.29	19.55±6.76	59.62±17.37	0.30±0.08	25.88±6.10	12.17±5.02
Nov 2005	27251±11401	148.86±64.98	7.34±2.60	39.37±8.54	13.53±5.26	32.90±10.43	0.38±0.05	15.98±2.49	10.63±3.45
Jan 2006	24844±6515	126.84±31.62	8.05±3.35	21.75±8.89	12.34±7.51	35.08±11.55	0.42±0.08	18.82±2.61	11.60±2.72
March 2006	21677±11147	131.18±52.42	5.56±3.07	22.25±7.58	8.79±4.40	35.16±16.36	0.36±0.16	16.68±6.65	9.26±3.89
May 2006	25215±16585	152.97±102.02	5.48±4.86	13.32±6.85	7.94±4.45	24.88±11.25	0.27±0.18	10.85±6.39	7.20±3.85

5.2 a. Iron

Iron content in sediments varies between 3584 to 59565 ppm during the months of July 2005 to May 2006. The bimonthly spatial Fe concentration ranges in sediments of 3.58 to 5.96 % found during the present study *(Table 5.1.7.),* is well within the reported Fe concentration ranges of 0.43 to 6.01 % and 0.73 to 8.60 % in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). Iron content in sediments averages to 35999 ± 12599 ppm, 29467 ± 12199 ppm, 27251 ± 11401 ppm, 24844 ± 6515 ppm, 21677 ± 11147 ppm and 25215 ± 16585 ppm respectively during the July, September, November, January, March and May months. Average Fe content in sediments (*Figure 5.1.1.)* showed the following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon.

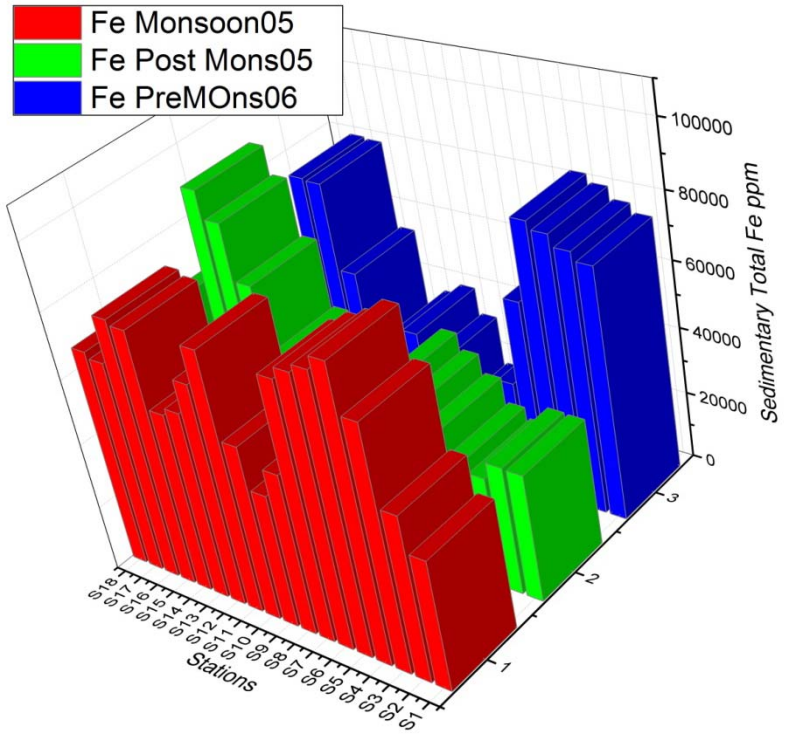

Figure 5.1.1. Seasonal variations of total iron (ppm) in sediments of the Muvattupuzha River

Table 5.1.7. Comparison of ranges/averages of total trace metal concentrations in sediments of the Muvattupuzha River with other Indian riverine/estuarine systems

Rivers/ Estuaries	Fe (%)	Mn (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Pb (ppm)	References
Periyar river	0.43-6.01	86-636	17-148	-	46-141	-	37-107	-	11-117	Maya (2005)
Periyar river	2.35	313	75	-	95	-	64	-	62	Maya (2005)
Chalakudy river	0.73-8.60	292-2554	31-149	-	58-126	-	33-168	-	23-116	Maya (2005)
Chalakudy river	4.02	737	86	-	90	-	82	-	65	Maya (2005)
Gomti river	-	82.6-263.1	2.22-19.13	-	6.53-29.76	1.38-35.03	3.06-101.73	0.34-8.38	6.27-75.33	Singh et al. (2005)
Gomti river	-	148	8.15	-	15.17	5	41.67	2.42	40.33	Singh et al. (2005)
Chitrapuzha river	2.6	245	101	16.4	62.6	28.5	177	12.9	22.4	Joseph(2002)
Kuttanad backwaters	6.88	540	156.3	61	52.7	31.7	138.8	2.0	54.9	Unnikrishnan (2000)
Cochin backwaters	5.4	451	109	19	48.5	31.2	196.7	1.8	34	Selvam et al. (2011)
Shale averages	4.72	850	90	19	68	45	95	0.3	20	Turekian and Wedepohl (1961)
Muvattupuzha river	3.58-5.96	18.81-498.45	3.74-44.64	0.10-17.54	0.23-93.99	1.76-48.04	5.96-77.77	0.07-0.83	1.79-23.59	Present study
Muvattupuzha river	2.74	173	20.75	7.44	28	12.53	38.75	0.35	10.17	Present study

The bimonthly average Fe concentration of 2.74 % in sediments found during the present study *(Table 5.1.7.),* agrees well with the reported average Fe concentration values of 2.35 %, 4.02 % and 2.60 % in sediments of the Periyar, Chalakudy and Chitrapuzha Rivers respectively (Joseph, 2002; Maya, 2005). However, the bimonthly average Fe concentration of 2.74 % in sediments found during the present study *(Table 5.1.7.),* is very lower than the reported average Fe concentration values of 6.88 % and 5.40 % in sediments of the Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Selvam et al. 2011).

5.2b. Manganese

Manganese content in sediments varies between 18.81 to 498.45 ppm during the months of July 2005 to May 2006. The bimonthly spatial Mn concentration ranges in sediments of 18.81 to 498.45 ppm found during the present study *(Table 5.1.7.),* is considerably lower than the reported Mn concentration ranges of 86 to 636 ppm and 292 to 2554 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). The bimonthly spatial Mn concentration ranges in sediments of 18.81 to 498.45 ppm found during the present study broadly agrees with the reported Mn concentration ranges of 82.6 to 263.1 ppm in sediments of the Gomti River which is a tributary of Ganges (Singh et al. 2005).

Manganese content in sediments averages to 205.78 ± 126.58 ppm, 273.80 ± 116.58 ppm, 148.86 ± 64.98 ppm, 126.84 ± 31.62 ppm, 131.18 ± 52.42 ppm and 152.97 ± 102.02 ppm respectively during the July, September, November, January, March and May months. Average Mn content in sediments (*Figure 5.1.2.)* showed the following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon. The bimonthly

average Mn concentration of 173 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Mn concentration of 313 ppm and 737 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). The bimonthly average Mn concentration of 173 ppm in sediments found during the present study *(Table 5.1.7.),* is higher than the reported average Mn concentration of 148 ppm in sediments of the Gomti River (Singh et al. 2005). However, the bimonthly average Mn concentration of 173 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Mn concentrations of 245 ppm, 540 ppm and 451.3 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

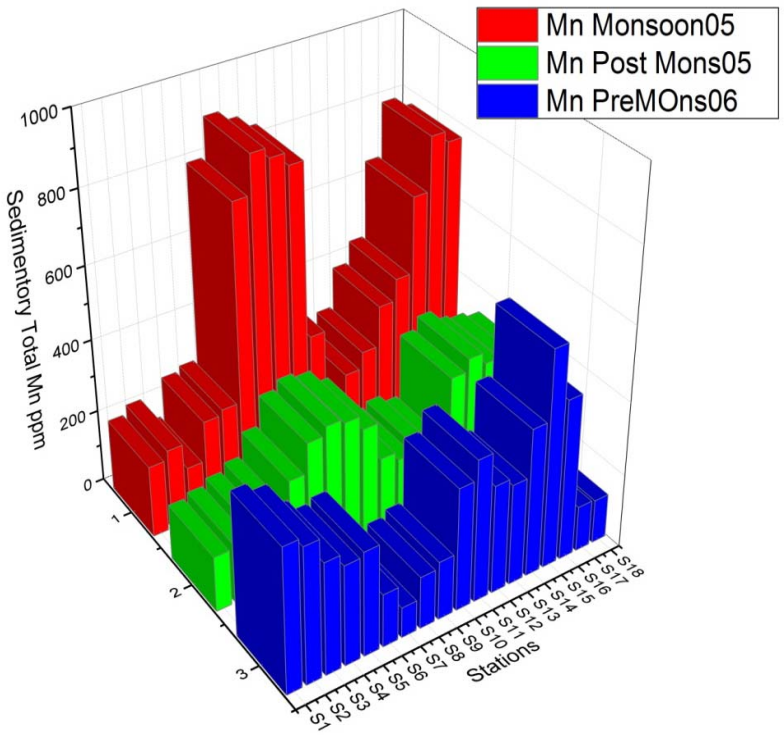

Figure 5.1.2. Seasonal variations of total manganese (ppm) in sediments of the Muvattupuzha River

5.2c. Cobalt

Cobalt content in sediments varies between 0.10 to 17.54 ppm during the months of July 2005 to May 2006. Cobalt content in sediments averages to 8.17 ± 2.36 ppm, 10.04 ± 4.12 ppm, 7.34 ± 2.60 ppm, 8.05 ± 3.35 ppm, 5.56 ± 3.07 ppm and 5.48 ± 4.86 ppm respectively during the July, September, November, January, March and May months. Average Co content in sediments (*Figure 5.1.3.)* showed the following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon. The bimonthly average Co concentration of 7.44 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Co concentrations of 16.4 ppm, 61 ppm and 18.95 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

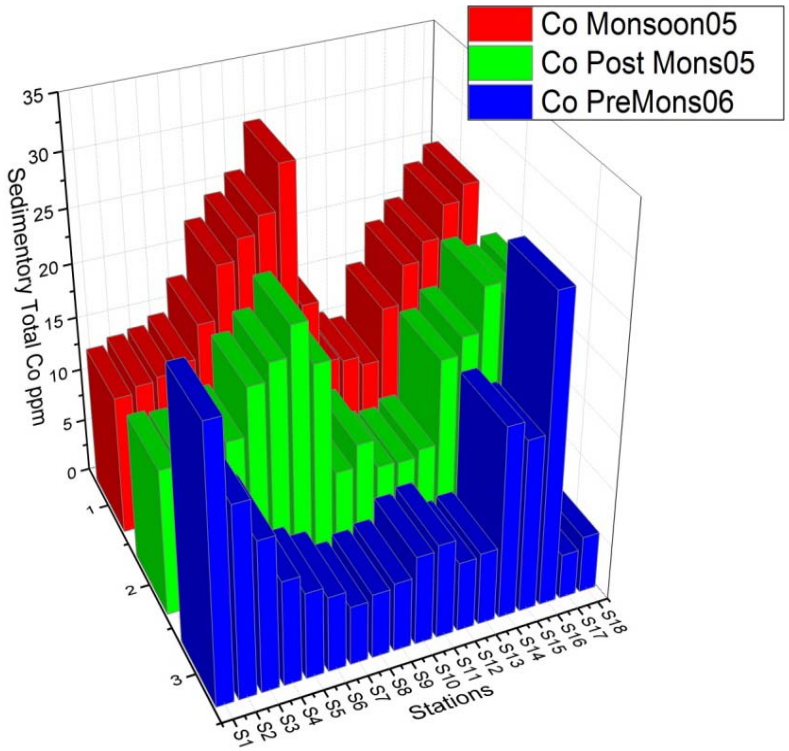

Figure 5.1.3. Seasonal variations of total cobalt (ppm) in sediments of the Muvattupuzha River

5.2d. Nickel

Nickel content in sediments varies between 0.23 to 93.99 ppm during the months of July 2005 to May 2006. The bimonthly spatial Ni concentration ranges in sediments of 0.23 to 93.99 ppm found during the present study *(Table 5.1.7.),* broadly agrees with the reported Ni concentration ranges of 46 to 141 ppm and 58 to 126 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). The bimonthly spatial Ni concentration ranges in sediments of 0.23 to 93.99 ppm found during the present study broadly agrees with the reported Ni concentration ranges of 6.53 to 29.76 ppm in sediments of the Gomti River (Singh et al. 2005).

Nickel content in sediments averages to 19.69 ± 7.68 ppm, 51.89 ± 9.29 ppm, 39.37 ± 8.54 ppm, 21.75 ± 8.89 ppm, 22.25 ± 7.58 ppm and 13.32 ± 6.85 ppm respectively during the July, September, November, January, March and May months. Average Ni content in sediments (*Figure 5.1.4.)* showed the following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon. The bimonthly average Ni concentration of 28 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Ni concentration of 95 ppm and 90 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). The bimonthly average Ni concentration of 28 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably higher than the reported average Ni concentration of 15.17 ppm in sediments of the Gomti River (Singh et al. 2005). However, the overall bimonthly average Ni concentration of 28 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Ni concentrations of 62.6 ppm, 52.7 ppm and 48.5 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

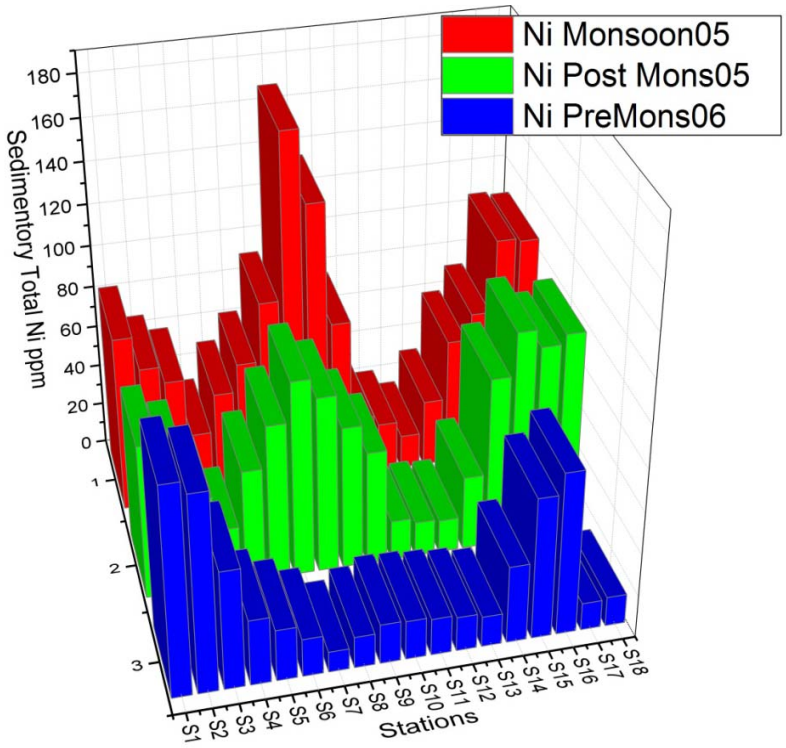

Figure 5.1.4. Seasonal variations of total nickel (ppm) in sediments of the Muvattupuzha River

5.2e. Copper

Copper content in sediments varies between 1.76 to 48.04 ppm during the months of July 2005 to May 2006. The bimonthly spatial Cu concentration ranges in sediments of 1.76 to 48.04 ppm found during the present study *(Table 5.1.7.),* is higher than the reported Cu concentration ranges of 1.38 to 35.03 ppm in sediments of the Gomti River (Singh et al. 2005).

Copper content in sediments averages to 13.03 ± 3.97 ppm, 19.55 ± 6.76 ppm, 13.53 ± 5.26 ppm, 12.34 ± 7.51 ppm, 8.79 ± 4.40 ppm and 7.94 ± 4.45 ppm respectively during the July, September, November, January, March and May months. Average Cu content in sediments (*Figure 5.1.5.)* showed the following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon. The bimonthly average Cu concentration of 12.53 ppm in

sediments found during the present study *(Table 5.1.7.),* is considerably higher than the reported average Cu concentration of 5 ppm in sediments of the Gomti River (Singh et al. 2005). But, the bimonthly average Cu concentration of 12.53 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Cu concentrations of 28.5 ppm, 31.7 ppm and 31.2 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

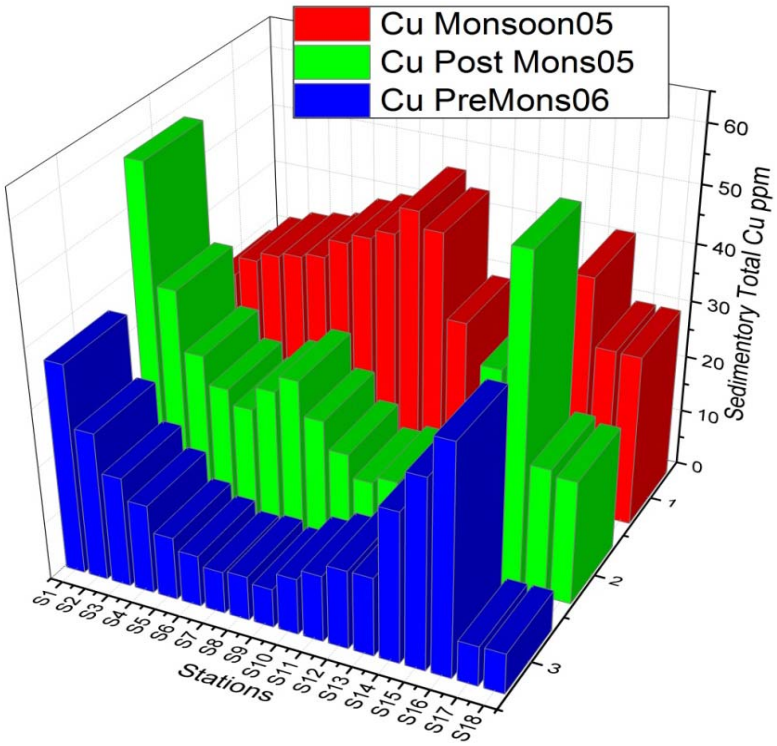

Figure 5.1.5. Seasonal variations of total copper (ppm) in sediments of the Muvattupuzha River

5.2f. Chromium

Chromium content in sediments varies between 3.74 to 44.64 ppm during the months of July 2005 to May 2006. The bimonthly spatial Cr

concentration ranges in sediments of 3.74 to 44.64 ppm found during the present study *(Table 5.1.7.),* is considerably lower than the reported Cr concentration ranges of 17 to 148 ppm and 31 to 149 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). However, the spatial Cr concentration ranges in sediments of 3.74 to 44.64 ppm found during the present study is higher than the reported Cr concentration ranges of 2.22 to 19.13 ppm in sediments of the Gomti River (Singh et al. 2005).

Chromium content in sediments averages to 36.28 ± 6.93 ppm, 25.88 ± 6.10 ppm, 15.98 ± 2.49 ppm, 18.82 ± 2.61 ppm, 16.68 ± 6.65 ppm and 10.85 ± 6.39 ppm respectively during the July, September, November, January, March and May months. Average Cr content in sediments (*Figure 5.1.6.)* showed the following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon. The bimonthly average Cr concentration of 20.75 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Cr concentration of 75 ppm and 86 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). The bimonthly average Cr concentration of 20.75 ppm in sediments found during the present study is higher than the reported average Cr concentration of 8.15 ppm in sediments of the Gomti River (Singh et al. 2005). Nevertheless, the bimonthly average Cr concentration of 20.75 ppm in sediments found during the present study *(Table 5.1.7.),* is very lower than the reported average Cr concentrations of 101 ppm, 156.3 ppm and 109 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

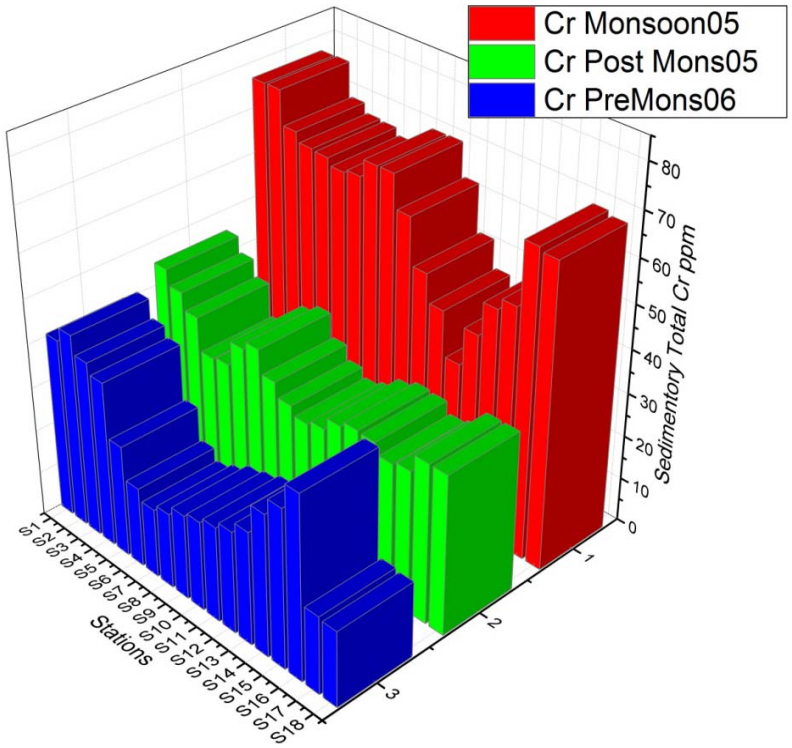

Figure 5.1.6. Seasonal variations of total chromium (ppm) in sediments of the Muvattupuzha River

5.2g. Zinc

Zinc content in sediments varies between 5.96 to 77.77 ppm during the months of July 2005 to May 2006. The bimonthly spatial Zn concentration ranges in sediments of 5.96 to 77.77 ppm found during the present study *(Table 5.1.7.),* is considerably lower than the reported Zn concentration ranges of 37 to 107 ppm and 33 to 168 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005).

Zinc content in sediments averages to 44.87 ± 15.61 ppm, 59.62 ± 17.37 ppm, 32.90 ± 10.43 ppm, 35.08 ± 11.55 ppm, 35.16 ± 16.36 ppm and 24.88 ± 11.25 ppm respectively during the July, September, November, January, March and May months. Average Zn content in sediments (*Figure 5.1.7.)* showed the following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon. The bimonthly spatial Zn concentration ranges in sediments of 5.96 to

77.77 ppm found during the present study *(Table 5.1.7.),* broadly agrees with the reported Zn concentration ranges of 3.06 to 101.73 ppm in sediments of the Gomti River (Singh et al. 2005). The bimonthly average Zn concentration of 38.75 ppm in sediments found during the present study is considerably lower than the reported average Zn concentration of 64 ppm and 82 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). The bimonthly average Zn concentration of 38.75 ppm in sediments found during the present study *(Table 5.1.7.),* is broadly agreeable with the reported average Zn concentration of 41.67 ppm in sediments of the Gomti River (Singh et al. 2005). However, the overall bimonthly average Zn concentration of 38.75 ppm in sediments obtained during the present study *(Table 5.1.7.),* is very lower than the reported average Zn concentrations of 177 ppm, 138.8 ppm and 196.7 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

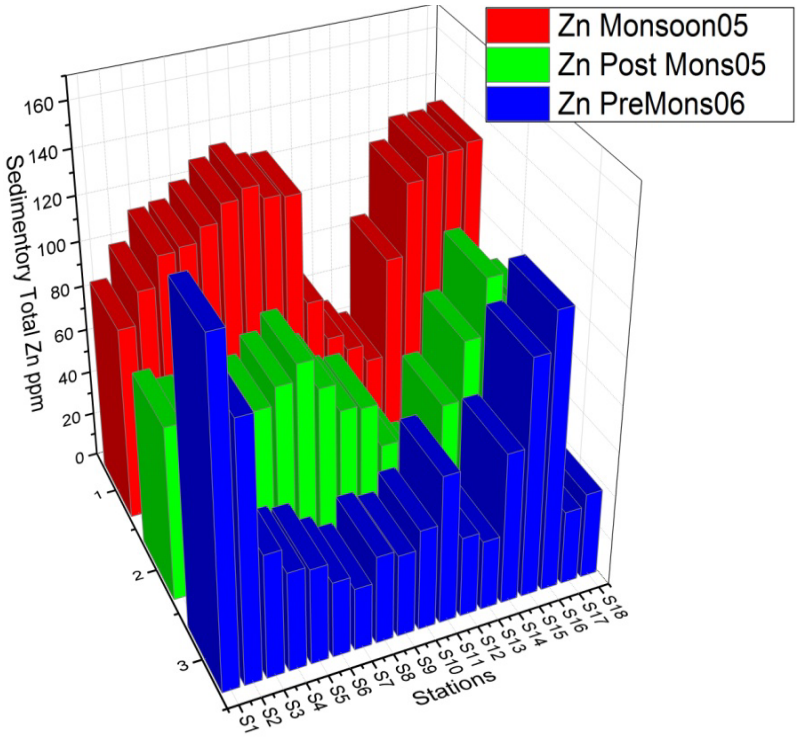

Figure 5.1.7. Seasonal variations of total zinc (ppm) in sediments of the Muvattupuzha River

5.2h. Cadmium

Cadmium content in sediments varies between 0.07 to 0.83 ppm during the months of July 2005 to May 2006. The bimonthly spatial Cd concentration ranges in sediments of 0.07 to 0.83 ppm found during the present study *(Table 5.1.7.),* is very low than the reported Cd concentration ranges of 0.34 to 8.38 ppm in sediments of the Gomti River (Singh et al. 2005).

Cadmium content in sediments averages to 0.36 ± 0.07 ppm, 0.30 ± 0.08 ppm, 0.38 ± 0.05 ppm, 0.42 ± 0.08 ppm, 0.36 ± 0.16 ppm and 0.27 ± 0.18 ppm respectively during the July, September, November, January, March and May months. Average Cd content in sediments (*Figure 5.1.8.)* showed the following decreasing order of seasonal values: post-monsoon > monsoon > pre-monsoon. The average Cd concentration of 0.35 ppm in sediments found during the present study *(Table 5.1.7.),* is very low than the reported average Cd concentration of 2.42 ppm in sediments of the Gomti River (Singh et al. 2005). On the other hand, the bimonthly average Cd concentration of 0.35 ppm in sediments found during the present study *(Table 5.1.7.),* is very lower than the reported average Cd concentrations of 12.9 ppm, 2.0 ppm and 1.8 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

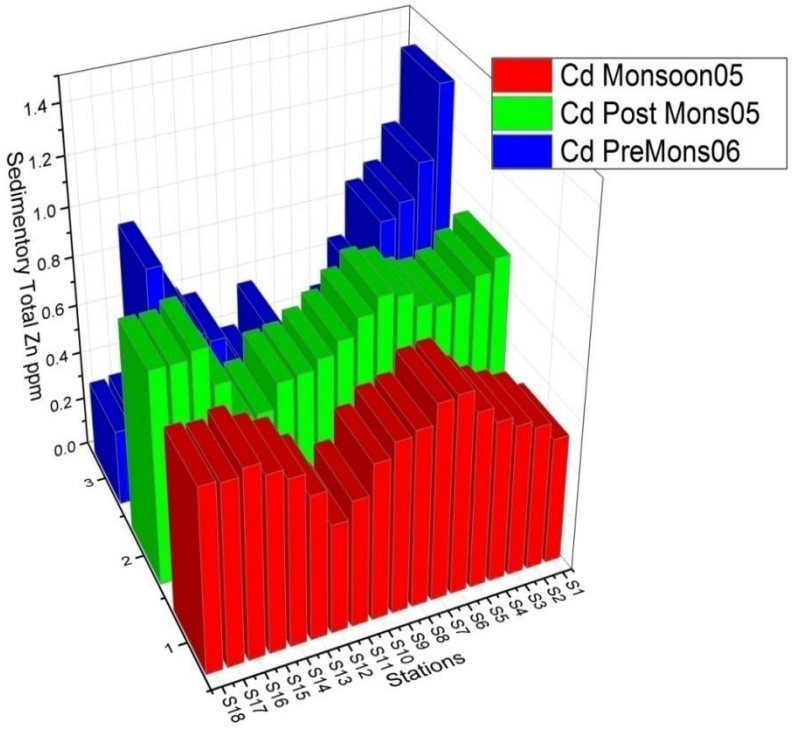

Figure 5.1.8. Seasonal variations of total cadmium (ppm) in sediments of the Muvattupuzha River

5.2i. Lead

Lead content in sediments varies between 1.79 to 23.59 ppm during the months of July 2005 to May 2006. The bimonthly spatial Pb concentration ranges in sediments of 1.79 to 23.59 ppm found during the present study *(Table 5.1.7.),* is considerably lower than the reported Pb concentration ranges of 11 to 117 ppm and 23 to 116 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). The bimonthly spatial Pb concentration ranges in sediments of 1.79 to 23.59 ppm found during the present study is considerably lower than the reported Pb concentration ranges of 6.27 to 75.33 ppm in sediments of the Gomti River (Singh et al. 2005).

Lead content in sediments averages to 10.13 ± 3.05 ppm, 12.17 ± 5.02 ppm, 10.63 ± 3.45 ppm, 11.60 ± 2.72 ppm, 9.26 ± 3.89 ppm and 7.20 ± 3.85 ppm respectively during the July, September, November, January, March and May months. Average Pb content in sediments (*Figure 5.1.9.)* showed the

following decreasing order of seasonal values: monsoon > post-monsoon > pre-monsoon. The bimonthly average Pb concentration of 10.17 ppm in sediments obtained during the present study is considerably lower than the reported average Pb concentration of 62 ppm and 65 ppm in sediments of the Periyar and Chalakudy Rivers respectively (Maya, 2005). Similarly, the bimonthly average Pb concentration of 10.17 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Pb concentration of 40.33 ppm in sediments of the Gomti River (Singh et al. 2005). On the other hand, the bimonthly average Pb concentration of 10.17 ppm in sediments found during the present study *(Table 5.1.7.),* is considerably lower than the reported average Pb concentrations of 22.4 ppm, 54.96 ppm and 33.95 ppm in sediments of the Chitrapuzha River, Kuttanad backwaters and Cochin backwaters respectively (Unnikrishnan, 2000; Joseph, 2002; Selvam et al. 2011).

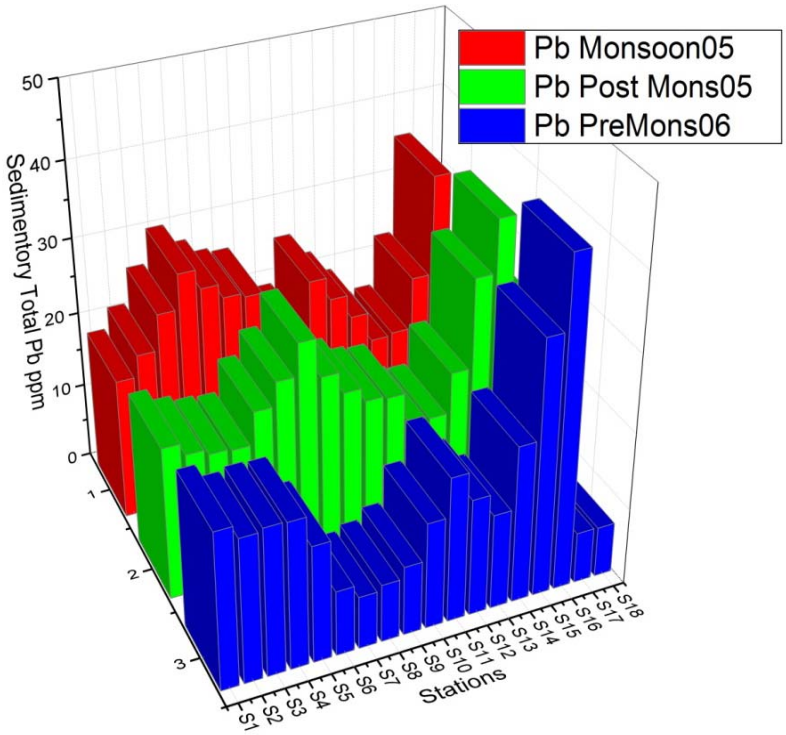

Figure 5.1.9. Seasonal variations of total lead (ppm) in sediments of the Muvattupuzha River

The seasonal trend of all total metals (except Cd) in sediments showed a decreasing order of concentrations which is as follows: monsoon > post-monsoon > pre-monsoon. The increase in concentration of total metals in sediments during the monsoon months (July/September) when compared to post-monsoon months (November/January) or pre-monsoon months (March/May) indicates the influence of land run-off materials on the trace metal accumulation in sediments of the Muvattupuzha River. The observed higher values for total trace metals during monsoon season than other seasons is due to enrichment of trace metal residues in sediments from agro-chemicals used in agricultural lands and municipal wastes through the land runoff washing process by heavy rain and strong water currents. The observed low concentrations of total metals in sediments during post-monsoon and pre-monsoon periods are possibly due to dilution process.

The bimonthly average concentration of metals in sediments of the Muvattupuzha River showed the respective orders of abundance:

Fe > Mn > Zn > Cr > Ni > Cu > Pb > Co > Cd (for July 2005)
Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > Cd (for September 2005)
Fe > Mn > Ni > Zn > Cr > Cu > Pb > Co > Cd (for November 2005)
Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > Cd (for January 2006)
Fe > Mn > Zn > Ni > Cr > Pb > Cu > Co > Cd (for March 2006)
Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > Cd (for May 2006)

The order of abundance of metals during different seasons showed that Fe was the most abundant metal which was followed by Mn and the least abundant metal was Cd. Of the 9 metals (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd &

Pb) studied the average concentrations of Zn, Cu, Cr, Ni, and Pb vary considerably between months.

5.3. A comparison of spatial and bi-monthly variations of trace metals in sediments with average shale values

A comparison of metal concentrations in sediment with the shale standard (Turekian and Wedepohl, 1961) is generally taken as a quick and practical method of tracing heavy metals enrichment in a given region (Taylor and McLennan, 1985). Naturally occurring trace metal levels in sediments depend on the geology of the catchment area but however due to anthropogenic loadings from point and non-point sources, sediments exhibit wide fluctuations in trace metal levels with the average value usually being higher than the normal shale value (Taylor and McLennan, 1985; Wedepohl, 1995). Hence, a comparison of spatial and bi-monthly variation of trace metals with respective average shale values (*Table 5.1.7.)*, indicated that Mn, Cu, Co, Cr and Zn concentrations were below the reported average shale metals values of 850 ppm for Mn, 45 ppm for Cu, 19 ppm for Co, 90 ppm for Cr and 95 ppm for Zn respectively (Turekian and Wedepohl, 1961). Also a comparison of spatial and bi-monthly variation of Fe concentrations in sediments usually did not exceed to the reported shale average value of 4.72 % in most stations except at stations S_{11} during July 2005 and at stations S_{15} and S_{16} during November 2005. Similarly, a comparison of spatial and bi-monthly variation of Ni concentrations in sediments didn't exceed the shale average value of 68 ppm in most stations during all months except at stations S_1, S_7, S_8, S_9, S_{11} and S_{12} during September 2005. A comparison of spatial and bi-monthly variation of Pb concentrations in sediments usually not exceeded the shale average value of 20 ppm in most stations except at stations S_{16} during May 2006. A

comparison of spatial and bi-monthly variation of Cd concentrations in sediments usually exceeds the shale average value of 0.3 ppm in most stations during all months except at stations S_6 to S_{14} and S_{17} to S_{18} during May 2006. Fe, Ni, Cd and Pb concentrations in sediments at certain sites exceeded respective shale average indicating its enrichment due to the influence of land-based anthropogenic inputs from point agricultural sources and non-point domestic sources in the study region (Forstner and Wittmann, 1983). A similar but higher enrichment of trace metals in sediments with respect to shale average standards were also noted from domestic, agricultural and industrial sources in the Cochin backwaters (Deepulal et al. 2011; Selvam et al. 2011).

5.4. Assessment of trace metal pollution status in sediments

In order to understand whether the geochemical distribution of individual metals in riverine systems is influenced by natural or anthropogenic factors, geochemical normalization and multivariate statistical methods are usually employed (Balachandran et al. 2006; Alkarkhi et al. 2008; Idris 2008). In the present study the heavy metal pollution status in sediments of the Muvattupuzha River basin was assessed by means of geo-statistical tools like Enrichment Factor (*Tables 5.1.8 to 5.2.3*), Contamination Factor (*Tables 5.2.4 to 5.2.9*), Pollution Load Index (*Tables A5.1.0 to A5.1.5*) and Geo-accumulation Index (*Tables 5.3.0 to 5.3.5*).

5.4.1. Enrichment Factor (EF)

In order to identify anomalous metal concentrations in sediments that arising due to granulometric and mineralological variability and hence to evaluate the abundance of metals, geochemical normalization of the trace metals data to a conservative element like Al, Fe, or Si, was usually employed (Chapman and Wang, 2001). To detect and quantify the anthropogenic

contribution of metals over natural inputs, the conservative elements such as Al or Fe, whose levels are unaffected by anthropogenic inputs is employed to identify the anomalous metal concentrations in the sediments. Iron has been chosen as a normalization element because of its origin being exclusively lithospheric (Schiff and Weisberg, 1999). In this study also iron has been used as a conservative tracer to differentiate natural sources from anthropogenic sources.

Enrichment Factor (EF) for each element was calculated using the formula, $EF = (M_s/Fe_s) \div (M_b/Fe_b)$ where M_s is the content of the metal in the sample, M_b is the world shale average of the metal, Fe_s is the content of Fe in sample, and Fe_b is the world shale average of Fe. Shale averages (Turekian and Wedepohl, 1961), as background levels were used here owing to the difficulty in obtaining a pristine environmental value in the study area, owing to complicated sediment texture and diverse anthropogenic stresses that are observed throughout the Muvattupuzha River.

During the present study EF was used to evaluate the magnitude of contamination and possible anthropogenic impacts in sediments of the Muvattupuzha River. It can indicate whether the trace metals are from natural weathering processes of rocks or from anthropogenic sources and reflect the status of environmental contamination. The assessment criteria are generally based on the EF values. If an EF value is between 0.5 and 1.5 (i.e., $0.5 \leq EF \leq 1.5$), it suggests that the trace metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). However, if a value of EF is greater than 1.5 (i.e., $EF > 1.5$), it suggests that a significant portion of trace metal is delivered from non-crustal materials or non-natural weathering processes. Instead, the trace metals are provided by point and non-point pollution sources (Zhang and Liu, 2002). However, EF values can also be

interpreted as the levels of trace metal pollution as suggested by Birch (2003) where EF < 1 indicates no enrichment, EF < 3 is minor, EF = 3 to 5 is moderate, EF = 5 to 10 is moderately severe, EF = 10 to 25 is severe, EF = 25 to 50 is very severe, and EF > 50 is extremely severe. Following the interpretation of Birch (2003) the EFs (≤1) for metals in sediment indicate its origin predominantly from lithogenous material and suggest the absence of contamination by these metals. Elements having EF values < 1 reveal a natural origin, whereas values > 1 indicate enrichment due to anthropogenic inputs which is also dominant in the study region.

The spatial and bimonthly variations of Enrichment Factor (EF) values of Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb in sediments at 18 stations from the upstream regions of the Muvattupuzha River are given in *Tables 5.1.8 to 5.2.3*.

The EF value ranges for Mn during the months of July, September, November, January, March and May were 0.03 to 0.59, 0.16 to 7.29, 0.13 to 0.52, 0.20 to 0.45, 0.16 to 0.60 and 0.20 to 0.58 respectively. Mn showed only EF < 1, at all stations during the months of July, November, January, March and May. During the month of September only the EF value for Mn at stations S_8, S_9, S_{17} and S_{18} are 2.46, 7.29, 1.07 and 0.98 respectively. The spatial segregation of Mn together with its minor (EF < 3, at S_{17} and at S_8) to moderately severe (EF > 5, at S_9) enrichment during September at these stations reveals a marginal contribution of this element from the nearby municipal areas. A similar but low EF value of Mn (0.2 to 0.8) was reported for the Cochin backwaters (Selvam et al. 2011).

The EF value ranges for Co during the months of July, September, November, January, March and May were 0.26 to 1.18, 0.32 to 11.78, 0.36 to 1.12, 0.06 to 1.14, 0.09 to 1.04 and 0.07 to 0.83 respectively. The EF value for

Co at stations S_1 and S_2 during July are 1.08 and 1.18 respectively whereas the EF value for Co at stations S_8, S_9, S_{10}, S_{17}, and S_{18} during September are 3.55, 11.78, 2.46, 1.35 and 1.34 respectively. The EF value for Co at stations S_5 and S_7 during November are 1.12 and 1.05 respectively whereas the EF value for Co at stations S_1, S_2, S_3, S_4, S_5, S_6, S_7, S_8, S_{17}, and S_{18} during January are 1.06, 0.99, 0.99, 1.06, 1.03, 1.10, 1.10, 1.13, 1.14 and 1.12 respectively. The EF value for Co at stations S_8 and S_9 during March are 1.00 and 1.04 respectively.

Co showed a minor enrichment (EF < 3) at stations S_1 and S_2 during July. Co also showed a minor enrichment (EF < 3) at stations S_{10}, S_{17} and S_{18}, a moderate enrichment (EF = 3 to 5) at station S_8 and a severe enrichment (EF = 10 to 25) at S_9 during September. Co showed a minor enrichment (EF < 3) at stations S_5 and S_7 during November and at stations S_1 to S_8, S_{17} and S_{18} during January and at stations S_8 and S_9 during March respectively. The monthly spatial segregation of Co together with its minor to moderate to severe enrichment at these stations indicates a marginal contribution of this element from the nearby municipal and agricultural areas. A similar but low EF value of Co (0.6 to 1.4) was reported for the Cochin backwaters (Selvam et al. 2011).

The EF value ranges for Ni during the months of July, September, November, January, March and May were 0.16 to 1.50, 0.17 to 17.64, 0.15 to 1.78, 0.27 to 0.96, 0.40 to 1.12 and 0.04 to 0.75 respectively. The EF value for Ni at station S_8 during July is 1.5 whereas its value at stations S_1, S_2, S_7, S_8, S_9, S_{10}, S_{17} and S_{18} during September are 1.70, 1.08, 1.50, 5.60, 17.64, 4.77, 2.21 and 2.05 respectively. The EF value for Ni at station S_1, S_2, S_3, S_5, S_6, S_7, S_8, S_9, S_{10}, S_{17} and S_{18} during November is 1.61, 1.51, 1.29, 1.11, 1.43, 1.70, 1.78, 1.75, 1.41, 1.76 and 1.21 whereas its value at stations S_1 and S_2 during March are 1.12 and 1.10 respectively.

Ni showed a minor enrichment (EF < 3) at only station S_8 during July. Ni also showed a minor enrichment (EF < 3) at stations S_1, S_2, S_3, S_{17} and S_{18}, a moderate enrichment (EF = 3 to 5) at station S_8 and S_{10} and a severe enrichment (EF = 10 to 25) at S_9 during September. Ni showed a minor enrichment (EF < 3) at stations S_1 to S_3, S_5 to S_{10}, S_{17} and S_{18} during September. Ni showed a minor enrichment (EF < 3) at stations S_1 and S_2 during March. The monthly spatial segregation of Ni together with its minor to moderate to severe enrichment at these stations indicates a marginal contribution of this element from the nearby municipal and agricultural areas. A similar but low EF value of Ni (0.4 to 0.9) was reported for the Cochin backwaters (Selvam et al. 2011).

The EF value ranges for Cu during the months of July, September, November, January, March and May were 0.18 to 1.21, 0.30 to 8.26, 0.15 to 2.23, 0.08 to 0.96, 0.28 to 0.63 and 0.12 to 0.72 respectively. The EF value for Cu at station S_1 and S_2 during July are 1.21 and 1.05 respectively whereas its value at stations S_8, S_9, S_{10} and S_{11} during September are 2.55, 8.26, 3.86 and 1.05 respectively. The EF value for Cu at station S_1, S_2 and S_3 during November are 2.23, 1.37 and 1.22 respectively.

Cu showed a minor enrichment (EF < 3) at only stations S_1 and S_2 during July. Cu also showed a minor enrichment (EF < 3) at stations S_8, S_{10} and S_{11}, a moderate enrichment (EF = 3 to 5) at only station S_{10} during September. A fairly minor enrichment (EF < 3) of Cu is noted at stations S_1 to S_3 during November. The monthly spatial segregation of Cu together with its minor to moderate enrichment at these stations indicates a marginal contribution of this element from the nearby municipal and agricultural areas. A similar spatial segregation of Cu with its moderate enrichment factor values of the ranges 3 to 5 in the south, central, and northern parts of the Cochin

backwaters that were affected by agricultural, domestic and industrial pollution were also reported (Martin et al. 2012).

The EF value ranges for Cr during the months of July, September, November, January, March and May were 0.28 to 3.44, 0.20 to 4.06, 0.13 to 0.50, 0.23 to 0.81, 0.21 to 0.58 and 0.05 to 1.13 respectively. The EF value for Cr at stations S_1 and S_2 during July is 3.44 and 2.06 respectively whereas its value at stations S_8, S_9, and S_{10} during September are 1.40, 4.06 and 1.49 respectively. The EF value for Cr at stations S_7, S_{17} and S_{18} during May is 1.02, 1.05 and 1.13 respectively.

Cr showed a minor enrichment (EF < 3) at stations S_1 and S_2, and a moderate enrichment (EF = 3 to 5) at station S_9 during July. A fairly minor enrichment (EF < 3) of Cr is noted at stations S_7, S_{17} and S_{18} during May. The monthly spatial segregation of Cr together with its minor to moderate enrichment at these stations indicates a marginal contribution of this element from the nearby urban and agricultural areas. A similar but low EF value of Cr (0.6 to 1.8) was reported for the Cochin backwaters (Selvam et al. 2011).

The EF value ranges for Zn during the months of July, September, November, January, March and May were 0.23 to 1.43, 0.38 to 9.11, 0.21 to 0.98, 0.25 to 1.15, 0.45 to 2.02 and 0.11 to 2.05 respectively. The EF value for Zn at stations S_1 and S_2 during July is 1.16 and 1.43 respectively whereas its value at stations S_1, S_8, S_9, S_{10}, S_{16}, S_{17} and S_{18} during September are 1.09, 3.06, 9.11, 2.29, 1.01, 1.33 and 1.25 respectively. The EF value for Zn at stations S_1 and S_2 during January is 1.15 and 1.00 respectively. The EF value for Zn at stations S_1, S_8, S_9, S_{10}, S_{11}, S_{17} and S_{18} during March is 1.14, 1.23, 1.24, 1.25, 2.02, 1.02 and 1.13 respectively whereas its value at stations S_7, S_{17} and S_{18} during May are 2.05, 1.53 and 1.75 respectively.

Zn showed a minor enrichment (EF < 3) at stations S_1 and S_2 during July and January. Zn showed a minor enrichment (EF < 3) at stations S_1 $S_{10,}$ $S_{16,}$ S_{17} and $S_{18,}$ and a moderate enrichment (EF = 3 to 5) at stations S_8 and S_9 during July respectively. Zn also showed a minor enrichment (EF < 3) at stations S_1, S_8, S_9, S_{10}, S_{11}, S_{17} and S_{18} during March and at stations S_7, S_{17} and S_{18} during May respectively. The monthly spatial segregation of Zn together with its minor to moderate enrichment at these stations indicates a marginal contribution of this element from the nearby municipal and agricultural areas. A similar spatial segregation of Cu with its moderate enrichment factor values of 5 in the south as well as central parts but increased to severe enrichment factor values of the ranges 15 to 25 in northern parts of the Cochin backwaters that were affected by agricultural, domestic and industrial pollution were also reported (Martin et al. 2012).

The EF value ranges for Cd during the months of July, September, November, January, March and May were 0.91 to 4.51, 1.01 to 11.23, 1.14 to 3.92, 1.16 to 5.13, 1.55 to 5.98 and 0.78 to 2.91 respectively. Cd showed minor enrichment factor values (EF < 3), at stations S_3 to S_{18} during July, at stations S_1 to S_7 and S_{11} to S_{18} during September, at stations S_5 to S_{18} during November, at stations S_7 to S_{18} during January, at stations S_2 to S_6, S_{11} to S_{12} and S_{14} to S_{16} during March and at all stations during May respectively. Cd showed moderate enrichment factor values (EF = 3 to 5), at stations S_1 to S_2 during July, at station S_7 during September, at stations S_1 to S_4 and S_9 during November, at stations S_2 to S_6 during January, and at stations S_2, S_7 to S_{10}, S_{13}, and S_{17} to S_{18} during March respectively. Cd showed a moderately severe enrichment factor value (EF = 5 to 10), at station S_1 during January and at station S_{10} during March respectively. Cd showed a severe enrichment factor value (EF = 10 to 25), at station S_9 during September only. The monthly

spatial segregation of Cd together with its minor to moderate to severe enrichment at these stations indicates a marginal contribution of this element from the nearby urban and agricultural areas. A similar spatial segregation of Cd with its extremely severe enrichment factor values of the ranges 60 to 150 in the south as well as central parts but increased to extremely severe enrichment factor values of very higher ranges 200 to 350 in northern parts of the Cochin backwaters that were affected by agricultural, domestic and industrial pollution were also reported (Martin et al. 2012).

The EF value ranges for Pb during the months of July, September, November, January, March and May were 0.51 to 1.27, 0.44 to 5.29, 0.58 to 1.40, 0.75 to 1.69, 0.75 to 2.24 and 0.38 to 1.25 respectively. Pb showed minor enrichment factor values (EF < 3), at stations S_1 to S_2 during July, at stations S_1 to S_4, S_8, S_{11} and S_{16} during September, at stations S_3 to S_{11} and S_{17} during November, at stations S_1 to S_{10} and S_{15} to S_{18} during January, at stations S_7 to S_{13} and S_{16} to S_{18} during March and at stations S_7 to S_8 and S_{15} to S_{18} during May respectively. Pb showed moderate enrichment factor values (EF = 3 to 5), at station S_9 to S_{10} during September only. The monthly spatial segregation of Pb together with its minor to moderate enrichment at these stations indicates a marginal contribution of this element from the nearby urban and agricultural areas. A similar spatial segregation of Pb with its moderately severe enrichment factor values of the ranges 6 to 10 in the south, central and northern parts of the Cochin backwaters that were affected by agricultural, domestic and industrial pollution were also reported (Martin et al. 2012).

EF values (> 2) of these metals together with its minor to moderate enrichment at certain locations showed a moderate anthropogenic impact on the trace metal concentration levels in the Muvattupuzha River sediments. Thus it can be deduced that metal pollution in the Muvattupuzha River

sediments comes entirely from anthropogenic processes enhancing metal concentrations. The high EF values (>1.5) for these trace metals (Zhang and Liu, 2002) at certain locations indicating some terrestrial input of contaminated sediment through river and their spatial segregation suggests anthropogenic sources in the study area which is mainly derived from human activities like sand or clay mining, agriculture or domestic waste discharges (Padmalal et al. 2008). Thus, metal geochemistry of the Muvattupuzha River is dominated by anthropogenic sources (Balachandran et al. 2006). The spatial difference in EF values of various metals may be due to the difference in the magnitude of input for each metal in the sediment from anthropogenic sources and/or the difference in the removal rate of each metal from the sediment by water currents (Balachandran et al. 2005; Balachandran et al. 2006).

5.4.2. Contamination Factor

The level of contamination of sediment by a metal is often expressed in terms of a contamination factor (Hakanson, 1980).

Contamination Factor (CF) = Metal content in sediment / Back ground value of metal

Here the world average concentration of elements reported for shale was taken as background values of trace meals in the study region (Turekian and Wedepohl, 1961). A CF < 1 refers to low contamination, $1 \leq CF \leq 3$ means moderate contamination, $3 \leq CF \leq 6$ indicates considerable contamination, and CF > 6 indicates very high contamination (Hakanson, 1980).

The spatial and bimonthly variations of Contamination Factor (CF) values of Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb in sediments at 18 stations from the upstream regions of the Muvattupuzha River are given in *Tables 5.2.4 to 5.2.9*. The CF value ranges for Fe during the months of July,

September, November, January, March and May were 0.13 to 1.26, 0.08 to 0.89, 0.30 to 1.21, 0.33 to 0.83, 0.21 to 0.79 and 0.08 to 0.98 respectively. Fe showed CF < 1, at all stations during the months of September, January, March and May which indicates a low level contamination by this element from the nearby areas. However Fe showed CF > 1, at station S_{11} situated nearby Thodupuzha municipal town during July and at station S_{15} situated nearby Moolamattom mini township colony and at S_{16} station arakkulam situated nearby Idukki dam tunnel phase outlet during November respectively which indicates a moderate level contamination of this element from these areas. Similar CF values for Fe in the ranges of 0.39 to 1.92 were reported for the Cochin backwaters (Deepulal et al. 2011).

The CF value ranges for Mn during the months of July, September, November, January, March and May were 0.02 to 0.48, 0.08 to 0.59, 0.09 to 0.27, 0.08 to 0.22, 0.08 to 0.34 and 0.02 to 0.41 respectively. Mn showed CF < 1, at all stations during the months of July, September, November, January, March and May which indicates a low level contamination by this element from the nearby areas. CF values for Mn in the ranges of 0.07 to 0.92 were also reported for the Cochin backwaters (Deepulal et al. 2011).

The CF value ranges for Co during the months of July, September, November, January, March and May were 0.14 to 0.67, 0.25 to 0.92, 0.11 to 0.60, 0.02 to 0.64, 0.07 to 0.70 and 0.01 to 0.78 respectively. Co showed CF < 1, at all stations during the months of July, September, November, January, March and May which indicates a low level contamination by this element from the nearby areas. Similar CF values for Co in the ranges of 0.18 to 1.03 were reported for the Cochin backwaters (Deepulal et al. 2011).

The CF value ranges for Ni during the months of July, September, November, January, March and May were 0.06 to 1.19, 0.11 to 1.38, 0.10 to 0.94, 0.13 to 0.60, 0.09 to 0.81 and 0.03 to 0.66 respectively. Ni showed CF > 1, at station S_8 situated at the confluence of Thodupuzha, Kaliar and Kothamangalam Rivers (Muvattupuzha-Triveni-Sangamam) during July and September respectively. Ni showed CF > 1, at station S_1 situated at Piravam being influenced by sand and clay mining, at S_7 station situated nearby the check dam for Muvattupuzha town, at station S_9 situated nearby Arakkuzha township, at station S_{17} situated nearby Kothamangalam township and at station S_{18} situated nearby kaliarpuzha agricultural area during September. The CF > 1 for Ni at these stations indicates a moderate level contamination of this element from these mining, urban and agricultural areas during July and September. CF values for Ni in the ranges of 0.12 to 1.30 were also reported for the Cochin backwaters (Deepulal et al. 2011).

The CF value ranges for Cu during the months of July, September, November, January, March and May were 0.16 to 0.52, 0.15 to 0.70, 0.10 to 1.07, 0.04 to 0.80, 0.10 to 0.40 and 0.04 to 0.48 respectively. Cu showed CF ≤ 1, at all stations during the months of July, September, November, January, March and May which indicates a low level contamination by this element from the nearby areas. CF values for Cu in the ranges of 1 to 3 indicating a moderate level of contamination by Cu from the Cochin backwaters were reported (Martin et al. 2012).

The CF value ranges for Cr during the months of July, September, November, January, March and May were 0.28 to 0.50, 0.13 to 0.40, 0.13 to 0.24, 0.16 to 0.26, 0.10 to 0.41 and 0.04 to 0.30 respectively. Cr showed CF < 1, at all stations during the months of July, September, November, January, March and May which indicates a low level contamination by this element

from the nearby areas. CF values for Cr in the ranges of 0.06 to 0.63 were also reported for the Cochin backwaters (Deepulal et al. 2011).

The CF value ranges for Zn during the months of July, September, November, January, March and May were 0.15 to 0.66, 0.24 to 0.82, 0.13 to 0.47, 0.11 to 0.65, 0.14 to 0.81 and 0.11 to 0.75 respectively. Zn showed CF < 1, at all stations during the months of July, September, November, January, March and May which indicates a low level contamination by this element from the nearby areas. CF values for Zn in the ranges of 4 to 16 indicating a considerable to very high level of contamination by Zn from the Cochin backwaters were reported (Martin et al. 2012).

The CF value ranges for Cd during the months of July, September, November, January, March and May were 0.59 to 1.45, 0.46 to 1.38, 0.94 to 1.47, 0.78 to 1.68, 0.61 to 2.76 and 0.22 to 1.85 respectively. Cd showed CF > 1, at stations S_3 to S_{11}, S_{15} to S_{18} during July, at stations S_5 to S_7, S_{14} to S_{16} during September, at stations S_1 to S_1, S_{14} to S_{18} during November, at stations S_1 to S_{12}, S_{15} to S_{18} during January, at stations S_1 to S_5, S_{10}, S_{14} to S_{16} during March, and at stations S_1 to S_4, S_{15} to S_{16} during May which indicates a moderate level contamination of this element from these mining, agricultural and municipal areas. High CF values for Cd in the ranges of 50 to 75 in the south and central parts but gets increased to very high CF values in the ranges 100 to 200 in the northern parts indicating a very high level of contamination by Cd in the entire Cochin estuary were reported (Martin et al. 2012).

The CF value ranges for Pb during the months of July, September, November, January, March and May were 0.17 to 0.84, 0.24 to 0.95, 0.34 to 0.98, 0.36 to 0.93, 0.24 to 0.96 and 0.09 to 1.18 respectively. Pb showed CF ≤ 1, at all stations during the months of July, September, November, January,

March and May which indicates a low level contamination by this element from the nearby areas. CF values for Pb in the ranges of 2 to 3 indicating a moderate level of contamination by this metal for the Cochin backwaters were reported (Martin et al. 2012).

In general, the contamination factors for metals like Fe, Mn, Co, Cu, Cr, Zn and Pb were ≤ 1 indicating a low level contamination and low level pollution load of these elements from the nearby areas whereas the contamination factors for metals like Ni and Cd were > 1 at certain locations indicating a moderate level contamination and moderate level pollution load of these elements from the nearby areas. The elevated values of CF for these metals at certain locations suggest the influence of human impact on the riverine sediments (Padmalal et al. 2008). Quite likely, anthropogenic materials from agricultural and urban sources and riverine input have influenced the elevated concentrations of these metals in the surface sediments.

5.4.3. Pollution Load Index (PLI)

The extent of pollution by metals has been assessed by employing the method based on pollution load index (PLI) as developed by Tomlinson et al. (1980), which is the geometric mean of the contamination factor of each metal present in the studied area (Tomlinson et al. 1980). It provides a summative indication of the overall level of heavy metal pollution in a particular sample.

PLI = [Product of 'n' number of CF values]$^{1/n}$

The PLI can provide some understanding to the public of the area concerned about the quality of a component of their environment, and indicates the trend spatially and temporally. In addition, it also provides valuable information to the decision makers on the pollution level of the area. According to Tomlinson et al. (1980), PLI values of 0, 1, or >1 suggest the

absence of baseline pollutants, the presence of them, or the progressive deterioration of sediment quality, respectively. The PLI value of > 1 is polluted whereas < 1 indicates no pollution.

The spatial and bimonthly variations of Pollution Load Index (PLI) values of Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb in sediments at 18 stations from the upstream regions of the Muvattupuzha River are given in *Tables A5.1.0 to A5.1.5*. The PLI value ranges for trace metals during the months of July, September, November, January, March and May were 0.16 to 0.64, 0.24 to 0.74, 0.22 to 0.58, 0.23 to 0.58, 0.18 to 0.62 and 0.05 to 0.68 respectively. The values of PLI for trace metals were found to be low (maximum value 0.74) during all months (i.e., PLI < 1) which showed only a minor metallic pollution or its mere presence and hence a major metallic pollution is quite insignificant in the upstream freshwater regions of the Muvattupuzha River. Selvam et al. (2011) also noted a low PLI (i.e., PLI < 1) in the downstream estuarine regions of the Muvattupuzha River. Since the values of PLI were found to be low (< 1) during all months indicating that this riverine ecosystem is not of a severe or major pollution concerns with respect to trace metal concentrations in sediments in the present scenario of human impacts.

5.4.4. Geo-accumulation Index

To understand current environmental status and trace metal pollution extent with respect to natural environment, geoaccumulation index (*I* geo) is used (Muller, 1969).

$$I\,\text{geo} = \log_2 (C_n/1.5B_n)$$

where C_n is the measured concentration of the element 'n' and Bn is the geochemical background value of element 'n' in average crust (Turekian and

Wedepohl, 1961).The 1.5 factor is introduced to include possible variations of the background values due to lithogenic effects.

Sediment quality based on the *I* geo values is given as: < 0 = practically unpolluted, 0 – 1 = unpolluted to moderately polluted, 1 – 2 = moderately polluted, 2 – 3 = moderately to strongly polluted, 3 – 4 = strongly polluted, 4 – 5 = strongly to extremely polluted, and > 5 = extremely polluted.

The spatial and bimonthly variations of Geo-accumulation Index (GAI or *I* geo) values of Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb in sediments at 18 stations from the upstream regions of the Muvattupuzha River are given in *Tables 5.3.0 to 5.3.5*. The *I* geo value ranges for Fe during the months of July, September, November, January, March and May were -3.51 to -0.25, -4.26 to -0.75, -2.30 to -0.31, -2.20 to -0.85, -2.81 to -0.92 and -4.30 to -0.62 respectively. The *I* geo value ranges for Mn during the months of July, September, November, January, March and May were -6.03 to -1.64, -4.19 to -1.35, -4.73 to -2.46, -4.16 to -2.79, -4.32 to -2.16 and -6.08 to -1.89 respectively. The *I* geo value ranges for Co during the months of July, September, November, January, March and May were -3.40 to -1.17, -2.56 to -0.70, -3.76 to -1.31, -5.97 to -1.24, -4.51 to -1.11 and -8.10 to -0.95 respectively. The *I* geo value ranges for Ni during the months of July, September, November, January, March and May were -4.58 to -0.33, -3.81 to -0.12, -3.91 to -0.67, -3.53 to -1.33, -3.98 to -0.88 and -8.79 to -1.17 respectively. The *I* geo value ranges for Cu during the months of July, September, November, January, March and May were -3.23 to -1.54, -3.28 to -1.11, -3.98 to -0.49, -5.26 to -0.91, -3.88 to -1.90 and -5.07 to -1.64 respectively. The *I* geo value ranges for Cr during the months of July, September, November, January, March and May were -2.44 to -1.60, -3.57 to -1.90, -3.57 to -2.64, -3.22 to -2.50, -3.95 to -1.86 and -5.17 to -2.33

respectively. The *I* geo value ranges for Zn during the months of July, September, November, January, March and May were -3.29 to -1.18, -2.67 to -0.87, -3.48 to -1.67, -3.83 to -1.99, -3.47 to -0.89 and -4.58 to -0.99 respectively. The *I* geo value ranges for Cd during the months of July, September, November, January, March and May were -1.34 to -0.05, -1.71 to -0.12, -0.67 to -0.03, -0.94 to 0.16, -1.31 to 0.88 and -2.79 to 0.30 respectively. The *I* geo value ranges for Pb during the months of July, September, November, January, March and May were -3.17 to -0.84, -2.67 to -0.66, -2.16 to -0.61, -2.07 to -0.68, -2.65 to -0.65 and -4.07 to -0.35 respectively.

From this classification criteria, all the sediments in the Muvattupuzha River could be approximately categorized as practically unpolluted with Fe, Mn, Ni, Co, Zn, Cu, Cr and Pb (*I* geo < 0 for each trace metal), and unpolluted to somewhat moderately polluted with Cd (*I* geo value 0 to 1). Based on the same classification criteria, sediments of the Cochin backwaters are also categorised similarly as practically unpolluted with Fe, Mn, Ni, Co, and Cr (*I* geo < 0 for each trace metal), and moderately polluted with Cu and Pb (*I* geo value 0 to 2 for both trace metals), moderately to heavily polluted with Zn (*I* geo value 0 to 3), and heavily to extremely polluted with Cd (*I* geo value 4 to 6), respectively indicating pollution concerns for metals like Cu, Pb, Zn and Cd in the respective environments because of anthropogenic activities (Martin et al. 2012).

5.5. Concluding remarks

Total trace metal concentrations in sediments were studied during the bimonthly intervals of July 2005 to May 2006 from the upstream stretch of the Muvattupuzha River at stations of Moolamattam to Piravam which is flowing through municipal townships and agricultural lands. The order of abundance

of various metals in sediments during different seasons showed that Fe was the most abundant metal which was followed by Mn and the least abundant metal was Cd. High EF values (> 1.5) for metals at certain sites indicates terrestrial input of contaminated sediment through the river and their spatial segregation suggests anthropogenic sources in the study area possibly derived from human activities like sand/clay mining, agricultural as well as domestic waste discharges. The contamination factors for the metals Fe, Mn, Co, Cu, Cr, Zn and Pb in sediments were ≤ 1 indicating a low level contamination and low level pollution load of these elements from the urban and agricultural areas whereas the contamination factors for metals like Ni and Cd were > 1 in sediments indicating a moderate level contamination and moderate level pollution load of these elements from the urban and agricultural areas. Since values of PLI for trace metals were found to be low (i.e. PLI < 1 with a maximum value 0.74) during all months indicates only a minor metallic pollution or its mere presence and hence a major metallic pollution is quite insignificant in the river. However EF investigations markedly highlighted anthropogenic controls on trace metals enrichment and its geochemical distribution in the river.

Table 5.1.8. Enrichment Factors (EF) for trace metals in sediments of the Muvattupuzha River during July 2005

Station position	Mn (EF)	Co (EF)	Ni (EF)	Cu (EF)	Zn (EF)	Cd (EF)	Cr (EF)	Pb (EF)
S1	0.38	1.08	0.48	1.21	1.16	4.51	3.44	1.27
S2	0.43	1.18	0.52	1.05	1.43	4.04	2.06	1.01
S3	0.03	0.58	0.27	0.40	0.71	1.56	0.70	0.60
S4	0.16	0.50	0.22	0.32	0.55	1.31	0.52	0.61
S5	0.20	0.56	0.19	0.37	0.66	1.43	0.54	0.61
S6	0.55	0.61	0.16	0.39	0.74	1.58	0.50	0.59
S7	0.59	0.63	0.16	0.41	0.81	1.66	0.49	0.58
S8	0.58	0.68	1.50	0.42	0.79	1.75	0.57	0.68
S9	0.55	0.86	0.80	0.50	0.79	1.84	0.60	0.73
S10	0.36	0.49	0.30	0.30	0.43	1.54	0.46	0.69
S11	0.08	0.26	0.19	0.18	0.23	0.91	0.28	0.51
S12	0.15	0.32	0.19	0.20	0.27	1.04	0.34	0.65
S13	0.30	0.47	0.22	0.30	0.38	1.66	0.47	0.72
S14	0.39	0.81	0.41	0.36	0.80	2.23	0.60	0.84
S15	0.23	0.55	0.35	0.41	0.62	1.31	0.36	0.63
S16	0.22	0.54	0.37	0.60	0.62	1.30	0.33	0.97
S17	0.43	0.59	0.45	0.36	0.76	1.66	0.53	0.60
S18	0.40	0.63	0.44	0.38	0.79	1.71	0.53	0.58
Average	**0.34**	**0.63**	**0.40**	**0.45**	**0.70**	**1.84**	**0.74**	**0.72**

Table 5.1.9. Enrichment Factors (EF) for trace metals in sediments of the Muvattupuzha River during September 2005

Station position	Mn (EF)	Co (EF)	Ni (EF)	Cu (EF)	Zn (EF)	Cd (EF)	Cr (EF)	Pb (EF)
S1	0.26	0.78	1.70	0.70	1.09	1.58	0.58	1.10
S2	0.20	0.54	1.08	0.58	0.89	1.22	0.47	1.02
S3	0.18	0.38	0.83	0.55	0.82	1.12	0.33	1.04
S4	0.17	0.32	0.30	0.52	0.77	1.01	0.28	1.06
S5	0.16	0.50	0.65	0.52	0.79	1.25	0.31	0.97
S6	0.55	0.78	0.94	0.61	0.85	1.53	0.36	0.93
S7	0.71	0.95	1.50	0.69	0.91	1.55	0.41	0.99
S8	2.46	3.55	5.60	2.55	3.06	4.08	1.40	1.01
S9	7.29	11.78	17.64	8.26	9.11	11.23	4.06	5.29
S10	0.58	2.46	4.77	3.86	2.29	3.52	1.49	3.51
S11	0.20	0.66	0.46	1.05	0.81	1.35	0.58	1.21
S12	0.27	0.58	0.37	0.34	0.61	1.01	0.41	0.76
S13	0.24	0.41	0.17	0.30	0.38	1.49	0.20	0.58
S14	0.39	0.59	0.41	0.32	0.80	1.72	0.31	0.59
S15	0.41	0.64	0.75	0.39	0.92	1.57	0.35	0.75
S16	0.71	0.74	0.94	0.50	1.01	1.70	0.40	1.16
S17	1.07	1.35	2.21	0.68	1.33	1.93	0.61	0.65
S18	0.98	1.34	2.05	0.60	1.25	1.83	0.55	0.44
Average	**0.94**	**1.57**	**2.35**	**1.28**	**1.54**	**2.26**	**0.73**	**1.28**

Table 5.2.0. Enrichment Factors (EF) for trace metals in sediments of the Muvattupuzha River during November 2005

Station position	Mn (EF)	Co (EF)	Ni (EF)	Cu (EF)	Zn (EF)	Cd (EF)	Cr (EF)	Pb (EF)
S1	0.20	0.76	1.61	2.23	0.91	3.06	0.50	0.94
S2	0.22	0.75	1.51	1.37	0.89	3.00	0.50	0.90
S3	0.36	0.36	1.29	1.22	0.98	3.92	0.63	1.16
S4	0.35	0.89	0.50	0.76	0.72	3.55	0.38	1.02
S5	0.42	1.12	1.11	0.33	0.89	2.70	0.36	1.06
S6	0.52	0.97	1.43	0.41	0.86	2.68	0.39	1.18
S7	0.49	1.05	1.70	0.43	0.86	2.64	0.36	1.40
S8	0.51	0.96	1.78	0.54	0.82	2.91	0.33	1.25
S9	0.43	0.99	1.75	0.55	0.86	3.09	0.38	1.21
S10	0.18	0.68	1.41	0.55	0.85	2.86	0.37	1.09
S11	0.13	0.46	0.25	0.40	0.39	2.65	0.36	1.05
S12	0.19	0.39	0.19	0.24	0.27	1.86	0.34	0.63
S13	0.19	0.39	0.15	0.15	0.21	1.44	0.31	0.58
S14	0.27	0.48	0.29	0.16	0.33	1.38	0.23	0.60
S15	0.23	0.43	0.73	0.30	0.40	1.22	0.15	0.73
S16	0.22	0.50	0.75	0.39	0.38	1.14	0.13	0.81
S17	0.49	0.94	1.76	0.46	0.81	2.83	0.32	1.15
S18	0.31	0.66	1.21	0.31	0.57	1.85	0.23	0.77
Average	**0.32**	**0.71**	**1.08**	**0.60**	**0.67**	**2.49**	**0.35**	**0.97**

Table 5.2.1. Enrichment Factors (EF) for trace metals in sediments of the Muvattupuzha River during January 2006

Station position	Mn (EF)	Co (EF)	Ni (EF)	Cu (EF)	Zn (EF)	Cd (EF)	Cr (EF)	Pb (EF)
S1	0.26	1.06	0.96	0.70	1.15	5.13	0.81	1.69
S2	0.25	0.99	0.77	0.65	0.99	4.47	0.66	1.42
S3	0.26	0.99	0.66	0.62	0.90	3.96	0.58	1.34
S4	0.28	1.06	0.56	0.58	0.80	3.51	0.49	1.23
S5	0.28	1.03	0.67	0.62	0.82	3.28	0.40	1.28
S6	0.28	1.10	0.73	0.63	0.82	3.06	0.42	1.21
S7	0.28	1.10	0.75	0.64	0.80	2.70	0.41	1.16
S8	0.35	1.13	0.75	0.43	0.83	2.91	0.45	1.20
S9	0.45	0.06	0.55	0.29	0.70	2.99	0.42	1.24
S10	0.36	0.57	0.39	0.08	0.58	2.45	0.32	1.00
S11	0.31	0.43	0.31	0.24	0.52	2.11	0.33	0.91
S12	0.28	0.41	0.27	0.35	0.37	2.41	0.35	0.79
S13	0.23	0.48	0.30	0.53	0.25	2.36	0.42	0.84
S14	0.30	0.70	0.41	0.34	0.43	1.16	0.28	0.75
S15	0.26	0.62	0.53	0.63	0.51	1.45	0.23	0.99
S16	0.20	0.68	0.72	0.96	0.79	1.94	0.25	1.13
S17	0.28	1.14	0.83	0.48	0.88	2.58	0.43	1.11
S18	0.27	1.12	0.88	0.42	0.84	2.55	0.40	1.09
Average	**0.29**	**0.81**	**0.61**	**0.51**	**0.72**	**2.83**	**0.43**	**1.13**

Table 5.2.2. Enrichment Factors (EF) for trace metals in sediments of the Muvattupuzha River during March 2006

Station position	Mn (EF)	Co (EF)	Ni (EF)	Cu (EF)	Zn (EF)	Cd (EF)	Cr (EF)	Pb (EF)
S1	0.29	0.81	1.12	0.52	1.14	3.91	0.58	0.82
S2	0.27	0.60	1.10	0.39	0.83	2.58	0.54	0.75
S3	0.21	0.46	0.75	0.34	0.55	1.98	0.51	0.77
S4	0.16	0.38	0.41	0.28	0.45	1.69	0.46	0.75
S5	0.24	0.47	0.48	0.29	0.54	2.10	0.39	0.84
S6	0.25	0.63	0.55	0.33	0.53	2.45	0.33	0.76
S7	0.31	0.93	0.58	0.45	0.56	3.33	0.40	1.03
S8	0.54	1.00	0.76	0.48	1.23	3.43	0.40	1.13
S9	0.60	1.04	0.91	0.39	1.24	3.58	0.39	1.34
S10	0.57	0.92	0.68	0.42	1.25	5.98	0.40	1.70
S11	0.52	0.68	0.48	0.46	2.02	2.44	0.41	2.24
S12	0.51	0.40	0.44	0.59	0.89	2.31	0.42	1.71
S13	0.55	0.61	0.40	0.63	0.93	4.19	0.48	1.04
S14	0.47	0.89	0.50	0.49	0.64	2.07	0.27	0.85
S15	0.44	0.09	0.74	0.44	0.58	1.55	0.21	0.95
S16	0.14	0.91	0.82	0.52	0.78	1.78	0.22	1.25
S17	0.54	0.99	0.78	0.52	1.02	3.83	0.52	1.14
S18	0.48	0.90	0.76	0.48	1.13	3.42	0.44	1.03
Average	**0.39**	**0.70**	**0.68**	**0.45**	**0.91**	**2.92**	**0.41**	**1.12**

Table 5.2.3. Enrichment Factors (EF) for trace metals in sediments of the Muvattupuzha River during May 2006

Station position	Mn (EF)	Co (EF)	Ni (EF)	Cu (EF)	Zn (EF)	Cd (EF)	Cr (EF)	Pb (EF)
S1	0.29	0.83	0.75	0.50	0.85	2.08	0.05	0.51
S2	0.26	0.53	0.61	0.31	0.64	1.90	0.10	0.43
S3	0.21	0.40	0.27	0.18	0.17	1.72	0.07	0.40
S4	0.20	0.21	0.13	0.13	0.11	1.67	0.05	0.38
S5	0.29	0.22	0.12	0.12	0.20	1.50	0.09	0.42
S6	0.23	0.37	0.13	0.22	0.48	2.11	0.23	0.40
S7	0.29	0.77	0.04	0.72	2.05	2.85	1.02	1.25
S8	0.33	0.62	0.28	0.53	1.06	2.65	0.96	1.02
S9	0.28	0.53	0.36	0.41	0.53	2.46	0.96	0.94
S10	0.58	0.44	0.22	0.25	0.33	0.78	0.29	0.59
S11	0.54	0.46	0.22	0.23	0.25	1.11	0.22	0.60
S12	0.41	0.44	0.24	0.29	0.27	1.47	0.29	0.61
S13	0.46	0.49	0.28	0.37	0.26	2.19	0.41	0.90
S14	0.36	0.72	0.44	0.52	0.58	1.56	0.35	0.93
S15	0.38	0.81	0.45	0.42	0.71	1.45	0.26	1.00
S16	0.43	0.82	0.53	0.51	0.72	1.84	0.31	1.24
S17	0.35	0.07	0.28	0.54	1.53	2.61	1.05	1.08
S18	0.36	0.81	0.37	0.59	1.75	2.91	1.13	1.15
Average	**0.35**	**0.53**	**0.32**	**0.38**	**0.69**	**1.94**	**0.23**	**0.77**

Table 5.2.4. Contamination Factors (CF) for trace metals in sediments of the Muvattupuzha River during July 2005

Station position	Fe (CF)	Mn (CF)	Co (CF)	Ni (CF)	Cu (CF)	Zn (CF)	Cd (CF)	Cr (CF)	Pb (CF)
S1	0.13	0.05	0.14	0.06	0.16	0.15	0.59	0.45	0.17
S2	0.23	0.10	0.27	0.12	0.24	0.33	0.93	0.47	0.23
S3	0.70	0.02	0.41	0.19	0.28	0.50	1.10	0.49	0.42
S4	0.96	0.16	0.48	0.21	0.30	0.53	1.26	0.50	0.58
S5	0.88	0.18	0.49	0.17	0.32	0.58	1.26	0.47	0.54
S6	0.85	0.47	0.52	0.13	0.33	0.63	1.34	0.42	0.50
S7	0.82	0.48	0.51	0.13	0.33	0.66	1.36	0.40	0.47
S8	0.79	0.46	0.54	1.19	0.34	0.62	1.39	0.45	0.54
S9	0.78	0.42	0.67	0.62	0.39	0.61	1.42	0.46	0.56
S10	0.94	0.34	0.46	0.29	0.28	0.40	1.45	0.43	0.65
S11	1.26	0.10	0.33	0.24	0.22	0.29	1.15	0.35	0.64
S12	0.97	0.15	0.32	0.18	0.19	0.26	1.01	0.33	0.63
S13	0.59	0.18	0.28	0.13	0.18	0.22	0.98	0.28	0.43
S14	0.47	0.19	0.39	0.19	0.17	0.38	1.05	0.28	0.40
S15	0.84	0.19	0.46	0.29	0.34	0.52	1.10	0.30	0.53
S16	0.87	0.19	0.47	0.32	0.52	0.54	1.12	0.29	0.84
S17	0.83	0.35	0.49	0.37	0.30	0.63	1.37	0.44	0.50
S18	0.83	0.33	0.52	0.37	0.31	0.65	1.41	0.44	0.48
Average	**0.76**	**0.24**	**0.43**	**0.29**	**0.29**	**0.47**	**1.18**	**0.40**	**0.51**

Table 5.2.5. Contamination Factors (CF) for trace metals in sediments of the Muvattupuzha River during September 2005

Station position	Fe (CF)	Mn (CF)	Co (CF)	Ni (CF)	Cu (CF)	Zn (CF)	Cd (CF)	Cr (CF)	Pb (CF)
S1	0.69	0.18	0.54	1.18	0.48	0.75	1.09	0.40	0.76
S2	0.82	0.16	0.44	0.89	0.47	0.73	0.99	0.38	0.84
S3	0.85	0.15	0.32	0.70	0.47	0.70	0.95	0.28	0.88
S4	0.89	0.15	0.29	0.27	0.47	0.68	0.90	0.25	0.94
S5	0.89	0.14	0.44	0.58	0.46	0.70	1.11	0.27	0.86
S6	0.87	0.48	0.67	0.81	0.53	0.73	1.33	0.31	0.81
S7	0.82	0.59	0.78	1.23	0.56	0.74	1.28	0.33	0.81
S8	0.23	0.58	0.83	1.31	0.60	0.72	0.96	0.33	0.24
S9	0.08	0.57	0.92	1.38	0.65	0.71	0.88	0.32	0.41
S10	0.18	0.10	0.44	0.86	0.70	0.41	0.63	0.27	0.63
S11	0.41	0.08	0.27	0.18	0.43	0.33	0.55	0.23	0.49
S12	0.45	0.12	0.26	0.17	0.15	0.28	0.46	0.19	0.35
S13	0.62	0.15	0.25	0.11	0.19	0.24	0.92	0.13	0.36
S14	0.69	0.27	0.40	0.28	0.22	0.55	1.18	0.21	0.41
S15	0.81	0.33	0.52	0.61	0.31	0.74	1.27	0.28	0.61
S16	0.81	0.58	0.60	0.76	0.41	0.82	1.38	0.32	0.95
S17	0.55	0.59	0.74	1.21	0.37	0.73	1.06	0.33	0.35
S18	0.59	0.57	0.78	1.20	0.35	0.73	1.07	0.32	0.26
Average	**0.62**	**0.32**	**0.53**	**0.76**	**0.43**	**0.63**	**1.00**	**0.29**	**0.61**

Table 5.2.6. Contamination Factors (CF) for trace metals in sediments of the Muvattupuzha River during November 2005

Station position	Fe (CF)	Mn (CF)	Co (CF)	Ni (CF)	Cu (CF)	Zn (CF)	Cd (CF)	Cr (CF)	Pb (CF)
S1	0.48	0.09	0.36	0.77	1.07	0.44	1.46	0.24	0.45
S2	0.44	0.10	0.33	0.66	0.60	0.39	1.32	0.22	0.39
S3	0.30	0.11	0.11	0.39	0.37	0.30	1.19	0.19	0.35
S4	0.33	0.12	0.29	0.16	0.25	0.24	1.17	0.13	0.34
S5	0.42	0.17	0.47	0.46	0.14	0.37	1.13	0.15	0.44
S6	0.49	0.26	0.47	0.70	0.20	0.42	1.31	0.19	0.58
S7	0.55	0.27	0.58	0.94	0.23	0.47	1.45	0.20	0.77
S8	0.50	0.26	0.47	0.88	0.27	0.40	1.44	0.16	0.62
S9	0.44	0.19	0.44	0.78	0.24	0.38	1.37	0.17	0.54
S10	0.43	0.08	0.29	0.61	0.24	0.37	1.23	0.16	0.47
S11	0.43	0.06	0.20	0.11	0.17	0.17	1.13	0.15	0.45
S12	0.56	0.10	0.22	0.10	0.13	0.15	1.03	0.19	0.35
S13	0.65	0.12	0.26	0.10	0.10	0.13	0.94	0.20	0.38
S14	0.84	0.22	0.40	0.24	0.14	0.27	1.16	0.19	0.50
S15	1.04	0.24	0.44	0.76	0.31	0.42	1.26	0.16	0.76
S16	1.21	0.26	0.60	0.90	0.47	0.45	1.37	0.15	0.98
S17	0.52	0.26	0.49	0.92	0.24	0.42	1.47	0.17	0.60
S18	0.78	0.24	0.51	0.94	0.25	0.44	1.45	0.18	0.60
Average	**0.58**	**0.18**	**0.39**	**0.58**	**0.30**	**0.35**	**1.27**	**0.18**	**0.53**

Table 5.2.7. Contamination Factors (CF) for trace metals in sediments of the Muvattupuzha River during January 2006

Station position	Fe (CF)	Mn (CF)	Co (CF)	Ni (CF)	Cu (CF)	Zn (CF)	Cd (CF)	Cr (CF)	Pb (CF)
S1	0.33	0.08	0.35	0.31	0.23	0.38	1.68	0.26	0.55
S2	0.37	0.09	0.37	0.29	0.24	0.37	1.66	0.25	0.53
S3	0.40	0.10	0.39	0.26	0.24	0.36	1.58	0.23	0.53
S4	0.44	0.12	0.46	0.25	0.25	0.35	1.53	0.22	0.54
S5	0.50	0.14	0.52	0.34	0.31	0.41	1.64	0.20	0.64
S6	0.54	0.15	0.60	0.40	0.34	0.44	1.66	0.23	0.66
S7	0.58	0.16	0.64	0.44	0.37	0.47	1.57	0.24	0.67
S8	0.48	0.17	0.54	0.36	0.20	0.40	1.39	0.21	0.57
S9	0.42	0.19	0.02	0.23	0.12	0.29	1.24	0.17	0.52
S10	0.49	0.18	0.28	0.20	0.04	0.29	1.21	0.16	0.49
S11	0.55	0.17	0.24	0.17	0.13	0.29	1.17	0.18	0.50
S12	0.51	0.14	0.21	0.14	0.18	0.19	1.23	0.18	0.41
S13	0.43	0.10	0.21	0.13	0.23	0.11	1.01	0.18	0.36
S14	0.67	0.20	0.47	0.27	0.23	0.29	0.78	0.19	0.50
S15	0.83	0.22	0.51	0.44	0.52	0.42	1.20	0.19	0.82
S16	0.83	0.16	0.57	0.60	0.80	0.65	1.61	0.21	0.93
S17	0.55	0.15	0.62	0.46	0.26	0.48	1.41	0.24	0.61
S18	0.56	0.15	0.63	0.50	0.23	0.47	1.44	0.23	0.62
Average	**0.53**	**0.15**	**0.42**	**0.32**	**0.27**	**0.37**	**1.39**	**0.21**	**0.58**

Table 5.2.8. Contamination Factors (CF) for trace metals in sediments of the Muvattupuzha River during March 2006

Station position	Fe (CF)	Mn (CF)	Co (CF)	Ni (CF)	Cu (CF)	Zn (CF)	Cd (CF)	Cr (CF)	Pb (CF)
S1	0.71	0.21	0.57	0.79	0.36	0.81	2.76	0.41	0.58
S2	0.74	0.20	0.44	0.81	0.29	0.61	1.90	0.40	0.55
S3	0.75	0.15	0.34	0.56	0.25	0.41	1.49	0.38	0.58
S4	0.79	0.13	0.30	0.33	0.22	0.35	1.34	0.37	0.59
S5	0.57	0.14	0.27	0.27	0.16	0.31	1.20	0.22	0.48
S6	0.41	0.10	0.26	0.23	0.14	0.22	1.00	0.14	0.31
S7	0.24	0.08	0.22	0.14	0.11	0.14	0.81	0.10	0.25
S8	0.25	0.14	0.25	0.19	0.12	0.31	0.87	0.10	0.28
S9	0.26	0.15	0.27	0.23	0.10	0.32	0.92	0.10	0.34
S10	0.26	0.15	0.24	0.18	0.11	0.33	1.58	0.10	0.45
S11	0.27	0.14	0.18	0.13	0.12	0.54	0.65	0.11	0.60
S12	0.26	0.13	0.11	0.11	0.16	0.24	0.61	0.11	0.45
S13	0.23	0.13	0.14	0.09	0.15	0.22	0.98	0.11	0.24
S14	0.54	0.26	0.48	0.27	0.26	0.35	1.11	0.15	0.46
S15	0.76	0.34	0.07	0.56	0.33	0.44	1.18	0.16	0.72
S16	0.77	0.11	0.70	0.63	0.40	0.60	1.36	0.17	0.96
S17	0.21	0.12	0.21	0.17	0.11	0.22	0.82	0.11	0.24
S18	0.23	0.11	0.21	0.18	0.11	0.26	0.80	0.10	0.24
Average	**0.46**	**0.15**	**0.29**	**0.33**	**0.20**	**0.37**	**1.19**	**0.19**	**0.46**

Table 5.2.9. Contamination Factors (CF) for trace metals in sediments of the Muvattupuzha River during May 2006

Station position	Fe (CF)	Mn (CF)	Co (CF)	Ni (CF)	Cu (CF)	Zn (CF)	Cd (CF)	Cr (CF)	Pb (CF)
S1	0.89	0.26	0.74	0.66	0.45	0.75	1.85	0.04	0.45
S2	0.91	0.24	0.48	0.56	0.28	0.58	1.73	0.09	0.40
S3	0.97	0.20	0.38	0.26	0.17	0.16	1.67	0.07	0.39
S4	0.98	0.19	0.21	0.13	0.13	0.11	1.63	0.05	0.37
S5	0.68	0.20	0.15	0.08	0.08	0.14	1.02	0.06	0.29
S6	0.29	0.07	0.11	0.04	0.06	0.14	0.61	0.07	0.12
S7	0.08	0.02	0.06	0.00	0.05	0.16	0.22	0.08	0.09
S8	0.09	0.03	0.06	0.03	0.05	0.10	0.25	0.09	0.10
S9	0.12	0.03	0.06	0.04	0.05	0.06	0.29	0.11	0.11
S10	0.42	0.24	0.19	0.09	0.11	0.14	0.33	0.12	0.25
S11	0.58	0.31	0.27	0.13	0.14	0.15	0.65	0.13	0.35
S12	0.52	0.21	0.23	0.12	0.15	0.14	0.76	0.15	0.32
S13	0.42	0.19	0.21	0.12	0.16	0.11	0.93	0.17	0.38
S14	0.61	0.22	0.44	0.27	0.32	0.36	0.96	0.21	0.57
S15	0.95	0.36	0.77	0.43	0.40	0.67	1.37	0.25	0.95
S16	0.95	0.41	0.78	0.51	0.48	0.69	1.75	0.30	1.18
S17	0.08	0.03	0.01	0.02	0.04	0.13	0.22	0.09	0.09
S18	0.08	0.03	0.06	0.03	0.05	0.14	0.23	0.09	0.09
Average	**0.53**	**0.18**	**0.29**	**0.20**	**0.18**	**0.26**	**0.91**	**0.12**	**0.36**

Table 5.3.0. Geo-accumulation Index (GAI) for trace metals in sediments of the Muvattupuzha River during July 2005

Station position	Fe (GAI)	Mn (GAI)	Co (GAI)	Ni (GAI)	Cu (GAI)	Zn (GAI)	Cd (GAI)	Cr (GAI)	Pb (GAI)
S1	-3.51	-4.90	-3.40	-4.58	-3.23	-3.29	-1.34	-1.73	-3.17
S2	-2.71	-3.94	-2.47	-3.64	-2.63	-2.19	-0.69	-1.67	-2.70
S3	-1.10	-6.03	-1.89	-2.97	-2.41	-1.59	-0.45	-1.62	-1.83
S4	-0.65	-3.26	-1.64	-2.85	-2.31	-1.51	-0.26	-1.60	-1.36
S5	-0.77	-3.07	-1.61	-3.14	-2.21	-1.37	-0.25	-1.66	-1.47
S6	-0.82	-1.69	-1.54	-3.49	-2.18	-1.26	-0.16	-1.84	-1.58
S7	-0.87	-1.64	-1.55	-3.54	-2.17	-1.18	-0.14	-1.90	-1.66
S8	-0.92	-1.70	-1.47	-0.33	-2.16	-1.27	-0.11	-1.73	-1.46
S9	-0.95	-1.82	-1.17	-1.27	-1.94	-1.29	-0.08	-1.69	-1.42
S10	-0.68	-2.14	-1.71	-2.39	-2.42	-1.91	-0.05	-1.80	-1.21
S11	-0.25	-3.92	-2.19	-2.64	-2.74	-2.38	-0.38	-2.10	-1.22
S12	-0.63	-3.32	-2.25	-3.03	-2.96	-2.52	-0.58	-2.20	-1.24
S13	-1.34	-3.09	-2.44	-3.51	-3.08	-2.75	-0.61	-2.44	-1.82
S14	-1.67	-3.02	-1.96	-2.95	-3.15	-1.99	-0.51	-2.40	-1.92
S15	-0.84	-2.96	-1.69	-2.37	-2.13	-1.53	-0.45	-2.32	-1.50
S16	-0.79	-2.97	-1.68	-2.24	-1.54	-1.47	-0.42	-2.37	-0.84
S17	-0.86	-2.08	-1.61	-2.01	-2.33	-1.25	-0.13	-1.78	-1.59
S18	-0.86	-2.18	-1.52	-2.04	-2.27	-1.20	-0.09	-1.77	-1.66
Average	**-1.12**	**-2.99**	**-1.88**	**-2.72**	**-2.44**	**-1.78**	**-0.37**	**-1.92**	**-1.65**

Table 5.3.1. Geo-accumulation Index (GAI) for trace metals in sediments of the Muvattupuzha River during September 2005

Station position	Fe (GAI)	Mn (GAI)	Co (GAI)	Ni (GAI)	Cu (GAI)	Zn (GAI)	Cd (GAI)	Cr (GAI)	Pb (GAI)
S1	-1.12	-3.05	-1.49	-0.35	-1.64	-0.99	-0.46	-1.90	-0.98
S2	-0.88	-3.20	-1.77	-0.76	-1.67	-1.04	-0.59	-1.97	-0.84
S3	-0.83	-3.28	-2.21	-1.10	-1.68	-1.11	-0.66	-2.41	-0.77
S4	-0.75	-3.34	-2.38	-2.48	-1.69	-1.14	-0.74	-2.57	-0.67
S5	-0.76	-3.39	-1.76	-1.37	-1.70	-1.10	-0.43	-2.47	-0.80
S6	-0.79	-1.64	-1.15	-0.88	-1.50	-1.03	-0.17	-2.28	-0.89
S7	-0.87	-1.35	-0.95	-0.28	-1.41	-1.01	-0.23	-2.17	-0.89
S8	-2.68	-1.38	-0.85	-0.19	-1.33	-1.07	-0.65	-2.19	-2.67
S9	-4.26	-1.39	-0.70	-0.12	-1.21	-1.07	-0.77	-2.24	-1.86
S10	-3.06	-3.85	-1.75	-0.80	-1.11	-1.86	-1.24	-2.48	-1.24
S11	-1.89	-4.19	-2.48	-3.02	-1.82	-2.19	-1.46	-2.68	-1.61
S12	-1.72	-3.63	-2.52	-3.16	-3.28	-2.43	-1.71	-3.00	-2.12
S13	-1.28	-3.33	-2.56	-3.81	-3.00	-2.67	-0.70	-3.57	-2.06
S14	-1.13	-2.47	-1.89	-2.41	-2.77	-1.45	-0.34	-2.81	-1.89
S15	-0.89	-2.17	-1.54	-1.30	-2.26	-1.02	-0.24	-2.40	-1.30
S16	-0.88	-1.38	-1.31	-0.97	-1.88	-0.87	-0.12	-2.21	-0.66
S17	-1.45	-1.36	-1.02	-0.31	-2.02	-1.04	-0.50	-2.16	-2.08
S18	-1.36	-1.39	-0.94	-0.32	-2.08	-1.03	-0.48	-2.21	-2.53
Average	**-1.48**	**-2.55**	**-1.63**	**-1.31**	**-1.89**	**-1.34**	**-0.64**	**-2.43**	**-1.44**

Table 5.3.2. Geo-accumulation Index (GAI) for trace metals in sediments of the Muvattupuzha River during November 2005

Station position	Fe (GAI)	Mn (GAI)	Co (GAI)	Ni (GAI)	Cu (GAI)	Zn (GAI)	Cd (GAI)	Cr (GAI)	Pb (GAI)
S1	-1.65	-4.00	-2.05	-0.97	-0.49	-1.78	-0.04	-2.64	-1.74
S2	-1.77	-3.93	-2.20	-1.17	-1.32	-1.94	-0.19	-2.76	-1.93
S3	-2.30	-3.76	-3.76	-1.93	-2.02	-2.33	-0.33	-2.96	-2.10
S4	-2.19	-3.69	-2.35	-3.20	-2.57	-2.66	-0.36	-3.57	-2.16
S5	-1.84	-3.10	-1.68	-1.69	-3.46	-2.02	-0.41	-3.34	-1.77
S6	-1.61	-2.55	-1.66	-1.10	-2.91	-1.84	-0.19	-2.99	-1.38
S7	-1.45	-2.46	-1.37	-0.68	-2.68	-1.67	-0.05	-2.94	-0.96
S8	-1.60	-2.56	-1.66	-0.77	-2.48	-1.89	-0.06	-3.20	-1.27
S9	-1.76	-2.99	-1.77	-0.95	-2.62	-1.98	-0.13	-3.16	-1.48
S10	-1.80	-4.25	-2.36	-1.31	-2.66	-2.04	-0.28	-3.22	-1.67
S11	-1.82	-4.73	-2.93	-3.80	-3.12	-3.18	-0.41	-3.28	-1.75
S12	-1.43	-3.86	-2.79	-3.86	-3.50	-3.35	-0.54	-3.00	-2.10
S13	-1.20	-3.62	-2.54	-3.91	-3.98	-3.48	-0.67	-2.89	-1.98
S14	-0.84	-2.75	-1.90	-2.62	-3.47	-2.45	-0.37	-2.98	-1.59
S15	-0.53	-2.62	-1.76	-0.99	-2.28	-1.84	-0.25	-3.23	-0.98
S16	-0.31	-2.53	-1.31	-0.74	-1.68	-1.73	-0.13	-3.31	-0.61
S17	-1.53	-2.54	-1.61	-0.71	-2.64	-1.83	-0.03	-3.16	-1.32
S18	-0.94	-2.64	-1.55	-0.67	-2.61	-1.76	-0.05	-3.08	-1.32
Average	**-1.48**	**-3.25**	**-2.07**	**-1.73**	**-2.58**	**-2.21**	**-0.25**	**-3.10**	**-1.56**

Table 5.3.3. Geo-accumulation Index (GAI) for trace metals in sediments of the Muvattupuzha River during January 2006

Station position	Fe (GAI)	Mn (GAI)	Co (GAI)	Ni (GAI)	Cu (GAI)	Zn (GAI)	Cd (GAI)	Cr (GAI)	Pb (GAI)
S1	-2.20	-4.16	-2.12	-2.26	-2.71	-1.99	0.16	-2.50	-1.44
S2	-2.01	-3.99	-2.03	-2.39	-2.64	-2.03	0.15	-2.61	-1.51
S3	-1.91	-3.86	-1.93	-2.52	-2.62	-2.07	0.07	-2.69	-1.49
S4	-1.78	-3.61	-1.70	-2.61	-2.56	-2.09	0.03	-2.79	-1.48
S5	-1.58	-3.43	-1.54	-2.16	-2.26	-1.88	0.13	-2.90	-1.23
S6	-1.47	-3.30	-1.33	-1.92	-2.13	-1.76	0.15	-2.73	-1.19
S7	-1.37	-3.19	-1.24	-1.77	-2.01	-1.68	0.06	-2.64	-1.16
S8	-1.65	-3.16	-1.48	-2.08	-2.88	-1.92	-0.11	-2.81	-1.39
S9	-1.85	-3.00	-5.97	-2.72	-3.63	-2.36	-0.27	-3.11	-1.54
S10	-1.60	-3.08	-2.42	-2.94	-5.26	-2.38	-0.31	-3.22	-1.61
S11	-1.44	-3.13	-2.65	-3.14	-3.50	-2.40	-0.36	-3.06	-1.59
S12	-1.55	-3.41	-2.83	-3.44	-3.06	-2.97	-0.28	-3.07	-1.89
S13	-1.81	-3.94	-2.86	-3.53	-2.72	-3.83	-0.58	-3.06	-2.07
S14	-1.16	-2.92	-1.67	-2.45	-2.73	-2.38	-0.94	-2.99	-1.58
S15	-0.86	-2.79	-1.55	-1.77	-1.53	-1.83	-0.33	-2.97	-0.87
S16	-0.85	-3.20	-1.40	-1.33	-0.91	-1.20	0.10	-2.85	-0.68
S17	-1.45	-3.29	-1.27	-1.72	-2.52	-1.64	-0.09	-2.67	-1.31
S18	-1.41	-3.29	-1.25	-1.59	-2.68	-1.66	-0.06	-2.73	-1.28
Average	**-1.55**	**-3.38**	**-2.07**	**-2.35**	**-2.69**	**-2.12**	**-0.14**	**-2.86**	**-1.41**

Table 5.3.4. Geo-accumulation Index (GAI) for trace metals in sediments of the Muvattupuzha River during March 2006

Station position	Fe (GAI)	Mn (GAI)	Co (GAI)	Ni (GAI)	Cu (GAI)	Zn (GAI)	Cd (GAI)	Cr (GAI)	Pb (GAI)
S1	-1.09	-2.87	-1.40	-0.92	-2.04	-0.89	0.88	-1.86	-1.36
S2	-1.02	-2.91	-1.77	-0.88	-2.37	-1.30	0.34	-1.91	-1.44
S3	-1.00	-3.28	-2.13	-1.41	-2.56	-1.87	-0.01	-1.98	-1.37
S4	-0.92	-3.54	-2.32	-2.19	-2.77	-2.08	-0.16	-2.03	-1.34
S5	-1.39	-3.46	-2.47	-2.45	-3.20	-2.28	-0.32	-2.76	-1.65
S6	-1.87	-3.85	-2.54	-2.73	-3.46	-2.80	-0.58	-3.47	-2.26
S7	-2.63	-4.32	-2.74	-3.42	-3.79	-3.47	-0.89	-3.95	-2.59
S8	-2.57	-3.46	-2.58	-2.96	-3.62	-2.27	-0.79	-3.90	-2.40
S9	-2.54	-3.28	-2.48	-2.68	-3.88	-2.23	-0.70	-3.89	-2.12
S10	-2.51	-3.32	-2.63	-3.07	-3.75	-2.18	0.07	-3.84	-1.74
S11	-2.48	-3.42	-3.04	-3.53	-3.61	-1.47	-1.20	-3.76	-1.32
S12	-2.51	-3.49	-3.82	-3.71	-3.27	-2.67	-1.31	-3.76	-1.74
S13	-2.68	-3.53	-3.40	-3.98	-3.34	-2.79	-0.61	-3.73	-2.63
S14	-1.48	-2.55	-1.64	-2.48	-2.52	-2.11	-0.43	-3.36	-1.71
S15	-0.98	-2.16	-4.51	-1.42	-2.18	-1.78	-0.35	-3.27	-1.06
S16	-0.97	-3.77	-1.11	-1.25	-1.90	-1.33	-0.14	-3.18	-0.65
S17	-2.81	-3.69	-2.83	-3.16	-3.75	-2.79	-0.87	-3.76	-2.61
S18	-2.69	-3.74	-2.83	-3.09	-3.76	-2.52	-0.91	-3.86	-2.65
Average	**-1.90**	**-3.37**	**-2.57**	**-2.52**	**-3.10**	**-2.16**	**-0.44**	**-3.24**	**-1.81**

Table 5.3.5. Geo-accumulation Index (GAI) for trace metals in sediments of the Muvattupuzha River during May 2006

Station position	Fe (GAI)	Mn (GAI)	Co (GAI)	Ni (GAI)	Cu (GAI)	Zn (GAI)	Cd (GAI)	Cr (GAI)	Pb (GAI)
S1	-0.76	-2.55	-1.02	-1.17	-1.75	-0.99	0.30	-5.17	-1.74
S2	-0.72	-2.67	-1.64	-1.43	-2.40	-1.36	0.20	-4.03	-1.92
S3	-0.63	-2.88	-1.96	-2.51	-3.12	-3.19	0.16	-4.50	-1.94
S4	-0.62	-2.97	-2.87	-3.53	-3.57	-3.79	0.12	-4.85	-2.02
S5	-1.14	-2.93	-3.36	-4.15	-4.20	-3.47	-0.56	-4.61	-2.38
S6	-2.39	-4.51	-3.84	-5.29	-4.56	-3.45	-1.31	-4.49	-3.70
S7	-4.30	-6.08	-4.68	-8.79	-4.79	-3.27	-2.79	-4.28	-3.99
S8	-3.99	-5.60	-4.68	-5.82	-4.91	-3.91	-2.58	-4.05	-3.96
S9	-3.67	-5.50	-4.58	-5.13	-4.94	-4.58	-2.37	-3.72	-3.76
S10	-1.83	-2.63	-3.02	-4.02	-3.82	-3.43	-2.18	-3.62	-2.59
S11	-1.36	-2.25	-2.47	-3.56	-3.47	-3.35	-1.21	-3.52	-2.10
S12	-1.54	-2.81	-2.71	-3.59	-3.31	-3.44	-0.98	-3.34	-2.24
S13	-1.83	-2.95	-2.85	-3.67	-3.24	-3.79	-0.69	-3.11	-1.97
S14	-1.29	-2.78	-1.76	-2.47	-2.22	-2.07	-0.64	-2.81	-1.39
S15	-0.66	-2.07	-0.97	-1.81	-1.90	-1.16	-0.13	-2.61	-0.66
S16	-0.66	-1.89	-0.95	-1.57	-1.64	-1.13	0.22	-2.33	-0.35
S17	-4.18	-5.69	-8.10	-6.03	-5.07	-3.56	-2.79	-4.11	-4.07
S18	-4.24	-5.73	-4.55	-5.68	-5.00	-3.43	-2.71	-4.07	-4.04
Average	**-1.99**	**-3.58**	**-3.11**	**-3.90**	**-3.55**	**-2.96**	**-1.11**	**-3.85**	**-2.49**

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Chapter 6

FRACTIONATION OF TRACE METALS IN SEDIMENTS OF THE MUVATTUPUZHA RIVER

6.1. Introduction

Trace metals are introduced anthropogenically as micro-pollutants into the aquatic environments from different sources such as industrial, agricultural and domestic effluents. Their fate, transport and pollution in aquatic systems are of wide environmental concern owing to its ecotoxic properties. Trace metal pollution of aquatic sediments is a pervasive problem which often constitutes a serious short term and long term risks for human beings, water quality and ecosystem health (Akcay et al. 2003; Sarkar et al. 2004; Sakan et al. 2009).

In aquatic sediments, heavy metals are partitioned in a number of chemical forms and exhibit different physico-chemical behaviours in terms of chemical interaction, mobility, bio-availability and potential toxicity (Tessier and Campbell, 1988; Li et al. 2000). The environmental behavior of trace metals is critically dependent on their associations with various sedimentary bound geochemical phases which influence the mobility, bioavailability and toxicity to organisms (Gibbs, 1973; Rauret, 1998; Tuzen, 2003). Eventhough total metal concentrations in water and sediments are often useful for

identifying hotspots of pollution that mediated by human sources of metal inputs but however cannot afford a powerful evidence regarding the mobility, storage, retention, bio-availability and toxicity of trace metals, since it depends on the chemical species by which they occur in aquatic environments (Devesa-Rey et al. 2010). Hence it is necessary to identify and quantify the chemical forms in which a metal is present in riverine sediment to gain a more precise understanding of the potential and actual impacts of elevated levels of metals in sediments and to evaluate processes of downstream transport, deposition and release under changing environmental conditions (Khairy et al. 2010).

The major mechanisms of accumulation of heavy metals in sediments lead to the existence of five categories; exchangeable, bound to carbonate, bound to reducible phases (iron & manganese), bound to organic matter and residual (Jain, 2004). These categories have different bio-geochemical behaviours with respect to remobilization under the changing environmental response and hydrodynamic conditions (Jain et al. 2007; Benson et al. 2013). Metals in exchangeable fraction are bound to the sediments by weak adsorption onto particles. Changes in ionic strength of the water are likely to affect the adsorption-desorption or ion-exchange process resulting in the uptake or release of metals at the sediment/water interface. Metals bound to carbonates are sensitive to pH changes with the lowering of pH being associated with the release of metal cations. Metal bound to Fe–Mn oxide fraction are unstable under reducing conditions which result in the release of metal ions to the dissolved fraction. Degradation of organic matter under oxidizing conditions can lead to the release of soluble metals bound to organic fractions. Residual fraction contains naturally occurring minerals which hold trace metals within their crystalline matrix.

Sequential extraction of metals in sediments as proposed by Tessier et al. (1979), is a multipurpose analytical tool which provides clues concerning their origin, mode of occurrence, bioavailability and toxicity. Metal speciation analysis, as proposed by Tessier et al. (1979), can be used to determine metal fractions released in controlled conditions, thus approximating metal leakage in the natural environment and hence in understanding the various pollution regimes and water-sediment diffusive fluxes or environmental compartment interactions within riverine systems (Jain, 2004). It is recognized that this method enables the prediction of possible metal impacts on biota in aquatic ecosystems (Benson et al. 2013).

Partition studies are not only useful for determining the degree of association of metals in sediments and to what extent they may be remobilized into the environment but also used for distinguishing those metals with a lithogenic origin from those with an anthropogenic origin (Forstner and Wittmann,1983). Hence the spatial variations of trace metal concentrations and its partitioning patterns in sediments are useful both in establishing the natural background levels and in assessing environmental contamination problems from anthropogenic sources in riverine systems (Chen et al. 2000). The fractions of heavy metals in sediments introduced by human activity show greater mobility and are hence "labile" which includes the metals bound to exchangeable, adsorptive, reducible and carbonate fractions (Salomons and Forstner, 1984). These are considered to be weakly binded metals with sediments which may equilibrate with the aqueous phase and thus become more rapidly bioavailable to aquatic organisms as the environmental parameters change (Salomons and Forstner, 1980; Pardo et al. 1990; Yang et

al. 2012). The metal present in the detrital and primary mineral phases can be regarded as a measure of the contribution by natural sources (Reimann and Caritat, 2005). In the absence of anthropogenic influences, trace metals in sediments are mainly associated with silicates and primary minerals which have limited mobility. The Fe–Mn oxide and organic matter have a scavenging effect and may provide a sink for heavy metals (Salomons and Forstner, 1984). The release of metals from this matrix will most likely be affected by the redox potential and pH (Soares et al. 1999).

The rationale of the sequential extraction procedure as proposed by Tessier et al. (1979) is that each successive reagent dissolves a different component so that the resulting elemental distributions can be used to infer information about the mobility and bioavailability of an element or its potential risks posed to the environment (Rauret, 1998; Filgueiras et al. 2002). Jain (2004) used a risk assessment code (RAC) to assess and estimate the environmental risks and possible damage effects to benthic organisms that caused by trace metal contaminated sediments in river Yamuna. The RAC considers the percentage fraction of metals that are exchangeable and associated with carbonates. In these fractions the metals are weakly bound to the sediment and present at a greater environmental risk since they are more bio-available to the aquatic system. The RAC classification defines risk levels as zero, low, medium, high and very high, depending on the percentage value (Perin et al., 1985). The metal concentrations associated with sediments in different phases of the Muvattupuzha River are discussed below.

Results and Discussion

6.2. Spatial and bimonthly variations of trace metal concentrations in different phases/fractions of sediments

The spatial and bimonthly variations of trace metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in the exchangeable, carbonate, Fe-Mn oxide/reducible, organic/sulphide, and residual fractions (or phases) of sediments at 18 stations from the upstream regions of the Muvattupuzha River are given in Annexure as *Tables A6.1.0. to A6.6.3*. The bimonthly mean values and standard deviations of trace metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in different phases of sediments at 18 stations from the upstream regions of the Muvattupuzha River are also given in *Tables 6.6.5. to 6.7.3.* In order to describe the seasonal variations of metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) in different phases of sediments, mean values of each element in different phases are calculated for the respective months of monsoon, post-monsoon and pre-monsoon periods were plotted and are shown in *Figures 6.1.1.* to *6.5.5.* respectively.

6.2a. Iron

Iron content in the exchangeable phase varies between 18.8 to 432.8 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, iron content averages to 251.3 ± 97.6 ppm, 199.8 ± 90.1 ppm, 180.5 ± 87.7 ppm, 164.2 ± 50.5 ppm, 138.6 ± 85.4 ppm and 168.0 ± 97.3 ppm respectively during the July, September, November, January, March and May months. Iron content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.1.*).

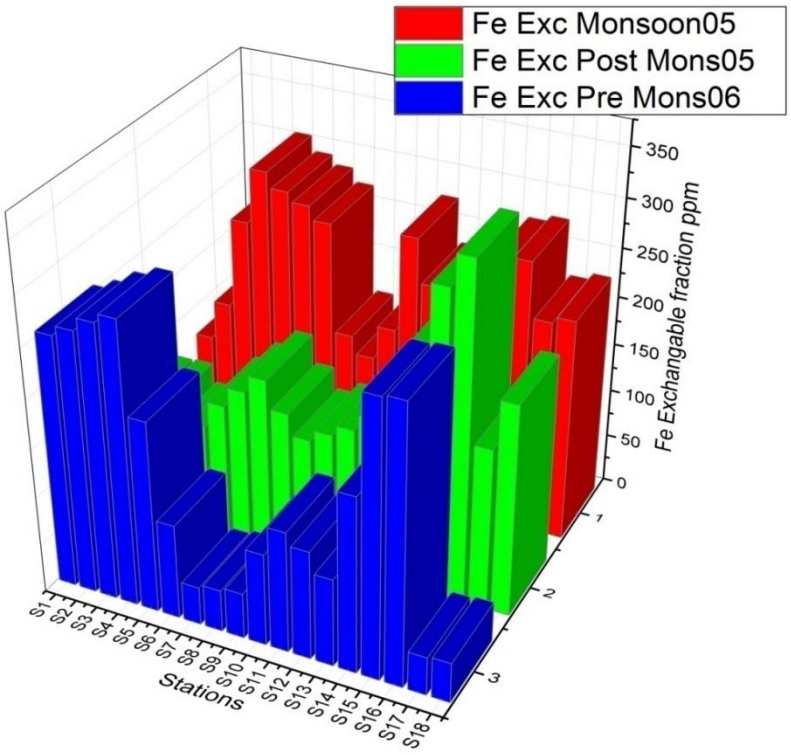

Figure 6.1.1. Seasonal variations of iron in the exchangeable fraction of sediments of the Muvattupuzha River

In the carbonate phase, iron content varies between 32.5 to 546.4 ppm during the months of July 2005 to May 2006. Iron content in the carbonate phase averages to 313.5 ± 110.3ppm, 250.6 ± 103.5 ppm, 224.9 ± 106.2ppm, 200.8 ± 60.8ppm, 170.8 ± 70.5 ppm and 179.2 ± 88.5 ppm respectively during the July, September, November, January, March and May months. In the carbonate phase, iron content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.2.*).

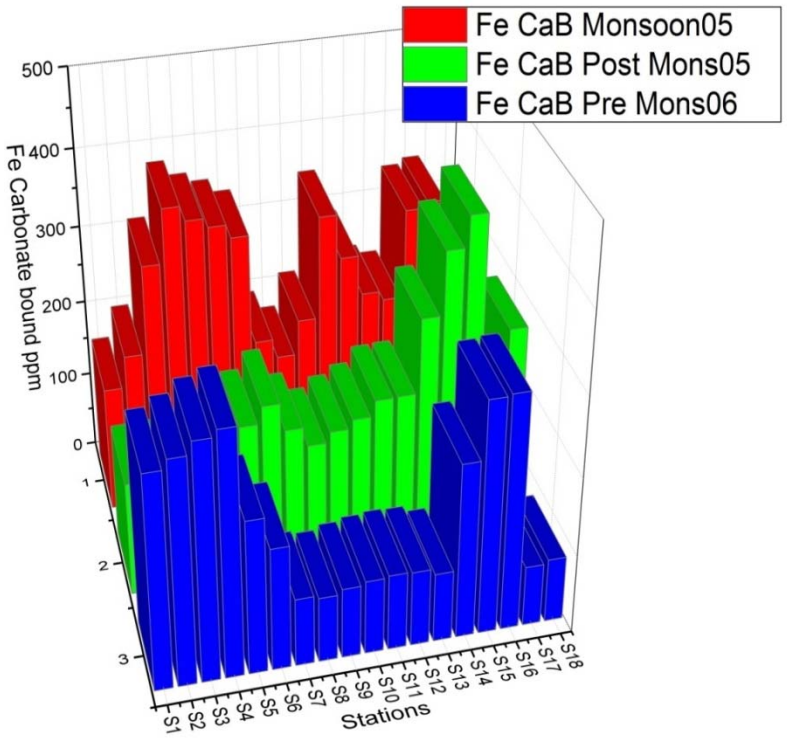

Figure 6.1.2. Seasonal variations of iron in the carbonate fraction of sediments of the Muvattupuzha River

Iron concentration in the Fe-Mn oxide phase varies between 234.4 to 2949.7 ppm during the periods of July 2005 to May 2006. In the Fe-Mn oxide phase, iron concentration averages to 2240.2 ± 851.5 ppm, 1811.4 ± 782.5 ppm, 1638.1 ± 770.5 ppm, 1476.2 ± 441.8 ppm, 1259.0 ± 755.4 ppm and 1557.2 ± 758.5 ppm respectively during the July, September, November, January, March and May months. Iron concentration in the Fe-Mn oxide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.3.*).

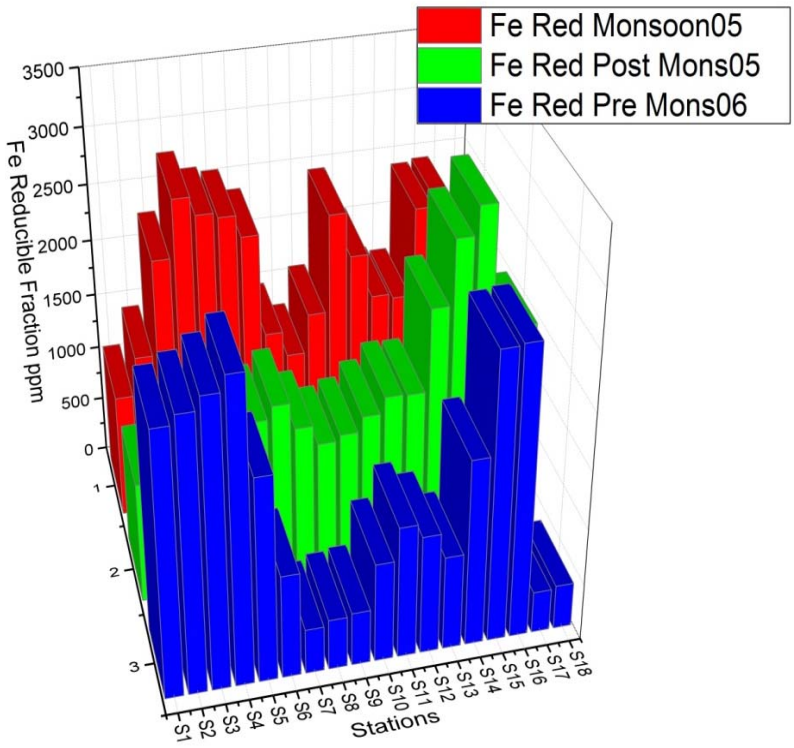

Figure 6.1.3. Seasonal variations of iron in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

In the organic/sulphide phase, iron content varies between 16.2 to 310.0 ppm during the months of July 2005 to May 2006. Iron content in the organic/sulphide phase averages to 180.1 ± 68.5 ppm, 144.4 ± 65.5 ppm, 131.2 ± 63.4 ppm, 117.8 ± 36.8 ppm, 100.3 ± 61.7 ppm and 124.3 ± 85.7 ppm respectively during the July, September, November, January, March and May months. In the organic/sulphide phase, iron content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.4.*).

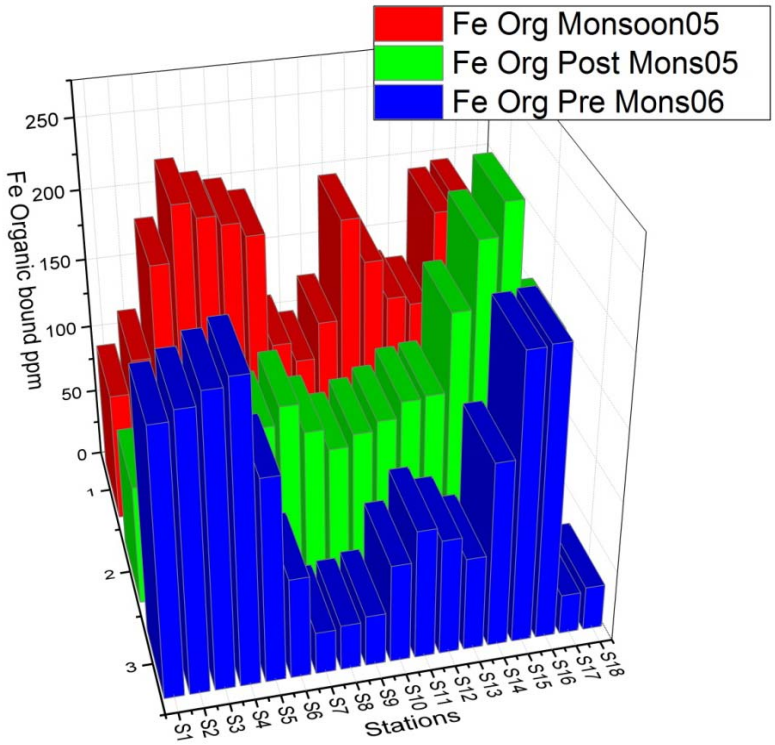

Figure 6.1.4. Seasonal variations of iron in the organic fraction of sediments of the Muvattupuzha River

Iron concentration in the residual phase varies between 3386.1 to 54004.3 ppm during the periods of July 2005 to May 2006. In the residual phase, iron concentration averages to 33062.2 ± 11356.8 ppm, 27086.2 ± 11342.5 ppm, 24931.7 ± 10433.5 ppm, 22926.7 ± 5947.5 ppm, 19965.3 ± 10250.7 ppm and 22982.8 ± 11450.5 ppm respectively during the July, September, November, January, March and May months. Iron concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.5.*).

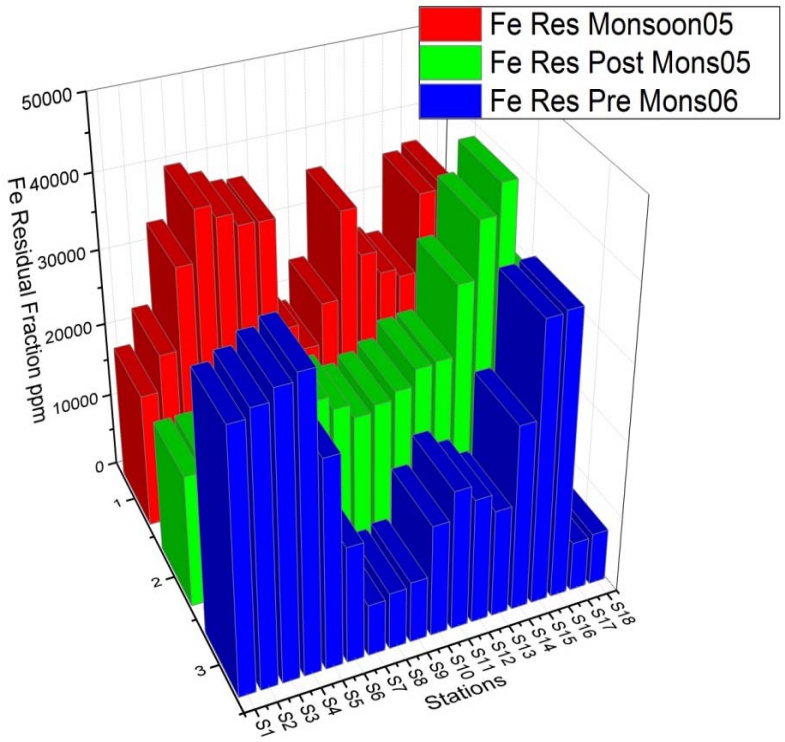

Figure 6.1.5. Seasonal variations of iron in the residual fraction of sediments of the Muvattupuzha River

6.2b. Manganese

Manganese content in the exchangeable phase varies between 1.13 to 32.49 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, manganese content averages to 12.73 ± 5.39 ppm, 17.19 ± 6.65 ppm, 8.78 ± 4.39 ppm, 7.28 ± 2.13 ppm, 7.57 ± 3.52 ppm and 9.36 ± 4.85 ppm respectively during the July, September, November, January, March and May months. Manganese content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.6.*).

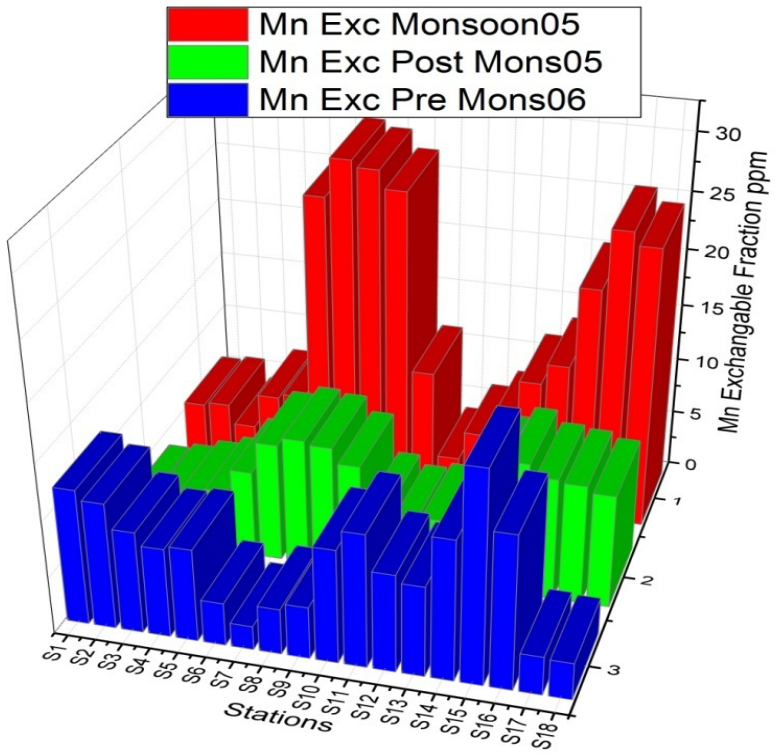

Figure 6.1.6. Seasonal variations of manganese in the exchangeable fraction of sediments of the Muvattupuzha River

In the carbonate phase, manganese content varies between 0.53 to 14.84 ppm during the months of July 2005 to May 2006. Manganese content in the carbonate phase averages to 5.31 ± 3.35 ppm, 7.15 ± 3.38 ppm, 3.63 ± 1.84 ppm, 3.01 ± 0.91ppm, 3.09 ± 1.45ppm and 3.88 ± 2.61 ppm respectively during the July, September, November, January, March and May months. In the carbonate phase, manganese content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.7.*).

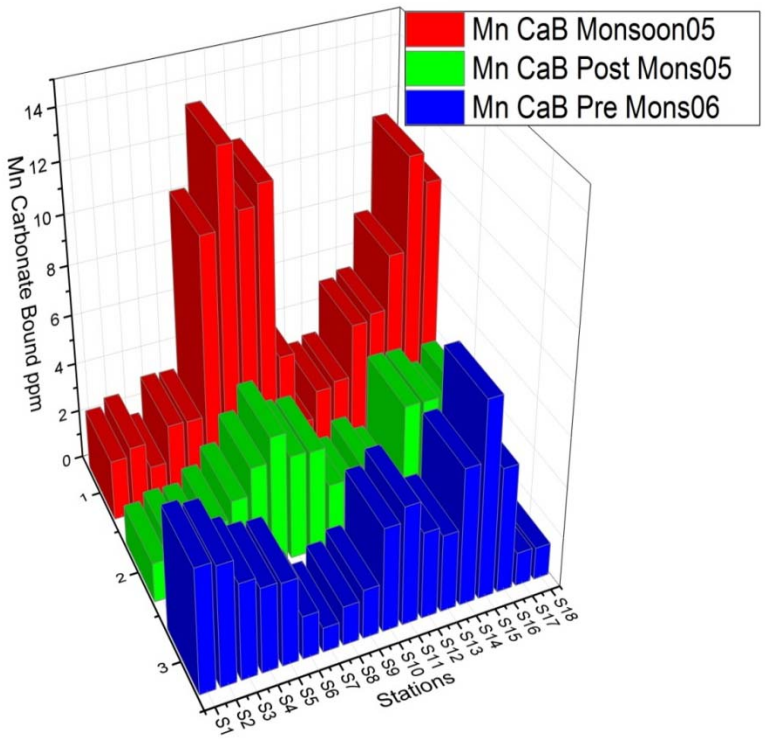

Figure 6.1.7. Seasonal variations of manganese in the carbonate fraction of sediments of the Muvattupuzha River

Manganese concentration in the Fe-Mn oxide phase varies between 5.52 to 160.97 ppm during the months of July 2005 to May 2006. In the Fe-Mn oxide phase, manganese concentration averages to 63.38 ± 25.58 ppm, 85.26 ± 28.68 ppm, 43.91 ± 21.08 ppm, 36.14 ± 10.47 ppm, 37.73 ± 12.57 ppm and 46.53 ± 12.85 ppm respectively during the July, September, November, January, March and May months. Manganese concentration in the Fe-Mn oxide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.8.*).

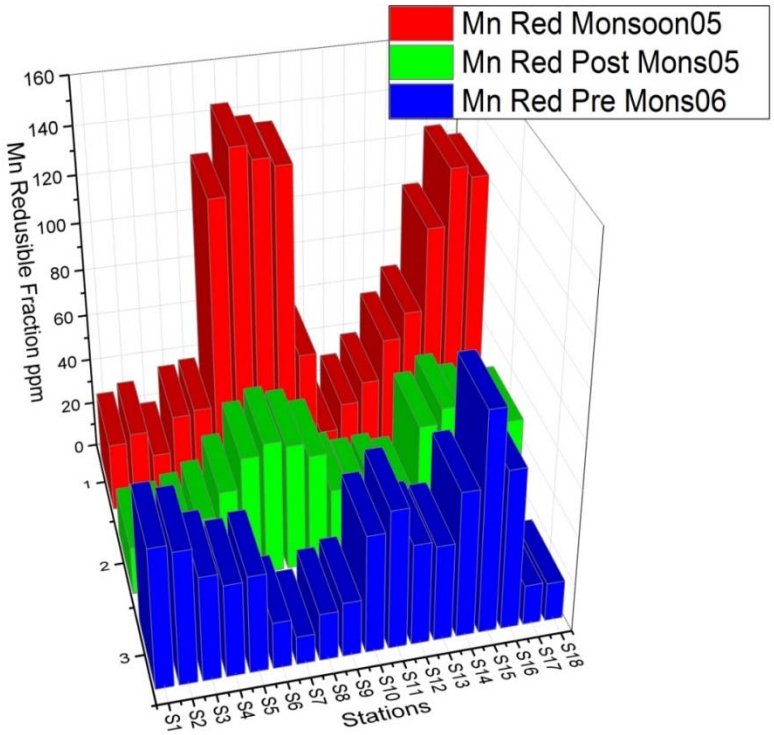

Figure 6.1.8. Seasonal variations of manganese in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

In the organic/sulphide phase, manganese content varies between 5.55 to 173.15 ppm during the periods of July 2005 to May 2006. Manganese content in the organic/sulphide phase averages to 68.10 ± 23.57 ppm, 92.20 ± 25.57 ppm, 47.32 ± 20.55 ppm, 39.14 ± 11.35 ppm, 40.71 ± 12.85 ppm and 50.31 ± 18.87 ppm respectively during the July, September, November, January, March and May months. In the organic/sulphide phase, manganese content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.1.9.*).

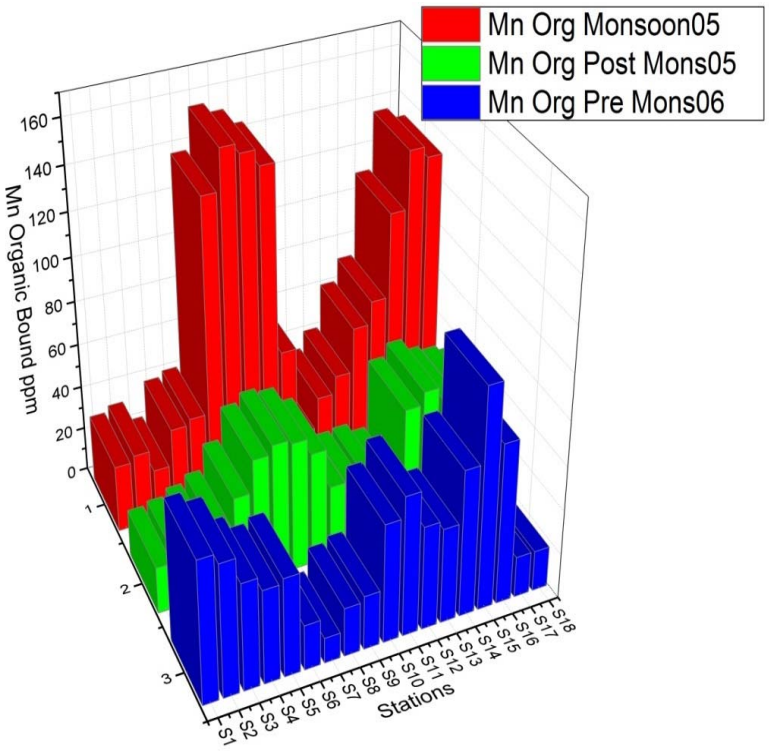

Figure 6.1.9. Seasonal variations of manganese in the organic fraction of sediments of the Muvattupuzha River

Manganese concentration in the residual phase varies between 6.08 to 129.76 ppm during the months of July 2005 to May 2006. In the residual phase, manganese concentration averages to 49.27 ± 27.85 ppm, 74.02 ± 33.55 ppm, 43.59 ± 16.52 ppm, 38.21 ± 8.35 ppm, 38.34 ± 9.68 ppm and 42.87 ± 15.65 ppm respectively during the July, September, November, January, March and May months. Manganese concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.0.*).

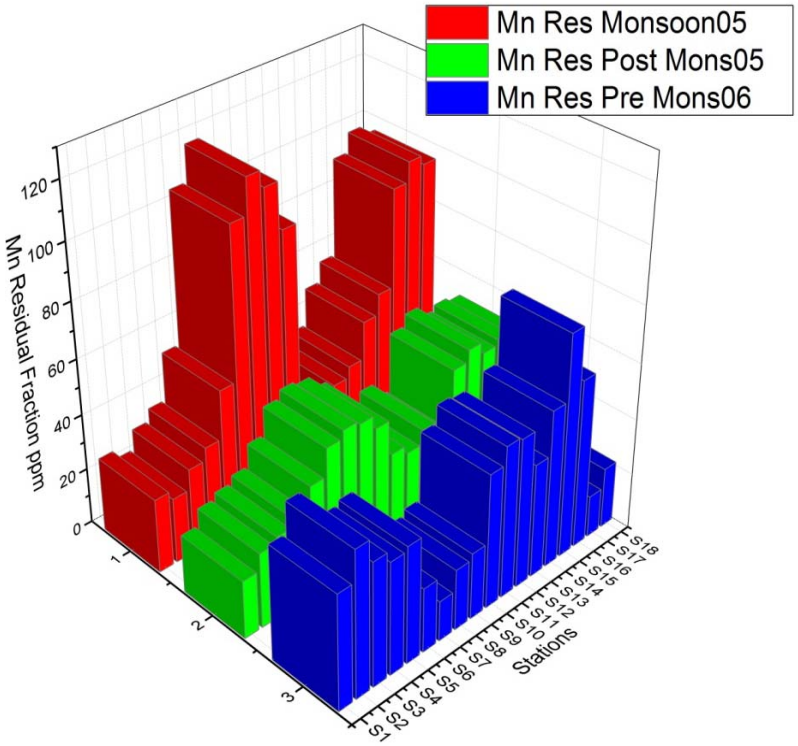

Figure 6.2.0. Seasonal variations of manganese in the residual fraction of sediments of the Muvattupuzha River

6.2c. Cobalt

Cobalt content in the exchangeable phase varies between 0.012 to 2.023 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, cobalt content averages to 0.936 ± 0.273 ppm, 1.153 ± 0.427 ppm, 0.839 ± 0.302 ppm, 0.922 ± 0.387 ppm, 0.633 ± 0.356 ppm and 0.625 ± 0.325 ppm respectively during the July, September, November, January, March and May months. Cobalt content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.1.*).

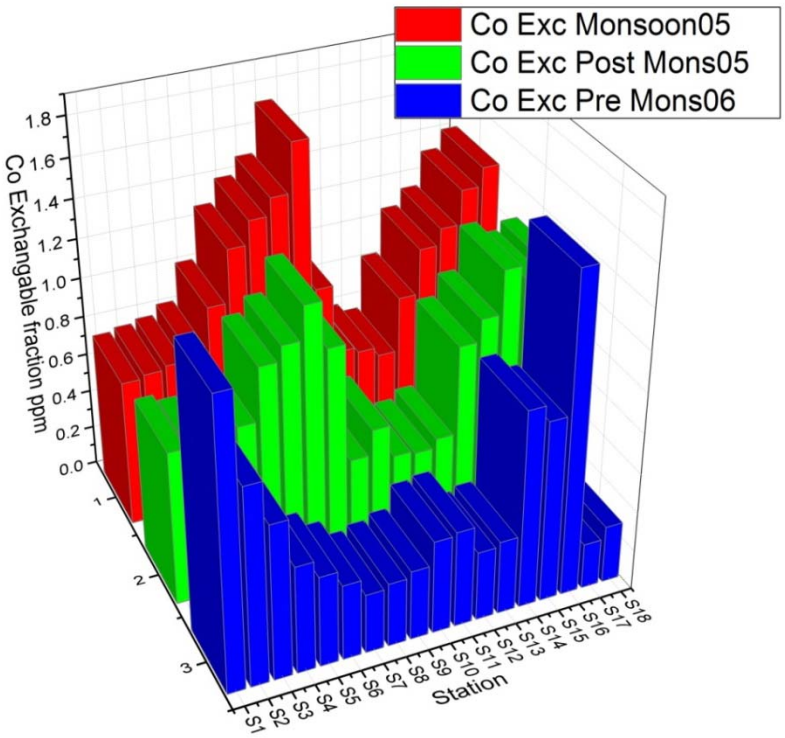

Figure 6.2.1. Seasonal variations of cobalt in the exchangeable fraction of sediments of the Muvattupuzha River

Cobalt concentration in the carbonate phase varies between 0.007 to 1.133 ppm during the months of July 2005 to May 2006. In the carbonate phase, cobalt concentration averages to 0.517 ± 0.151ppm, 0.629 ± 0.257 ppm, 0.462 ± 0.163 ppm, 0.501 ± 0.165 ppm, 0.351 ± 0.165 ppm and 0.346 ± 0.151 ppm respectively during the July, September, November, January, March and May months. Cobalt concentration in the carbonate phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.2.*).

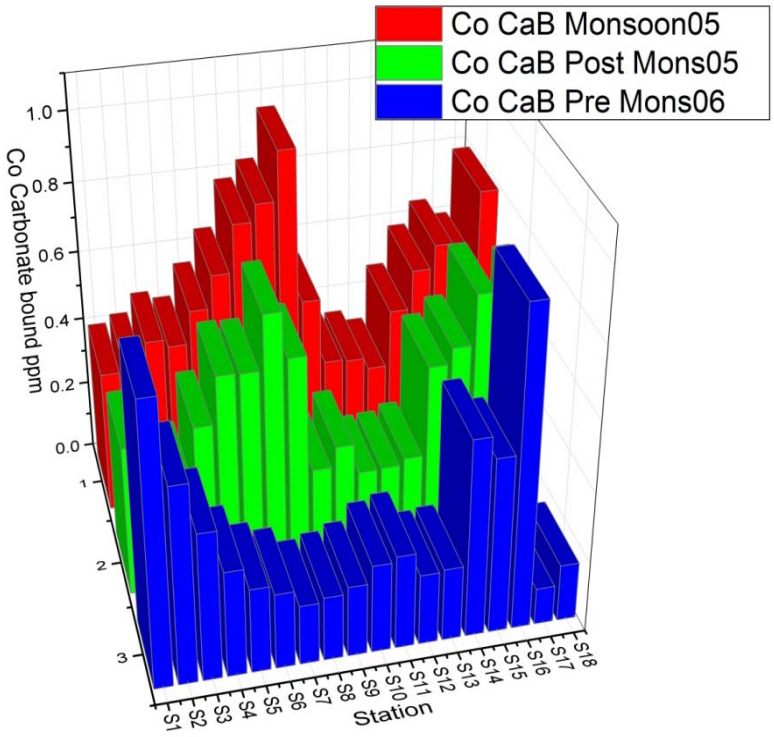

Figure 6.2.2. Seasonal variations of cobalt in the carbonate fraction of sediments of the Muvattupuzha River

In the Fe-Mn oxide phase, cobalt content varies between 0.011 to 1.780 ppm during the periods of July 2005 to May 2006. Cobalt content in the Fe-Mn oxide phase averages to 0.848 ± 0.232 ppm, 1.042 ± 0.405 ppm, 0.770 ± 0.251 ppm, 0.833 ± 0.305 ppm, 0.598 ± 0.302 ppm and 0.587 ± 0.308 ppm respectively during the July, September, November, January, March and May months. In the Fe-Mn oxide phase, cobalt content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.3.*).

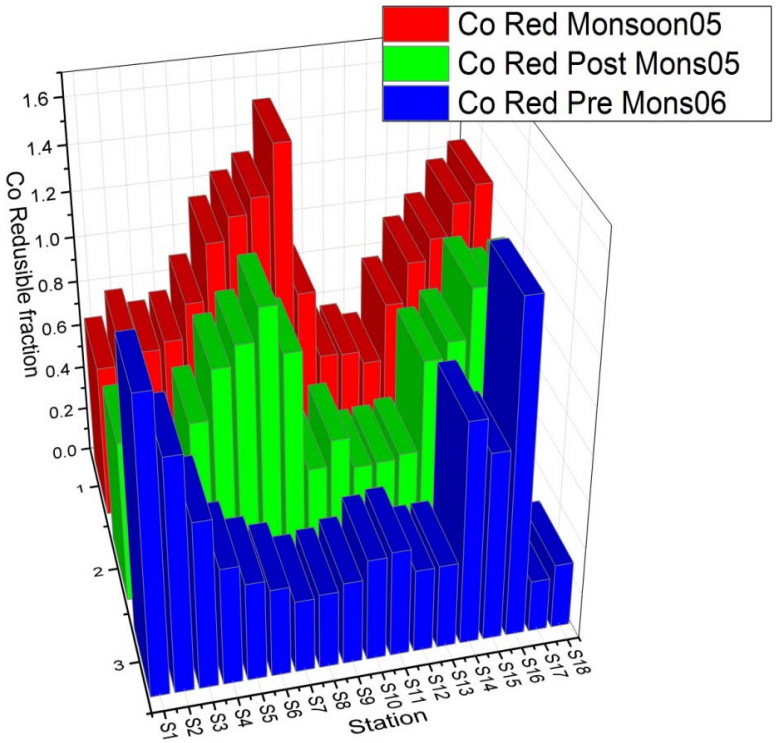

Figure 6.2.3. Seasonal variations of cobalt in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

Cobalt content in the organic/sulphide phase varies between 0.021 to 3.920 ppm during the periods of July 2005 to May 2006. In the organic/sulphide phase, cobalt content averages to 1.818 ± 0.533 ppm, 2.221 ± 0.929 ppm, 1.621 ± 0.585 ppm, 1.781 ± 0.752 ppm, 1.229 ± 0.685 ppm and 1.210 ± 0.856 ppm respectively during the July, September, November, January, March and May months. Cobalt content in the organic/sulphide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.4.*).

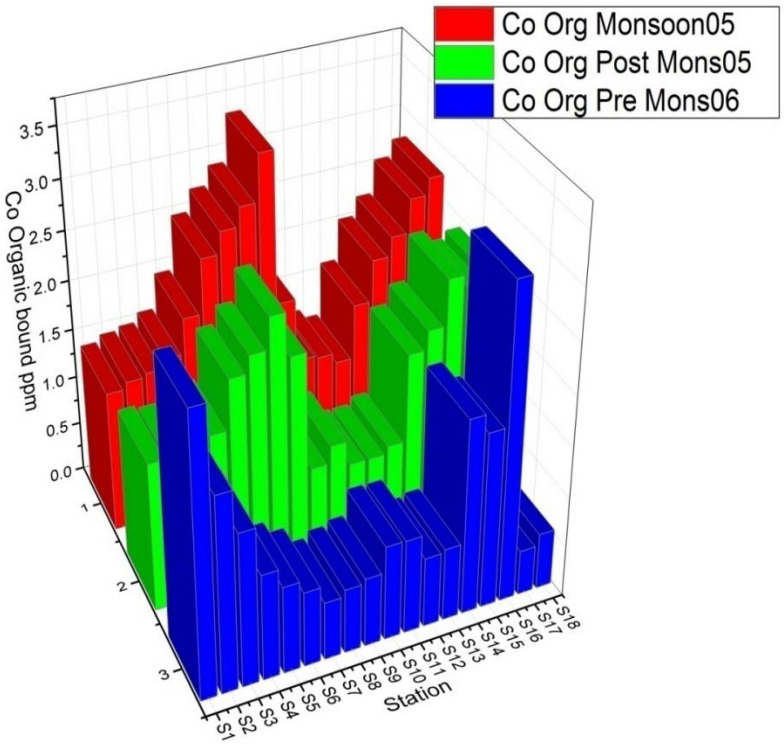

Figure 6.2.4. Seasonal variations of cobalt in the organic fraction of sediments of the Muvattupuzha River

Cobalt concentration in the residual phase varies between 0.052 to 8.710 ppm during the months of July 2005 to May 2006. In the residual phase, cobalt concentration averages to 4.065 ± 1.180 ppm, 4.999 ± 2.045 ppm, 3.658 ± 1.302 ppm, 4.025 ± 1.605 ppm, 2.764 ± 1.152 ppm and 2.728 ± 1.857 ppm respectively during the July, September, November, January, March and May months. Cobalt concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.5.*).

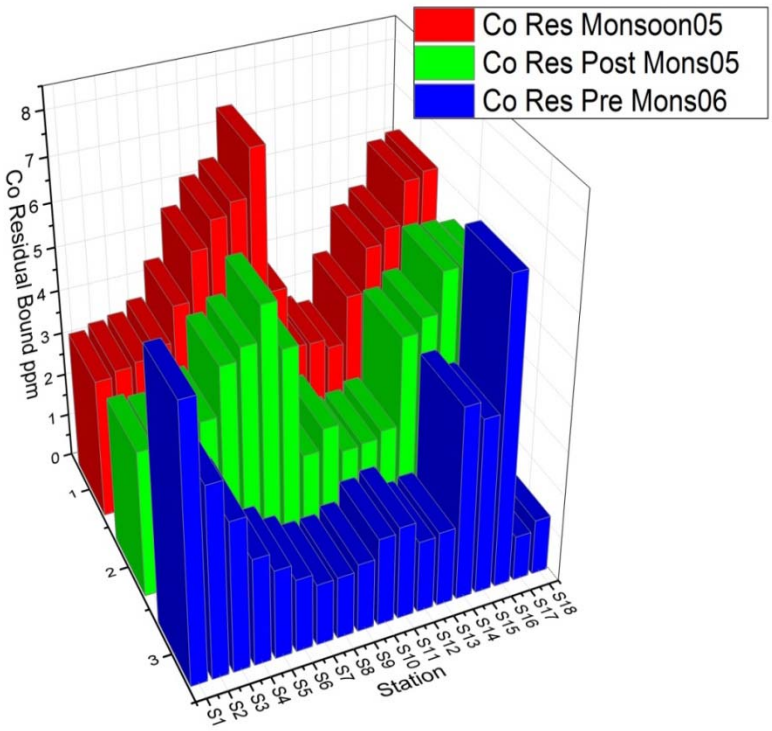

Figure 6.2.5. Seasonal variations of cobalt in the residual fraction of sediments of the Muvattupuzha River

6.2d. Nickel

Nickel content in the exchangeable phase varies between 0.02 to 8.16 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, nickel content averages to 1.70 ± 1.15 ppm, 4.45 ± 2.08 ppm, 3.38 ± 1.65 ppm, 1.86 ± 0.75 ppm, 1.91 ± 1.08 ppm and 1.15 ± 0.85 ppm respectively during the July, September, November, January, March and May months. Nickel content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.6.*).

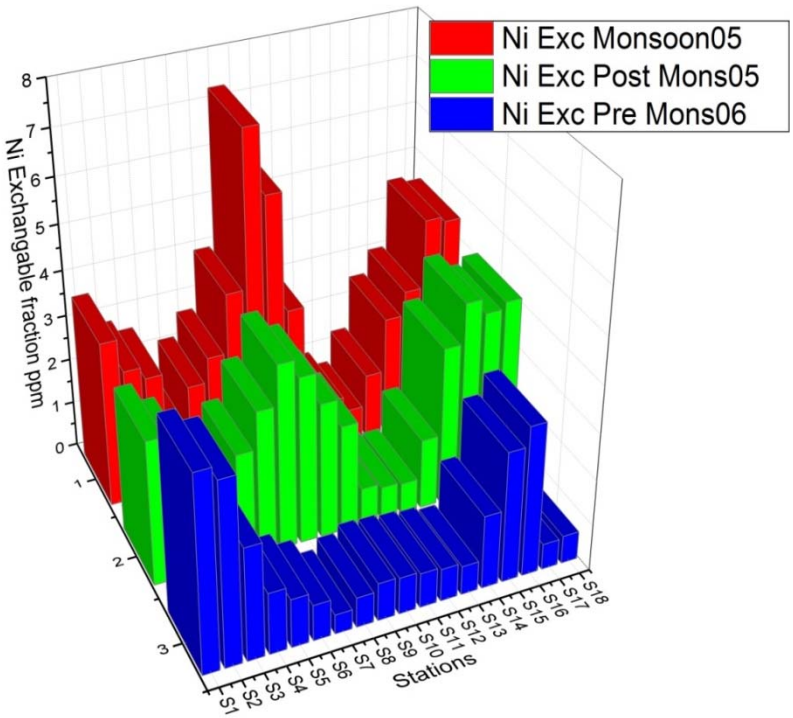

Figure 6.2.6. Seasonal variations of nickel in the exchangeable fraction of sediments of the Muvattupuzha River

In the carbonate phase, nickel content varies between 0.01 to 4.24 ppm during the periods of July 2005 to May 2006. Nickel content in the carbonate phase averages to 0.88 ± 0.65 ppm, 2.31 ± 1.30 ppm, 1.76 ± 0.97 ppm, 0.97 ± 0.40 ppm, 0.99 ± 0.71 ppm and 0.59 ± 0.35 ppm respectively during the July, September, November, January, March and May months. In the carbonate phase, nickel content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.7.*).

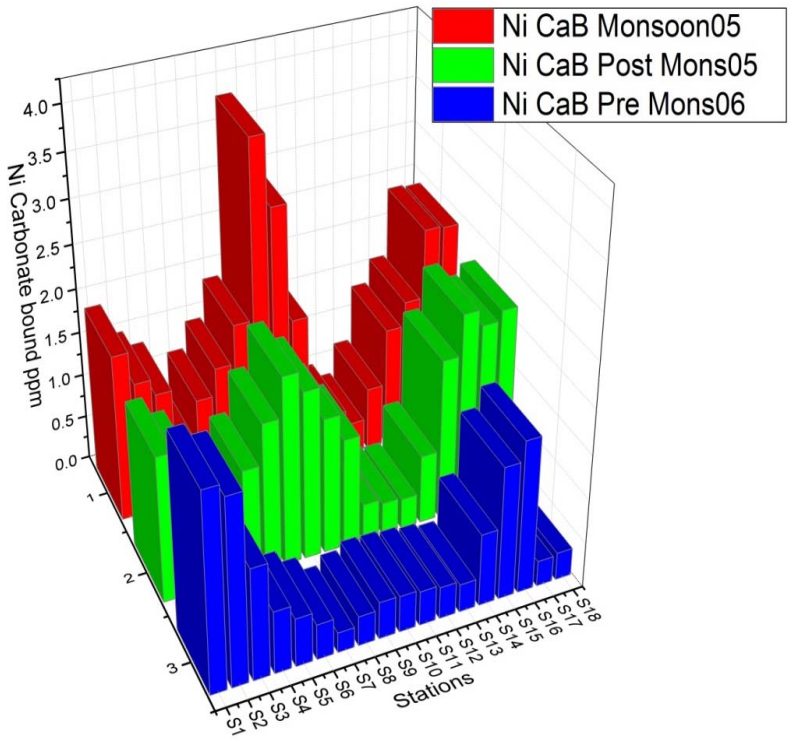

Figure 6.2.7. Seasonal variations of nickel in the carbonate fraction of sediments of the Muvattupuzha River

Nickel content in the Fe-Mn oxide phase varies between 0.01 to 3.90 ppm during the periods of July 2005 to May 2006. In the Fe-Mn oxide phase, nickel content averages to 0.83 ± 0.74 ppm, 2.16 ± 1.22 ppm, 1.64 ± 0.90 ppm, 0.91 ± 0.33 ppm, 0.93 ± 0.36 ppm and 0.56 ± 0.28 ppm respectively during the July, September, November, January, March and May months. Nickel content in the Fe-Mn oxide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.8.*).

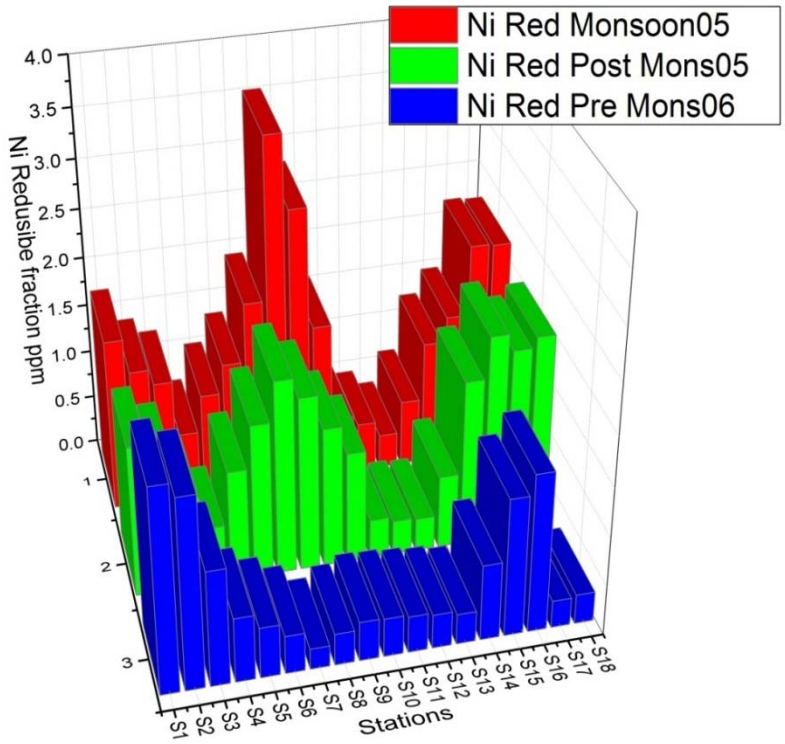

Figure 6.2.8. Seasonal variations of nickel in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

In the organic/sulphide phase, nickel content varies between 0.02 to 7.14 ppm during the periods of July 2005 to May 2006. Nickel content in the organic/sulphide phase averages to 1.49 ± 1.07 ppm, 3.95 ± 2.24 ppm, 2.99 ± 1.65 ppm, 1.64 ± 0.67 ppm, 1.68 ± 1.22 ppm and 1.00 ± 0.85 ppm respectively during the July, September, November, January, March and May months. In the organic/sulphide phase, nickel content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.2.9.*).

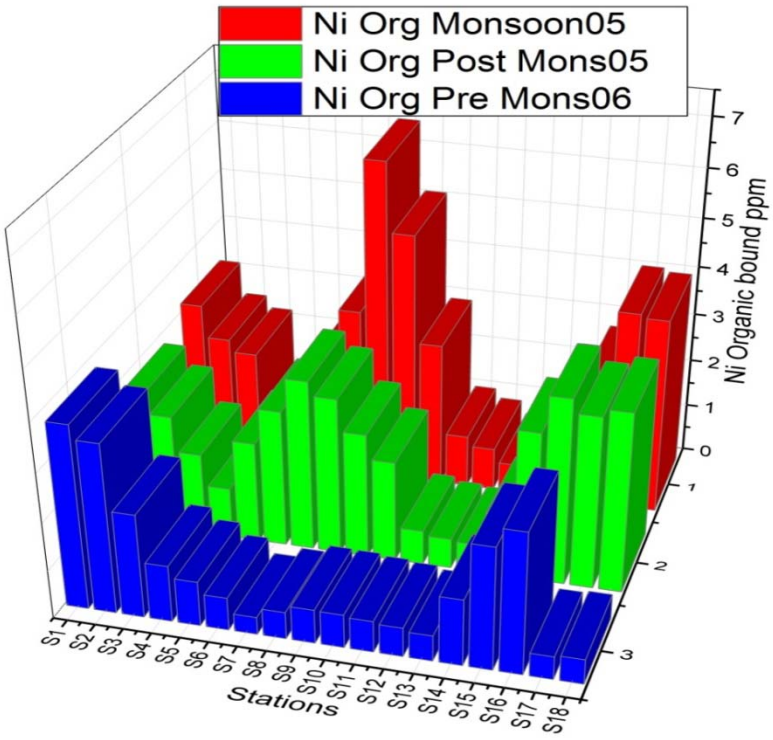

Figure 6.2.9. Seasonal variations of nickel in the organic fraction of sediments of the Muvattupuzha River

Nickel concentration in the residual phase varies between 0.16 to 64.44 ppm during the months of July 2005 to May 2006. In the residual phase, nickel concentration averages to 13.55 ± 10.25 ppm, 35.58 ± 20.01 ppm, 26.91 ± 14.60 ppm, 14.82 ± 5.94 ppm, 15.26 ± 11.08 ppm and 9.14 ± 5.65 ppm respectively during the July, September, November, January, March and May months. Nickel concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.0.*).

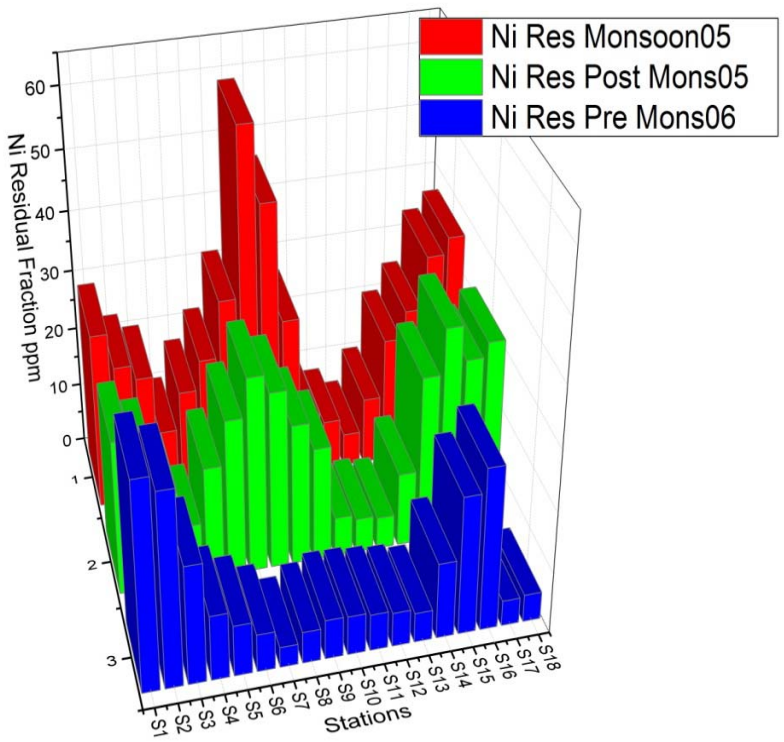

Figure 6.3.0. Seasonal variations of nickel in the residual fraction of sediments of the Muvattupuzha River

6.2e. Copper

Copper content in the exchangeable phase varies between 0.61 to 15.50 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, copper content averages to 4.43 ± 1.38 ppm, 6.66 ± 2.31 ppm, 4.59 ± 3.31 ppm, 4.21 ± 2.55 ppm, 2.98 ± 1.48 ppm and 2.72 ± 1.13 ppm respectively during the July, September, November, January, March and May months. Copper content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.1.*).

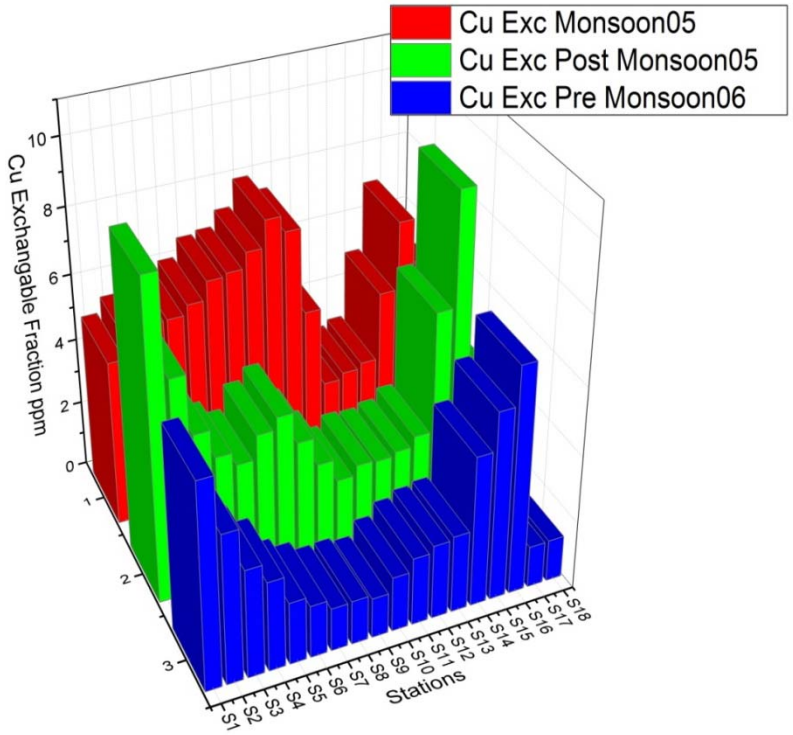

Figure 6.3.1. Seasonal variations of copper in the exchangeable fraction of sediments of the Muvattupuzha River

In the carbonate phase, copper content varies between 0.10 to 3.47 ppm during the periods of July 2005 to May 2006. Copper content in the carbonate phase averages to 0.83 ± 0.30 ppm, 1.32 ± 0.51 ppm, 0.87 ± 0.55 ppm, 0.79 ± 0.53 ppm, 0.51 ± 0.31 ppm and 0.49 ± 0.30 ppm respectively during the July, September, November, January, March and May months. In the carbonate phase, copper content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.2.*).

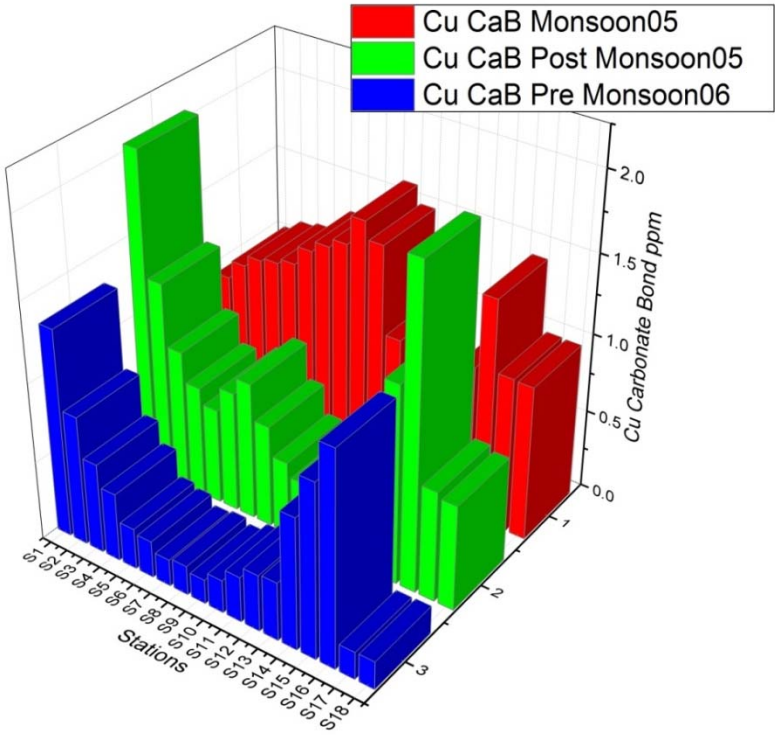

Figure 6.3.2. Seasonal variations of copper in the carbonate fraction of sediments of the Muvattupuzha River

Copper concentration in the Fe-Mn oxide phase varies between 0.16 to 2.53 ppm during the months of July 2005 to May 2006. In the Fe-Mn oxide phase, copper concentration averages to 0.75 ± 0.21 ppm, 1.08 ± 0.35 ppm, 0.77 ± 0.53 ppm, 0.71 ± 0.38 ppm, 0.52 ± 0.23 ppm and 0.48 ± 0.21 ppm respectively during the July, September, November, January, March and May months. Copper concentration in the Fe-Mn oxide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.3.*).

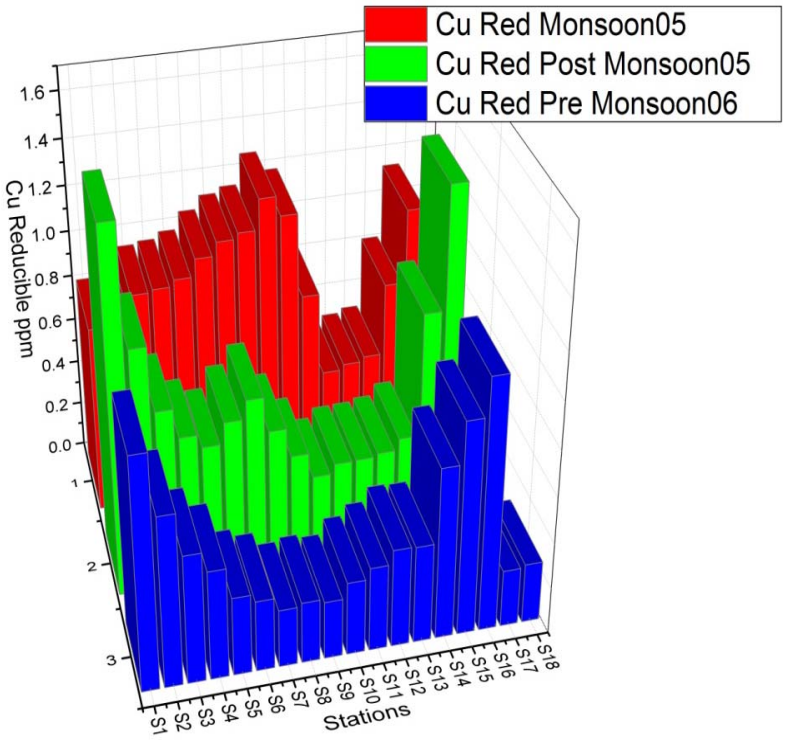

Figure 6.3.3. Seasonal variations of copper in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

In the organic/sulphide phase, copper content varies between 0.38 to 14.33 ppm during the periods of July 2005 to May 2006. Copper content in the organic/sulphide phase averages to 3.58 ± 1.23 ppm, 5.59 ± 2.09 ppm, 3.73 ± 1.85 ppm, 3.39 ± 1.78 ppm, 2.27 ± 1.36 ppm and 2.09 ± 1.25 ppm respectively during the July, September, November, January, March and May months. In the organic/sulphide phase, copper content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.4.*).

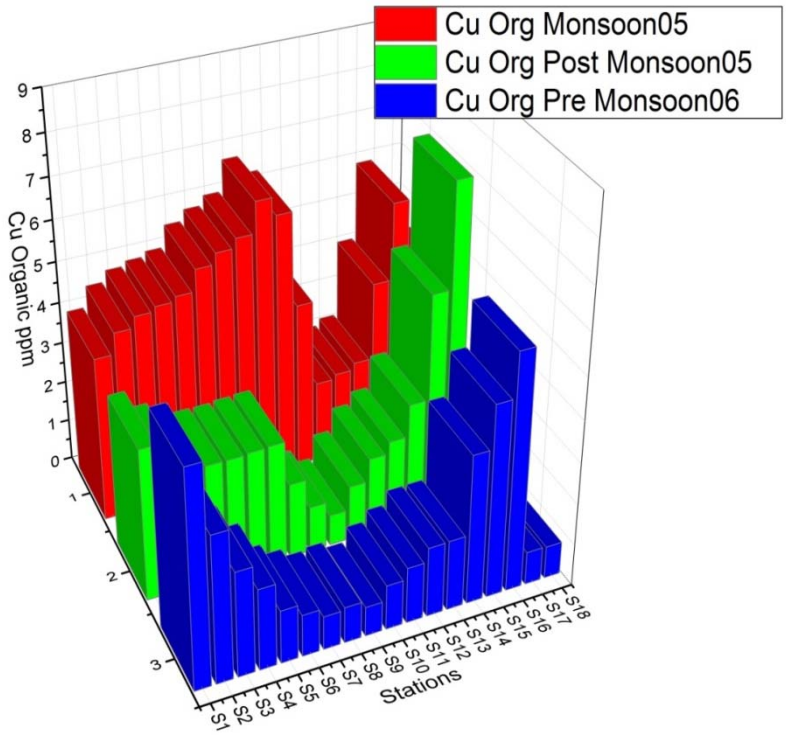

Figure 6.3.4. Seasonal variations of copper in the organic fraction of sediments of the Muvattupuzha River

Copper concentration in the residual phase varies between 0.44 to 11.04 ppm during the months of July 2005 to May 2006. In the residual phase, copper concentration averages to 3.34 ± 0.88 ppm, 4.77 ± 1.50 ppm, 3.44 ± 1.85 ppm, 3.16 ± 1.71 ppm, 2.39 ± 0.98 ppm and 2.11 ± 0.95 ppm respectively during the July, September, November, January, March and May months. Copper concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.5.*).

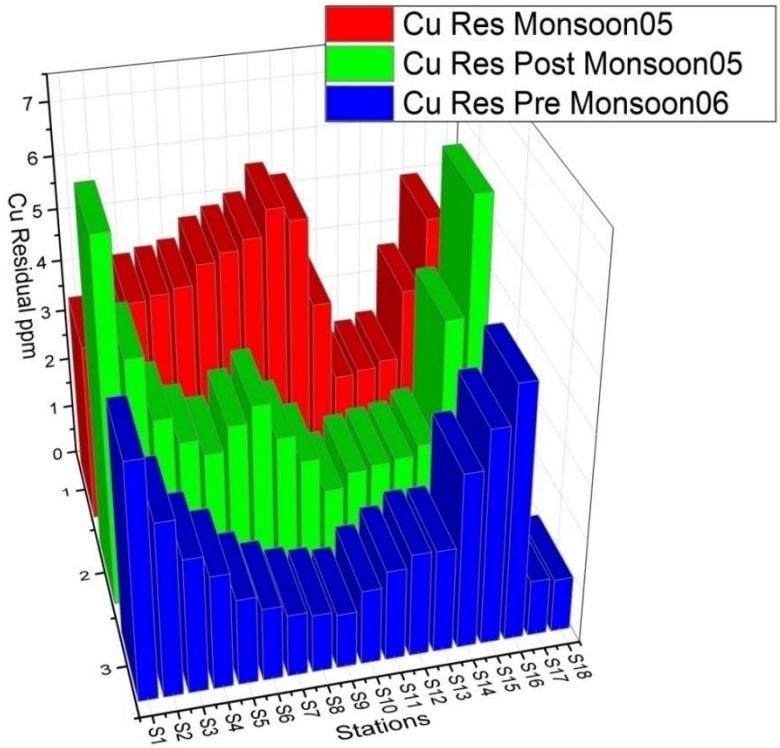

Figure 6.3.5. Seasonal variations of copper in the residual fraction of sediments of the Muvattupuzha River

6.2f. Chromium

Chromium content in the exchangeable phase varies between 0.013 to 0.325 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, chromium content averages to 0.260 ± 0.048 ppm, 0.184 ± 0.046 ppm, 0.112 ± 0.021 ppm, 0.132 ± 0.020 ppm, 0.117 ± 0.074 ppm and 0.073 ± 0.050 ppm respectively during the July, September, November, January, March and May months. Chromium content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.6.*).

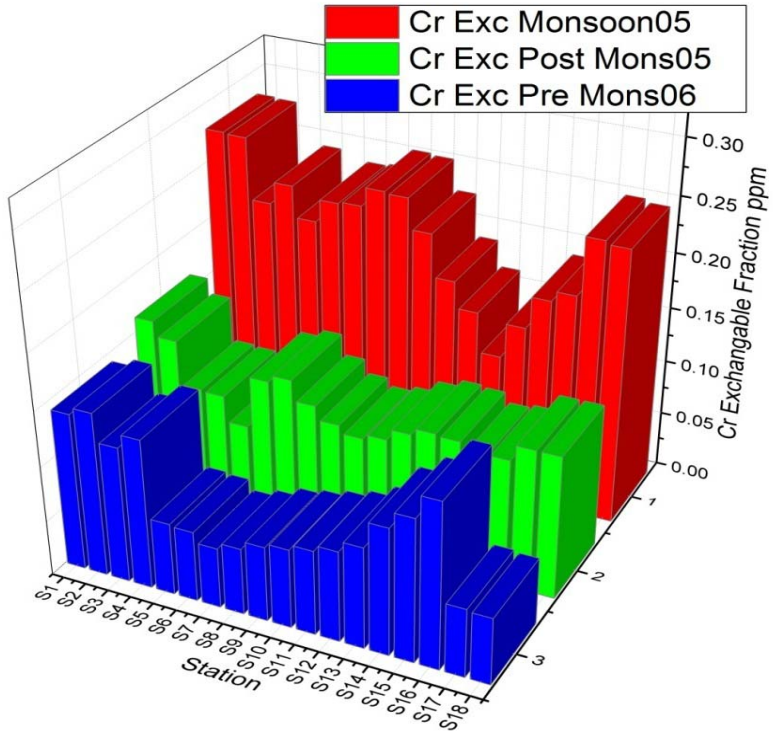

Figure 6.3.6. Seasonal variations of chromium in the exchangeable fraction of sediments of the Muvattupuzha River

Chromium concentration in the carbonate phase varies between 0.13 to 2.21 ppm during the months of July 2005 to May 2006. In the carbonate phase, chromium concentration averages to 1.78 ± 0.39 ppm, 1.21 ± 0.35 ppm, 0.67 ± 0.14 ppm, 0.82 ± 0.15 ppm, 0.71 ± 0.53 ppm and 0.42 ± 0.32 ppm respectively during the July, September, November, January, March and May months. Chromium concentration in the carbonate phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.7.*).

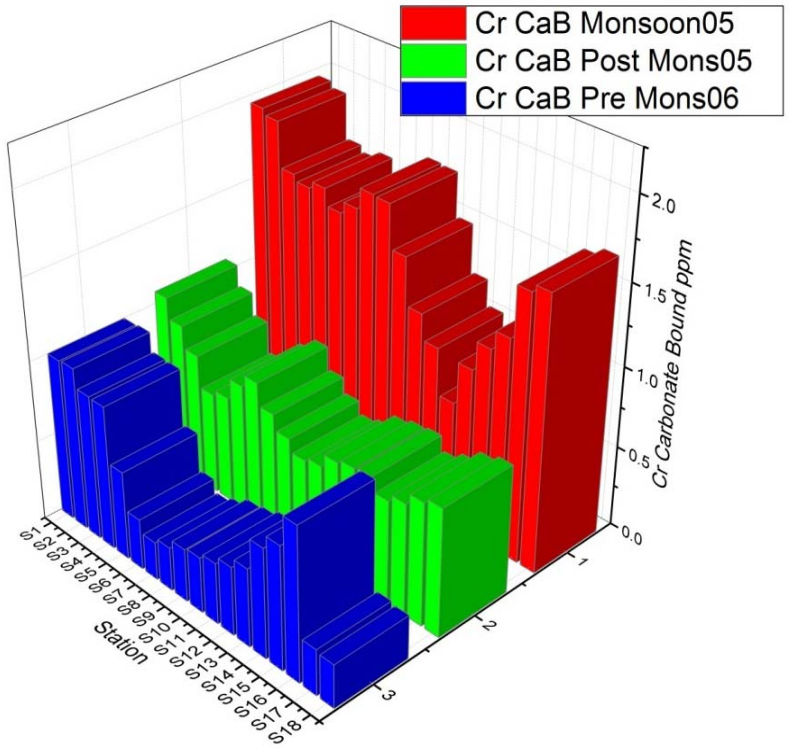

Figure 6.3.7. Seasonal variations of chromium in the carbonate fraction of sediments of the Muvattupuzha River

In the Fe-Mn oxide phase, chromium content varies between 0.65 to 11.34 ppm during the periods of July 2005 to May 2006. Chromium content in the Fe-Mn oxide phase averages to 9.06 ± 1.78 ppm, 6.42 ± 1.61 ppm, 3.86 ± 0.67 ppm, 4.59 ± 0.71 ppm, 4.00 ± 0.78 ppm and 2.46 ± 0.87 ppm respectively during the July, September, November, January, March and May months. In the Fe-Mn oxide phase, chromium content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.8.*).

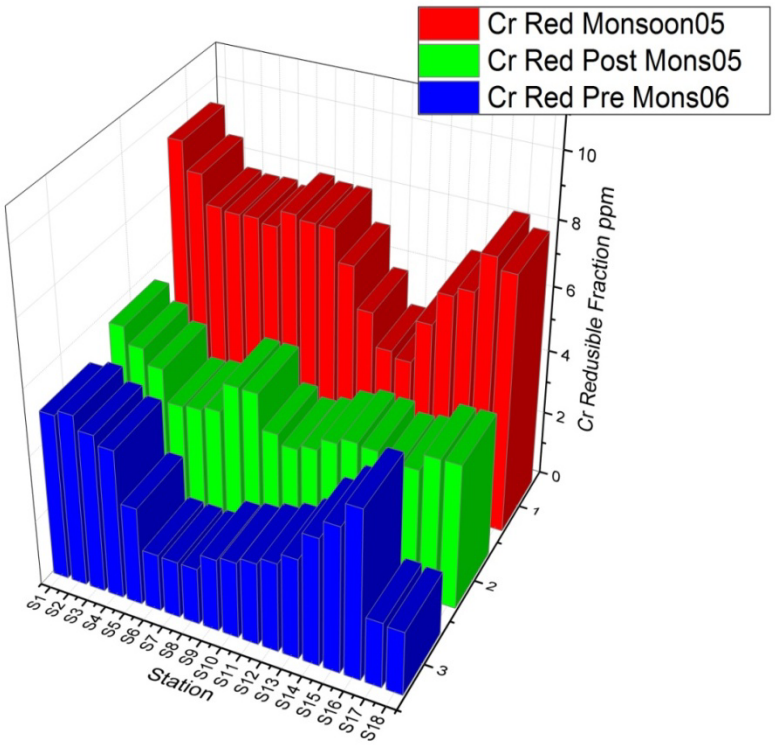

Figure 6.3.8. Seasonal variations of chromium in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

Chromium content in the organic/sulphide phase varies between 1.43 to 11.45 ppm during the periods of July 2005 to May 2006. In the organic/sulphide phase, chromium content averages to 9.15 ± 2.01 ppm, 6.14 ± 1.65 ppm, 3.38 ± 0.68 ppm, 4.20 ± 0.73 ppm, 3.05 ± 0.75 ppm and 2.68 ± 0.78 ppm respectively during the July, September, November, January, March and May months. Chromium content in the organic/sulphide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.3.9.*).

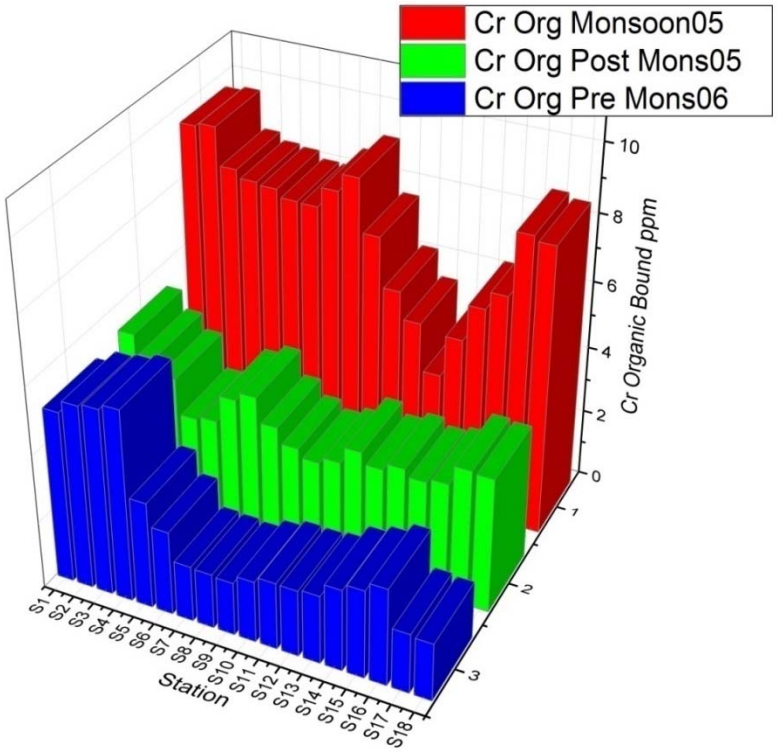

Figure 6.3.9. Seasonal variations of chromium in the organic fraction of sediments of the Muvattupuzha River

Chromium concentration in the residual phase varies between 1.26 to 23.37 ppm during the months of July 2005 to May 2006. In the residual phase, chromium concentration averages to 19.03 ± 3.60 ppm, 13.77 ± 3.20 ppm, 8.48 ± 1.28 ppm, 9.98 ± 1.36 ppm, 8.84 ± 1.35 ppm and 5.56 ± 1.25 ppm respectively during the July, September, November, January, March and May months. Chromium concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.4.0.*).

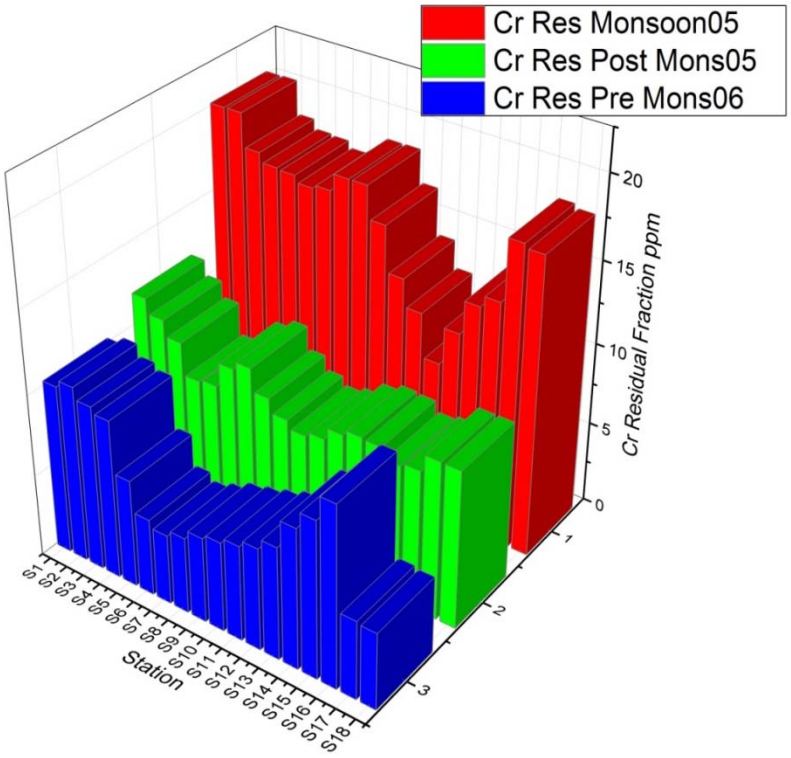

Figure 6.4.0. Seasonal variations of chromium in the residual fraction of sediments of the Muvattupuzha River

6.2g. Zinc

Zinc content in the exchangeable phase varies between 0.44 to 9.26 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, zinc content averages to 5.01 ± 2.01 ppm, 6.91 ± 2.24 ppm, 3.46 ± 1.34 ppm, 3.72 ± 1.37 ppm, 3.70 ± 1.65 ppm and 2.42 ± 1.85 ppm respectively during the July, September, November, January, March and May months. Zinc content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.4.1.*).

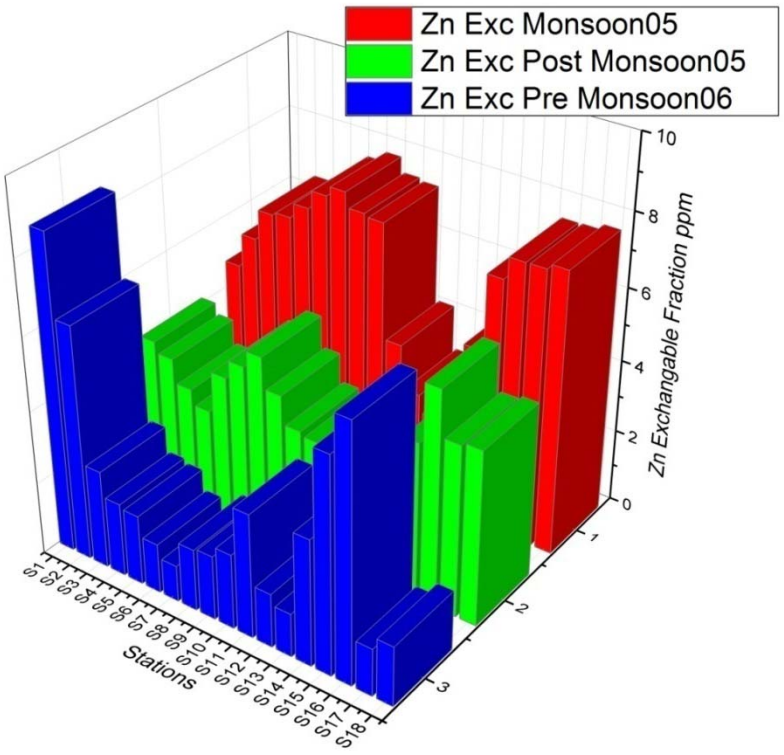

Figure 6.4.1. Seasonal variations of zinc in the exchangeable fraction of sediments of the Muvattupuzha River

In the carbonate phase, zinc content varies between 0.30 to 6.36 ppm during the periods of July 2005 to May 2006. Zinc content in the carbonate phase averages to 3.43 ± 1.38 ppm, 4.75 ± 1.54 ppm, 2.37 ± 0.92 ppm, 2.55 ± 0.95 ppm, 2.53 ± 0.98 ppm and 1.66 ± 0.96 ppm respectively during the July, September, November, January, March and May months. In the carbonate phase, zinc content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.4.2.*).

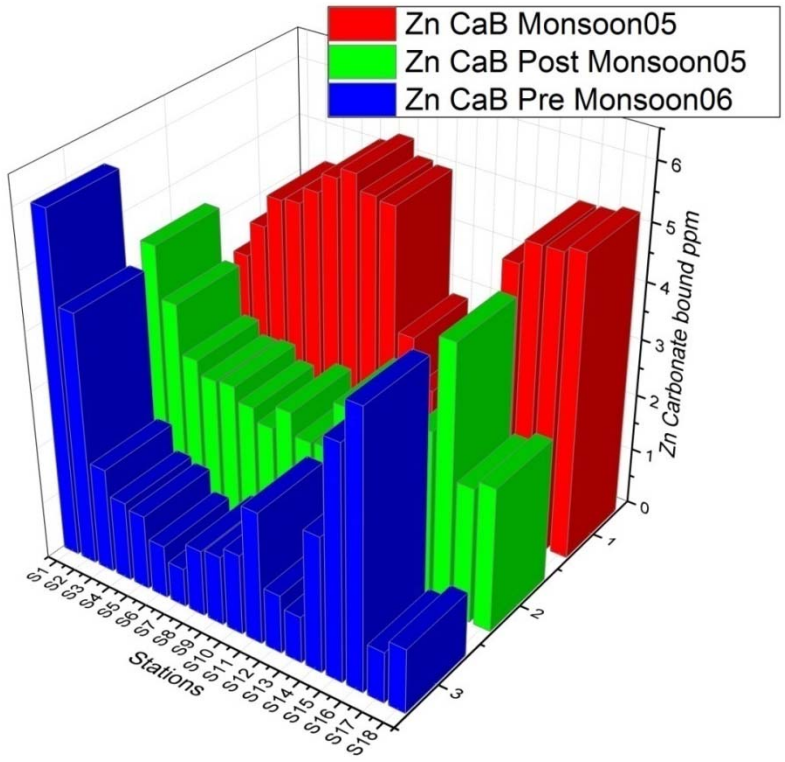

Figure 6.4.2. Seasonal variations of zinc in the carbonate fraction of sediments of the Muvattupuzha River

Zinc concentration in the Fe-Mn oxide phase varies between 0.58 to 12.50 ppm during the months of July 2005 to May 2006. In the Fe-Mn oxide phase, zinc concentration averages to 6.77 ± 2.72 ppm, 9.40 ± 3.04 ppm, 4.66 ± 1.80 ppm, 5.04 ± 1.95 ppm, 5.00 ± 1.88 ppm and 3.24 ± 1.77 ppm respectively during the July, September, November, January, March and May months. Zinc concentration in the Fe-Mn oxide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.4.3.*).

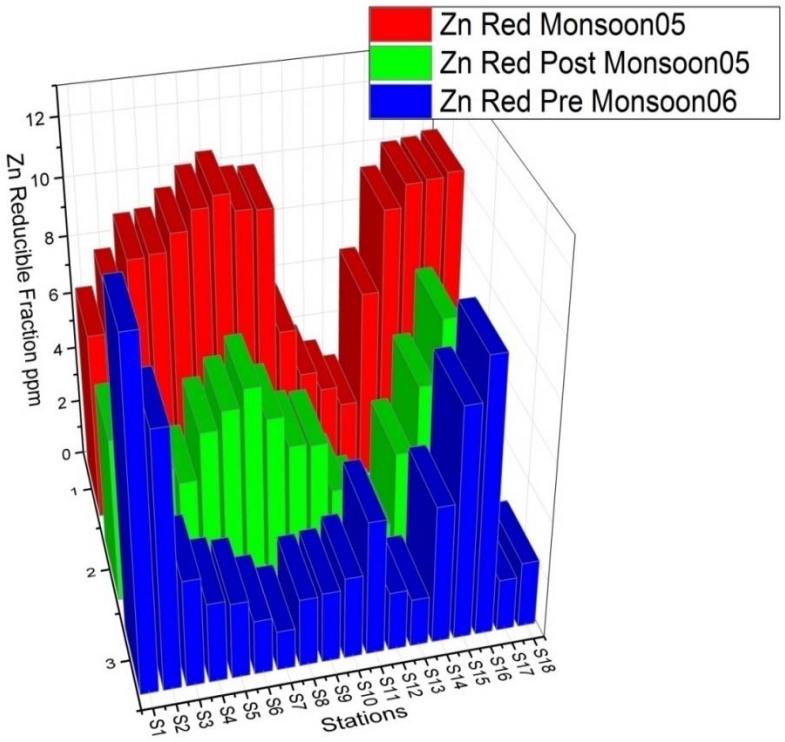

Figure 6.4.3. Seasonal variations of zinc in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

Zinc content in the organic/sulphide phase varies between 0.85 to 23.88 ppm during the periods of July 2005 to May 2006. In the organic/sulphide phase, zinc content averages to 12.94 ± 5.19 ppm, 17.84 ± 5.75 ppm, 8.96 ± 3.45 ppm, 9.68 ± 3.85 ppm, 9.71 ± 3.44 ppm and 6.34 ± 3.35 ppm respectively during the July, September, November, January, March and May months. Zinc content in the organic/sulphide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.4.4.*).

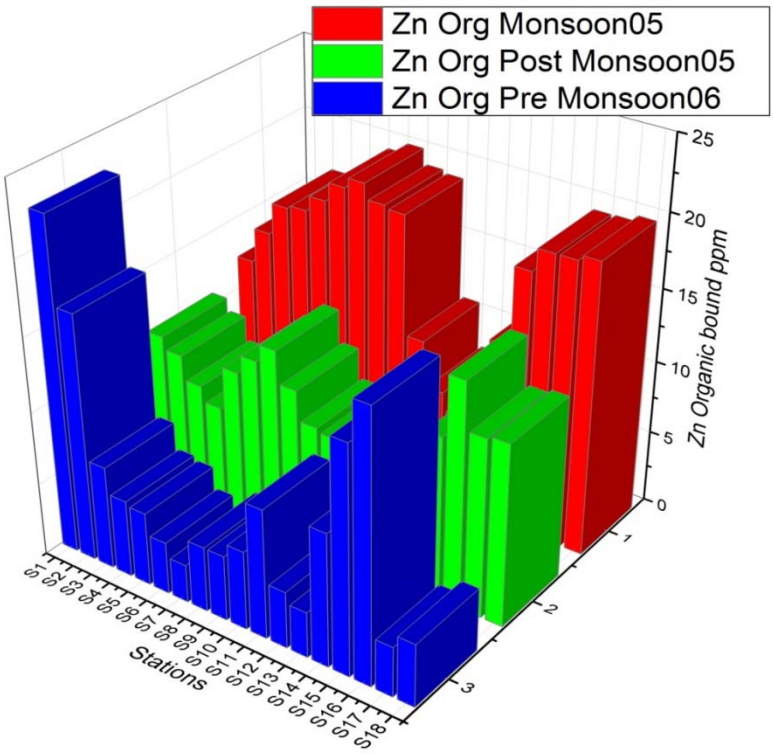

Figure 6.4.4. Seasonal variations of zinc in the organic fraction of sediments of the Muvattupuzha River

Zinc concentration in the residual phase varies between 2.13 to 32.72 ppm during the months of July 2005 to May 2006. In the residual phase, zinc concentration averages to 19.98 ± 6.01 ppm, 25.71 ± 6.70 ppm, 15.31 ± 3.98 ppm, 16.12 ± 4.40 ppm, 16.09 ± 4.22 ppm and 10.57 ± 3.65 ppm respectively during the July, September, November, January, March and May months. Zinc concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.4.5.*).

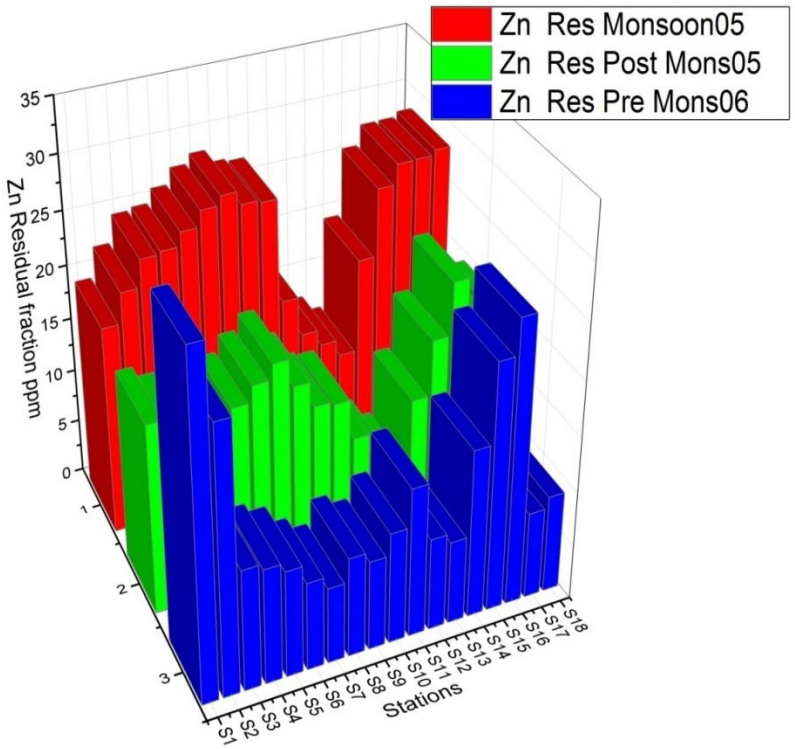

Figure 6.4.5. Seasonal variations of zinc in the residual fraction of sediments of the Muvattupuzha River

6.2h. Cadmium

Cadmium content in the exchangeable phase varies between 0.023 to 0.380 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, cadmium content averages to 0.152 ± 0.032 ppm, 0.126 ± 0.037 ppm, 0.165 ± 0.023 ppm, 0.182 ± 0.037 ppm, 0.153 ± 0.075 ppm and 0.117 ± 0.084 ppm respectively during the July, September, November, January, March and May months. Cadmium content in the exchangeable phase showed higher values during the post-monsoon months when compared to monsoon or pre-monsoon months (*Figure 6.4.6.*).

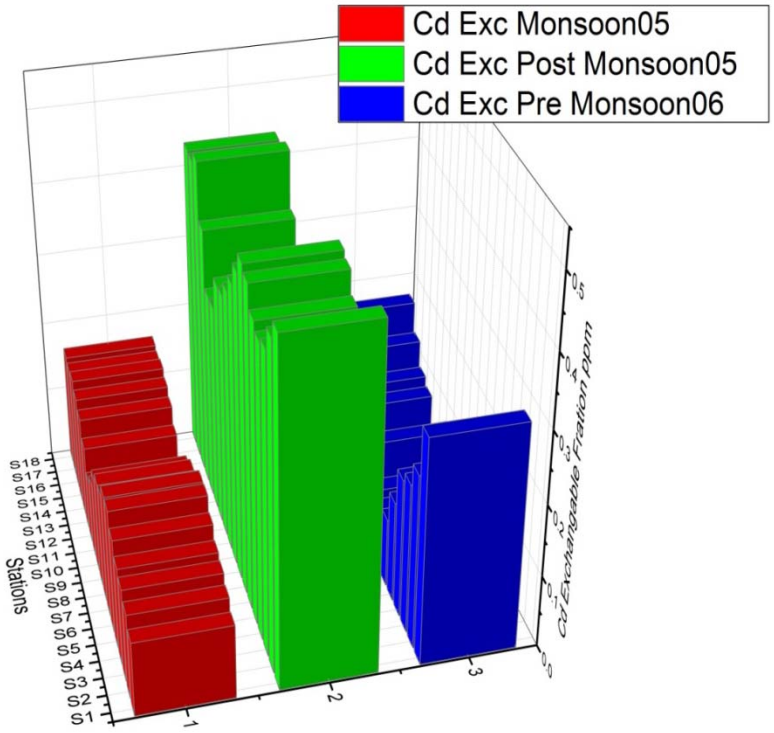

Figure 6.4.6. Seasonal variations of cadmium in the exchangeable fraction of sediments of the Muvattupuzha River

In the carbonate phase, cadmium content varies between 0.0068 to 0.0972 ppm during the periods of July 2005 to May 2006. Cadmium content in the carbonate phase averages to 0.0372 ± 0.0081 ppm, 0.0308 ± 0.0088 ppm, 0.0402 ± 0.0060 ppm, 0.0446 ± 0.0096 ppm, 0.0371 ± 0.0200 ppm and 0.0289 ± 0.0200 ppm respectively during the July, September, November, January, March and May months. In the carbonate phase, cadmium content showed higher values during the post-monsoon months when compared to monsoon or pre-monsoon months (*Figure 6.4.7.*).

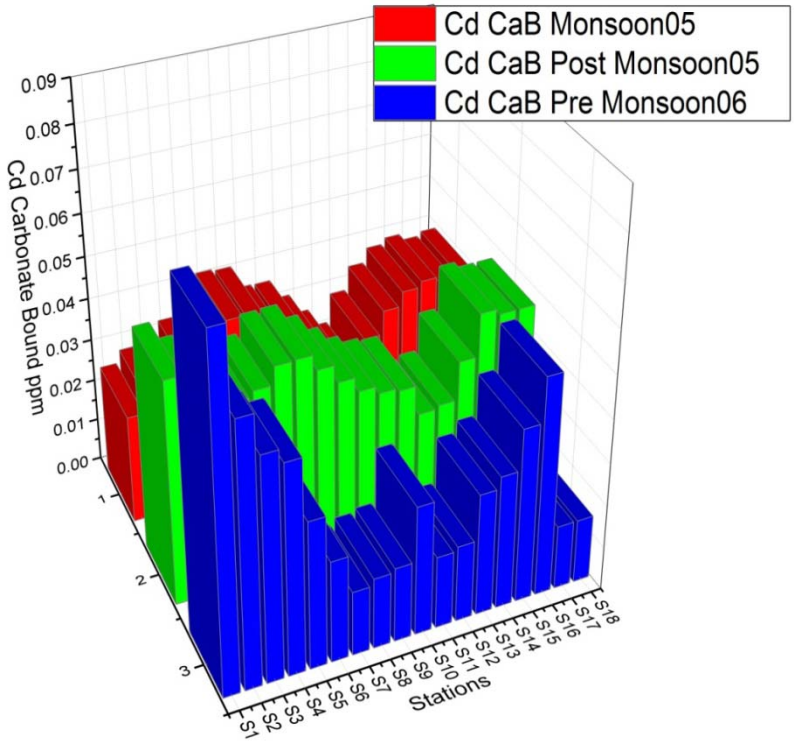

Figure 6.4.7. Seasonal variations of cadmium in the carbonate fraction of sediments of the Muvattupuzha River

Cadmium concentration in the Fe-Mn oxide phase varies between 0.0020 to 0.0298 ppm during the months of July 2005 to May 2006. In the Fe-Mn oxide phase, cadmium concentration averages to 0.0114 ± 0.0027 ppm, 0.0093 ± 0.0031 ppm, 0.0122 ± 0.0018 ppm, 0.0137 ± 0.0030 ppm, 0.0114 ± 0.0061 ppm and 0.0088 ± 0.0064 ppm respectively during the July, September, November, January, March and May months. Cadmium concentration in the Fe-Mn oxide phase showed higher values during the post-monsoon months when compared to monsoon or pre-monsoon months (*Figure 6.4.8.*).

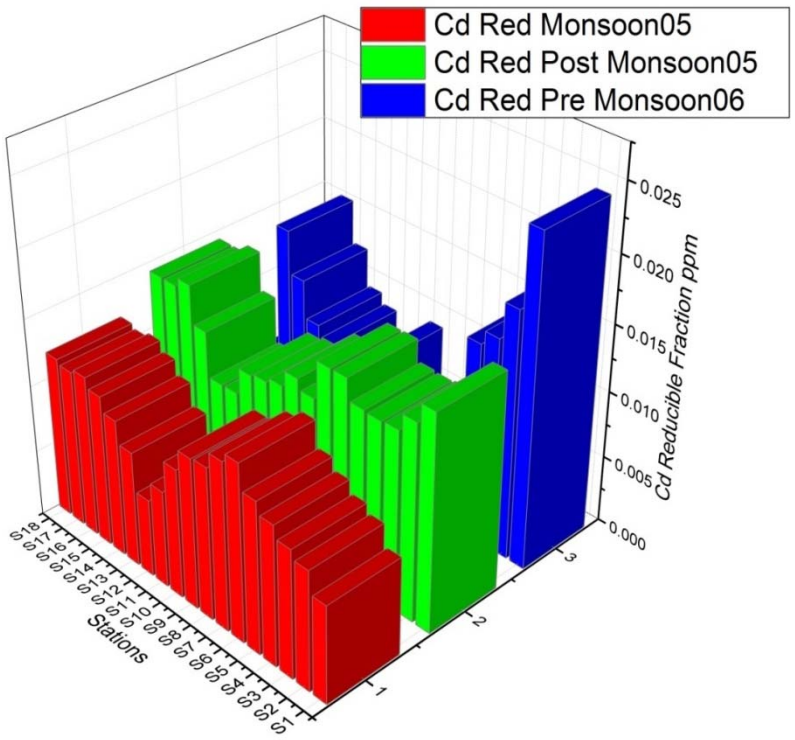

Figure 6.4.8. Seasonal variations of cadmium in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

In the organic/sulphide phase, cadmium content varies between 0.0060 to 0.0649 ppm during the periods of July 2005 to May 2006. Cadmium content in the organic/sulphide phase averages to 0.0360 ± 0.0081 ppm, 0.0298 ± 0.0097 ppm, 0.0392 ± 0.0061 ppm, 0.0406 ± 0.0110 ppm, 0.0341 ± 0.0150 ppm and 0.0277 ± 0.0200 ppm respectively during the July, September, November, January, March and May months. In the organic/sulphide phase, cadmium content showed higher values during the post-monsoon months when compared to monsoon or pre-monsoon months (*Figure 6.4.9.*).

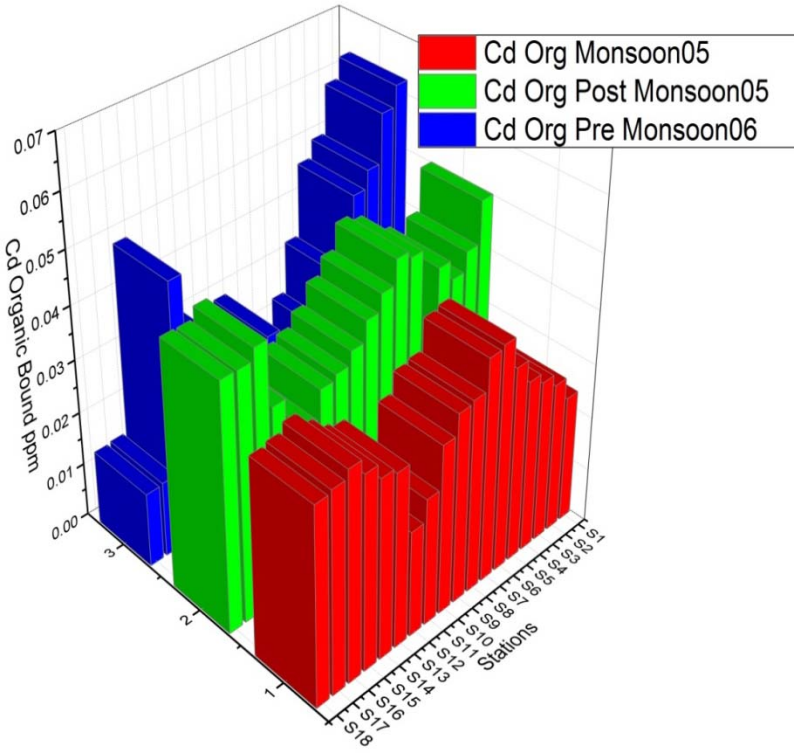

Figure 6.4.9. Seasonal variations of cadmium in the organic fraction of sediments of the Muvattupuzha River

Cadmium concentration in the residual phase varies between 0.0120 to 0.1797 ppm during the months of July 2005 to May 2006. In the residual phase, cadmium concentration averages to 0.0685 ± 0.0157 ppm, 0.0554 ± 0.0183 ppm, 0.0745 ± 0.0112 ppm, 0.0802 ± 0.0192 ppm, 0.0684 ± 0.0367 ppm and 0.0546 ± 0.0360 ppm respectively during the July, September, November, January, March and May months. Cadmium concentration in the residual phase phase showed higher values during the post-monsoon months when compared to monsoon or pre-monsoon months (*Figure 6.5.0.*).

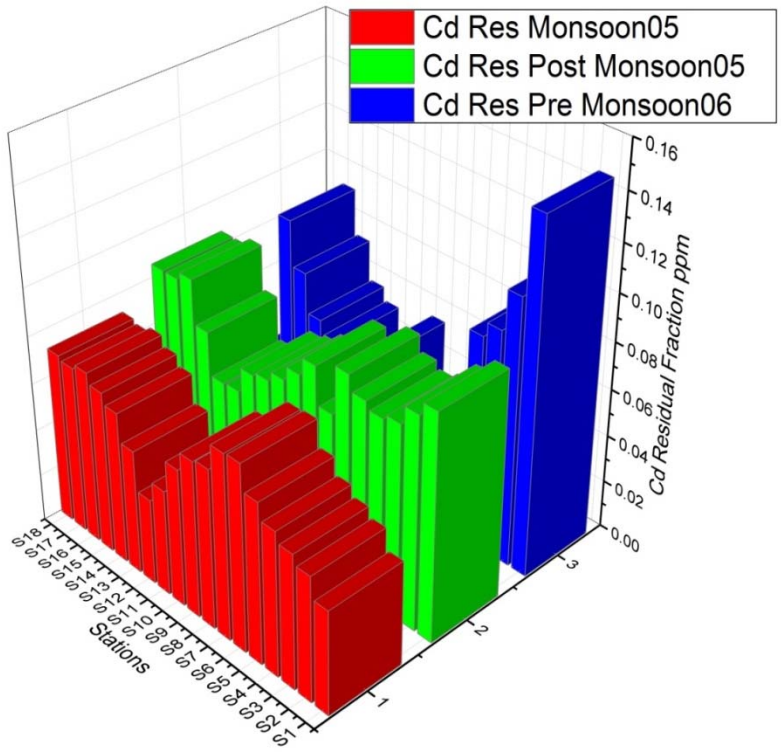

Figure 6.5.0. Seasonal variations of cadmium in the residual fraction of sediments of the Muvattupuzha River

6.2i. Lead

Lead content in the exchangeable phase varies between 1.35 to 16.58 ppm during the periods of July 2005 to May 2006. In the exchangeable phase, lead content averages to 7.27 ± 2.17 ppm, 8.75 ± 3.58 ppm, 7.61 ± 2.44 ppm, 8.62 ± 2.01 ppm, 6.68 ± 2.45 ppm and 5.13 ± 2.48 ppm respectively during the July, September, November, January, March and May months. Lead content in the exchangeable phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.5.1.*).

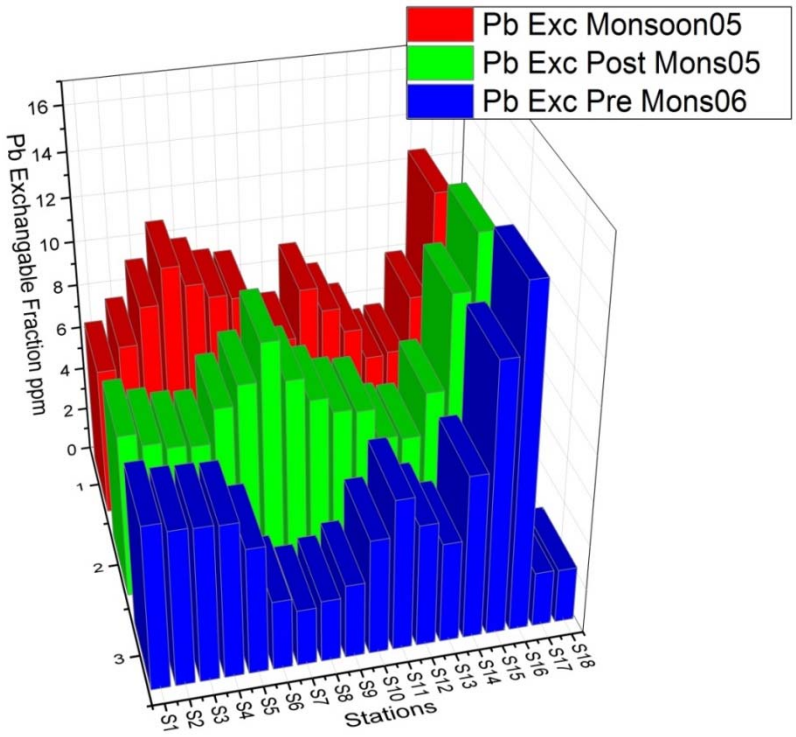

Figure 6.5.1. Seasonal variations of lead in the exchangeable fraction of sediments of the Muvattupuzha River

In the carbonate phase, lead content varies between 0.019 to 0.275 ppm during the periods of July 2005 to May 2006. Lead content in the carbonate phase averages to 0.105 ± 0.038 ppm, 0.131 ± 0.063 ppm, 0.110 ± 0.043 ppm, 0.123 ± 0.034 ppm, 0.092 ± 0.045 ppm and 0.075 ± 0.042 ppm respectively during the July, September, November, January, March and May months. In the carbonate phase, lead content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.5.2.*).

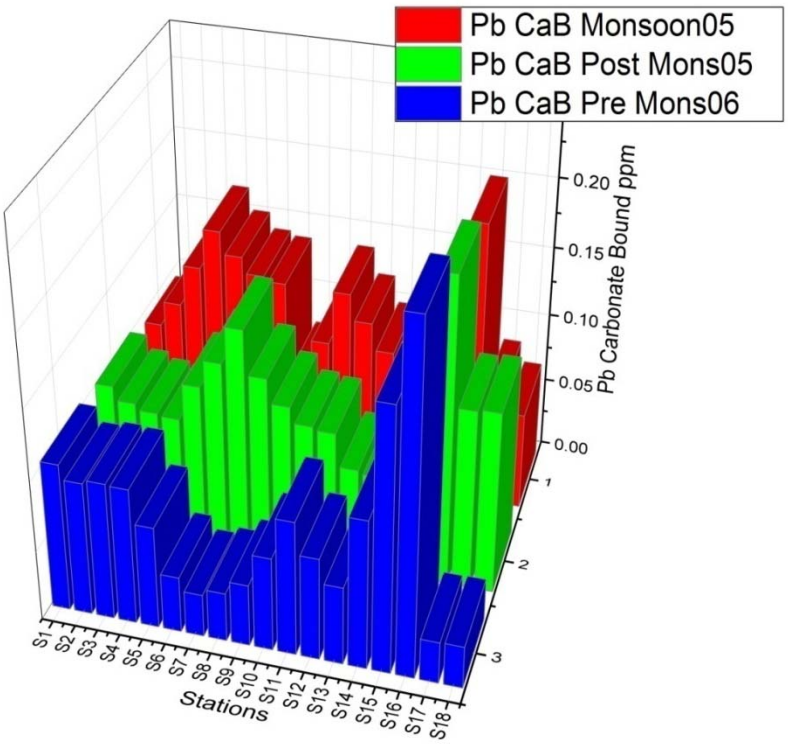

Figure 6.5.2. Seasonal variations of lead in the carbonate fraction of sediments of the Muvattupuzha River

Lead concentration in the Fe-Mn oxide phase varies between 0.04 to 1.03 ppm during the months of July 2005 to May 2006. In the Fe-Mn oxide phase, lead concentration averages to 0.49 ± 0.15 ppm, 0.55 ± 0.22 ppm, 0.45 ± 0.22 ppm, 0.48 ± 0.15 ppm, 0.42 ± 0.16 ppm and 0.33 ± 0.15 ppm respectively during the July, September, November, January, March and May months. Lead concentration in the Fe-Mn oxide phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.5.3.*).

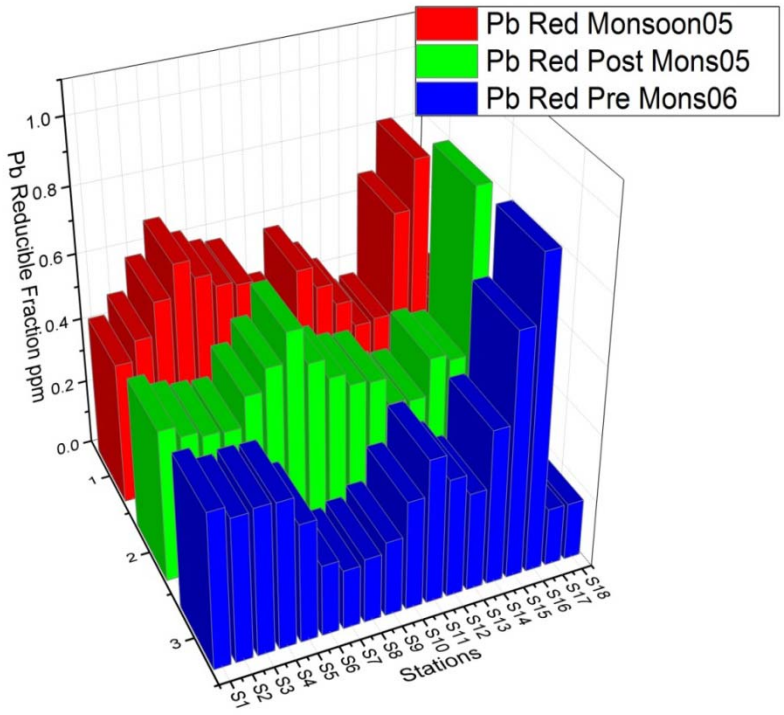

Figure 6.5.3. Seasonal variations of lead in the Fe-Mn oxide fraction of sediments of the Muvattupuzha River

In the organic/sulphide phase, lead content varies between 0.22 to 3.48 ppm during the periods of July 2005 to May 2006. Lead content in the organic/sulphide phase averages to 1.36 ± 0.50 ppm, 1.70 ± 0.82 ppm, 1.43 ± 0.56 ppm, 1.58 ± 0.44 ppm, 1.20 ± 0.62 ppm and 0.94 ± 0.65 ppm respectively during the July, September, November, January, March and May months. In the organic/sulphide phase, lead content showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.5.4.*).

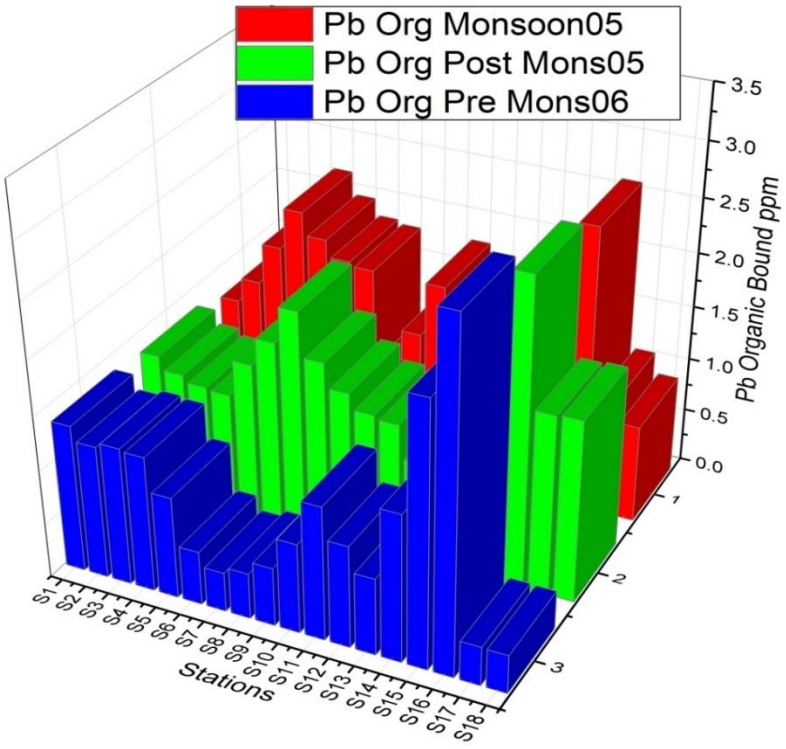

Figure 6.5.4. Seasonal variations of lead in the organic fraction of sediments of the Muvattupuzha River

Lead concentration in the residual phase varies between 0.18 to 1.83 ppm during the months of July 2005 to May 2006. In the residual phase, lead concentration averages to 1.21 ± 0.31 ppm, 1.36 ± 0.32 ppm, 1.26 ± 0.21 ppm, 1.32 ± 0.17 ppm, 1.17 ± 0.24 ppm and 0.91 ± 0.22 ppm respectively during the July, September, November, January, March and May months. Lead concentration in the residual phase showed higher values during the monsoon months when compared to post-monsoon or pre-monsoon months (*Figure 6.5.5.*).

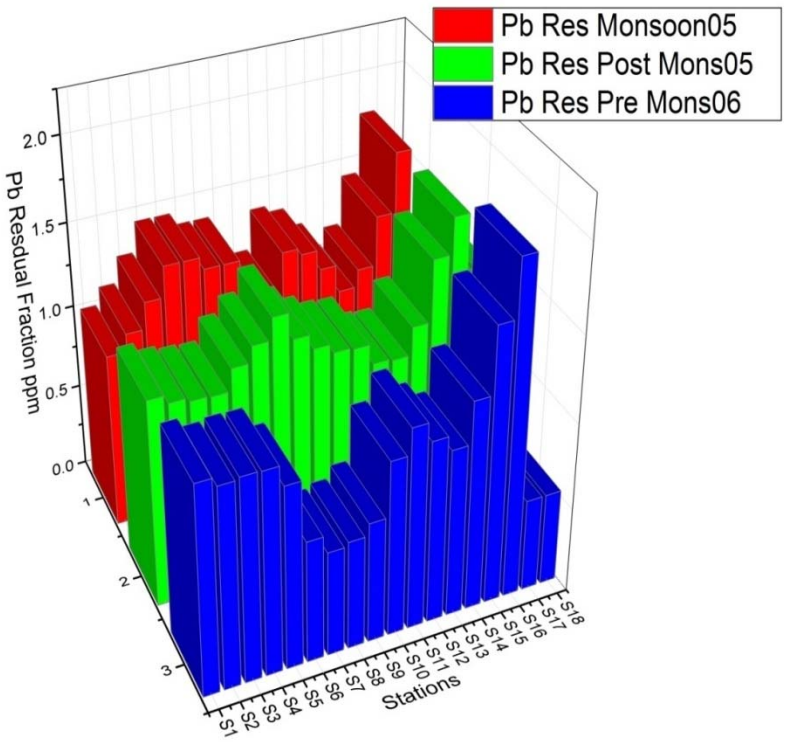

Figure 6.5.5. Seasonal variations of lead in the residual fraction of sediments of the Muvattupuzha River

In general, consistent with the high total metal concentrations in the bulk sediments, except Cd the bimonthly variations of other trace metals (Fe, Mn, Co, Ni, Cu, Cr, Zn & Pb) in the exchangeable, carbonate, Fe-Mn oxide, organic/sulphide, and residual fractions of sediments also showed maximum values during the monsoon months (July/September) when compared to post-monsoon months (November/January) or pre-monsoon months (March/May) showing the influence of monsoon derived land run-off materials in the trace metal fractions in sediments of the Muvattupuzha River.

6.3. Trace metal partitioning in sediments

Trace metal partitioning in sediments were assessed by comparing the trace metal concentrations expressed in percentage that associated in various sedimentary phases/fractions (exchangeable, carbonate, Fe-Mn oxide, organic/sulphide & residual) with respect to the total trace metal concentrations in bulk sediments (Singh et al. 2005). Metal fractionation in various sedimentary phases helps to describe the mechanisms of selective phase accumulation and the role of mineralization, complexation by organic matter, adsorption-desorption processes, redox changes, chemical diagenesis and remobilization with regard to metal availability to organisms (Nair et al. 1991; Nair and Balchand, 1993). The bimonthly variations of trace metal concentrations (Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd & Pb) expressed in percentage that associated in various sedimentary phases/fractions (exchangeable, carbonate, Fe-Mn oxide, organic/sulphide & residual) with respect to the total trace metal concentrations in bulk sediments of the Muvattupuzha River are given in Annexure as *Tables A6.1.0. to A6.6.3*. The percentage of iron, manganese, cobalt, nickel, copper, chromium, zinc, cadmium and lead that can be extractable from the exchangeable, carbonate, Fe-Mn oxide, organic/sulphide and residual fractions (or phases) of sediments follows the respective orders of abundance as shown below:

$Fe_{residual} > Fe_{Fe\text{-}Mn\ oxide} > Fe_{carbonate} > Fe_{exchangeable} > Fe_{organic}$
$Mn_{residual} = Mn_{organic} > Mn_{Fe\text{-}Mn\ oxide} > Mn_{exchangeable} > Mn_{carbonate}$
$Co_{residual} > Co_{organic} > Co_{Fe\text{-}Mn\ oxide} > Co_{exchangeable} > Co_{carbonate}$
$Ni_{residual} > Ni_{exchangeable} > Ni_{organic} > Ni_{Fe\text{-}Mn\ oxide} = Ni_{carbonate}$
$Cu_{exchangeable} > Cu_{residual} > Cu_{organic} > Cu_{Fe\text{-}Mn\ oxide} > Cu_{carbonate}$
$Cr_{residual} > Cr_{organic} = Cr_{Fe\text{-}Mn\ oxide} > Cr_{carbonate} > Cr_{exchangeable}$
$Zn_{residual} > Zn_{organic} > Zn_{Fe\text{-}Mn\ oxide} > Zn_{exchangeable} > Zn_{carbonate}$
$Cd_{exchangeable} > Cd_{residual} > Cd_{organic} = Cd_{carbonate} > Cd_{Fe\text{-}Mn\ oxide}$
$Pb_{exchangeable} > Pb_{organic} > Pb_{residual} > Pb_{Fe\text{-}Mn\ oxide} > Pb_{carbonate}$

A comparison of iron concentrations in different sedimentary phases (*Tables A6.1.0. to A6.1.5.*), with respect to total iron concentrations in bulk sediments showed that exchangeable Fe ranges from 0.33 to 0.73 %, carbonate Fe ranges from 0.64 to 0.97 %, reducible Fe ranges from 4.35 to 6.56 %, organic Fe ranges from 0.39 to 0.56 % and residual Fe ranges from 90 to 95 % respectively. Eventhough the relative contributions of Fe from labile fractions were quite small, their presence was also quite recognisable. Fractionation profile of iron in bed sediments of the Muvattupuzha River indicates that a major portion (> 90%) is associated with residual fraction characterizing stable compounds in sediments which cannot be remobilized under normal conditions encountered in the nature. A lesser amount of Fe (4 to 6 %) is associated with reducible fractions. A small amount (< 1%) of Fe is also noted in carbonate, exchangeable and organic labile fractions. In the fractionation profile for iron when compared with other fractions, Jain et al. (2007) also reported a major portion of iron that associated with residual fractions in sediments of Lake Nainital, Uttaranchal. In the fractionation profile for iron, Nair and Balchand (1993) also reported a major amount of total Fe (85 to 97%) that associated with residual fractions whereas only a nominal amount of total Fe that associated with reducible, carbonate, exchangeable and organic fractions in sediments of the Cochin backwaters.

An evaluation of manganese concentrations in different sedimentary phases with respect to total manganese concentrations in bulk sediments showed that exchangeable Mn ranges from 4.09 to 6.54 %, carbonate Mn ranges from 1.51 to 2.98 %, reducible Mn ranges from 25 to 30 %, organic Mn ranges from 30 to 35 % and residual Mn ranges from 30 to 35 % respectively. The fractionation profile of manganese in sediments indicates that it is mostly bound to organic, reducible and residual fractions, the rest being associated

with exchangeable and carbonate fractions. This indicates that Mn occurred in the form of stable organic complexes and metal sulphides in bed sediments of the Muvattupuzha River. Nair and Balchand (1993) also noted a similar significant amount of manganese that associated with organic/sulfide fraction in sediments of the Cochin backwaters. Prasad et al. (2006) also reported a high quantity of manganese that associated with the organic fraction in sediments of the Ackenkovil River.

An assessment of cobalt concentrations in different sedimentary phases with respect to total cobalt concentrations in bulk sediments showed that exchangeable Co ranges from 10 to 12 %, carbonate Co ranges from 5 to 7 %, reducible Co ranges from 10 to 14 %, organic Co ranges from 20 to 24 % and residual Co ranges from 45 to 53 % respectively. The fractionation profile of cobalt indicates that it is mostly bound to residual fraction, the rest being associated with organic, reducible, exchangeable and carbonate fractions. Nair and Balchand (1993) also noted a similar predominant quantity of cobalt species that locked up in residual phase which was followed by a moderate quantity of cobalt species that associated with organic/sulphide phase in sediments of the Cochin backwaters.

A comparison of nickel concentrations in different sedimentary phases with respect to total nickel concentrations in bulk sediments showed that exchangeable Ni ranges from 8 to 9 %, carbonate Ni ranges from 4 to 5 %, reducible Ni ranges from 4 to 5 %, organic Ni ranges from 6 to 8 % and residual Ni ranges from 63 to 73 % respectively. The fractionation profile of nickel indicates that it is mostly bound to residual fraction, the rest being associated with exchangeable, organic, reducible and carbonate fractions. Nair and Balchand (1993) also noted a similar major quantity of nickel species that associated with residual phase which was followed by a moderate quantity of

nickel species that associated with organic/sulphide phase and carbonate phase in sediments of the Cochin backwaters.

The association of copper species in different sedimentary phases with respect to total copper concentrations in bulk sediments showed that exchangeable Cu ranges from 30 to 35 %, carbonate Cu ranges from 4 to 7 %, reducible Cu ranges from 5 to 9 %, organic Cu ranges from 20 to 29 % and residual Cu ranges from 24 to 35 % respectively. Fractionation profile of copper indicates that a moderate portion is bound to exchangeable fraction at most of the sites. Another moderate portion of copper is bound to organic fraction at most of the sites probably due to its pronounced tendency for complexation with organic matter (Samanidou and Fytianos, 1987; Pardo et al. 1993; Pempkowiak et al. 1999). In the fractionation profile of copper in sediments of the Cochin backwaters, Nair et al. (1991) also noted similar proportions of copper that is associated in exchangeable, organic/suphide and residual fractions with some spatial variations due to the ability of copper species to interchange under different environmental conditions. Prasad et al. (2006) also noted a similar fractionation profile for copper with maximum exchangeable copper content in sediments of the Achenkovil River.

The association of chromium concentrations in different sedimentary phases with respect to total chromium concentrations in bulk sediments showed that exchangeable Cr ranges from 0.40 to 0.75 %, carbonate Cr ranges from 3 to 5 %, reducible Cr ranges from 17 to 25 %, organic Cr ranges from 17 to 25 % and residual Cr ranges from 50 to 55 % respectively. The fractionation profile of chromium (50 to 55 %) indicates that it is mostly bound to residual fraction, the rest being associated with organic, reducible, carbonate and exchangeable fractions. About 17 to 25 % of chromium is associated with reducible and oxidizable (organic) fractions respectively. Nair

and Balchand (1993) also reported a similar percentage wise chromium profile with maximum chromium concentrations in residual fraction which was followed by moderate chromium concentrations in organic/sulphide phase in sediments of the Cochin backwaters.

A comparison of zinc concentrations in different sedimentary phases with respect to total zinc concentrations in bulk sediments showed that exchangeable Zn ranges from 7 to 12 %, carbonate Zn ranges from 5 to 8 %, reducible Zn ranges from 10 to 15 %, organic Zn ranges from 20 to 30 % and residual Zn ranges from 40 to 50 % respectively. The fractionation profile of zinc indicates that it is mostly bound to residual fraction, the rest being associated with organic, reducible, exchangeable and carbonate fractions. Nair et al. (1991) also noted similar proportions of zinc with maximum concentrations in residual phase which was followed by minimum concentrations in organic/sulphide phase, carbonate phase and reducible phase in sediments of the Cochin backwaters. Prasad et al. (2006) also noted a similar fractionation profile with minor exchangeable and carbonate zinc contents in sediments of the Achenkovil River.

An assessment of cadmium concentrations in different sedimentary phases with respect to total cadmium concentrations in bulk sediments showed that exchangeable Cd ranges from 40 to 45 %, carbonate Cd ranges from 8 to 11 %, reducible Cd ranges from 2 to 4%, organic Cd ranges from 8 to 11 % and residual Cd ranges from 15 to 20 % respectively. About 40 to 45 % of the cadmium was associated in the exchangeable fraction and may be easily remobilized by changes in environmental conditions. Toxic nature of cadmium and its association with exchangeable fraction in sediments may cause deleterious effects to aquatic life. Nair et al. (1991) also noted a high concentration of exchangeable cadmium in sediments from the freshwater

upstream regions of the Cochin backwaters. Prasad et al. (2006) also noted a similar fractionation profile with a major amount of exchangeable cadmium content in sediments of the Achenkovil River.

A comparison of lead concentrations in different sedimentary phases with respect to total lead concentrations in bulk sediments showed that exchangeable Pb ranges from 70 to 75 %, carbonate Pb ranges from 0.5 to 1.2 %, reducible Pb ranges from 1 to 6 %, organic Pb ranges from 10 to 15 % and residual Pb ranges from 9 to 18 % respectively. A significant amount of the lead (70 to 75 %) was found to be associated with exchangeable fraction and may pose risk to aquatic life. The very high association of lead with exchangeable fraction indicates dominance of anthropogenic sources through domestic wastes and municipal sewage. A similar concentration profile for lead with detectable amounts in residual phase and carbonate phase in sediments was also reported for the Cochin backwaters (Nair et al. 1991).

The ability to accumulate metal species in sediments depends on particle size, composition of sediment and changes in environmental conditions of pH, Eh, salinity and concentrations of organic and inorganic complexing agents (Calmano and Forstner, 1983). The percentage amount of iron, manganese, cobalt, nickel, copper, chromium, zinc, cadmium and lead that can be extractable from the exchangeable, carbonate, Fe-Mn oxide, organic/sulphide and residual fractions/phases of sediments follows the respective orders of abundance:

Pb > Cd > Cu > Zn > Ni > Co > Mn > Cr > Fe (exchangeable fraction)
Cd > Zn > Cu > Co > Ni > Cr > Mn > Pb > Fe (carbonate fraction)
Mn > Cr > Zn > Co > Cu > Fe > Pb > Ni > Cd (Fe-Mn oxide/reducible fraction)
Mn > Zn > Cu > Cr > Co > Pb > Cd > Ni > Fe (organic/sulphide fraction)
Fe > Ni > Cr > Co > Zn > Mn > Cu > Cd > Pb (residual fraction)

Trace metals present in the exchangeable fraction of sediments correspond to the most loosely bound forms that are readily mobile and hence can be released by merely changing the ionic strength of the medium which constitutes to an immediate nutrient reservoir for aquatic organisms (Tessier et. al. 1979; Tessier and Cambell, 1987). In the exchangeable fraction of sediments, metals like Pb (70 to 75 %), Cd (40 to 45 %) and Cu (30 to 35 %) showed a high dynamic association/partition indicating high enrichment, metals like Zn (7 to 12 %), Co (10 to 12 %) and Ni (8 to 9 %) showed a moderate association indicating moderate enrichment, metals like Mn (4 to 6 %) showed a minor association indicating minor enrichment whereas metals like Cr (0.4 to 0.8 %) and Fe (0.3 to 0.7 %) showed a very low minor association indicating very low minor enrichment. A similar high enrichment of cadmium was noted by Nair et al. (1991) in the exchangeable phase of sediments from the upper reaches of the Cochin backwaters. Moderate association of zinc was also noted by Nair et al. (1991) in the exchangeable phase of sediments of the Cochin backwaters. A similar moderate enrichment of cobalt, copper and nickel was also noted by Nair and Balchand (1993) in the exchangeable phase of sediments from the upper freshwater regions of the Cochin backwaters. Minor enrichment of iron, manganese and chromium was also noted by Nair et al. (1991) and Nair and Balchand (1993) in the exchangeable phase of sediments from the upper reaches of the Cochin backwaters. However, contrary to the major association of lead in the exchangegable phase of sediments in the Muvattupuzha River, Nair et al. (1991) noted only a minor association of lead in the exchangegable phase of sediments in the Cochin backwaters. A high percentage of light minerals (quartz & feldspars) and clay minerals (kaolinite, illite & gibbsite) and organics in the sediments may possibly act as an adsorbent, retaining metals

through ion-exchange processes with a net result of enhancing trace metal levels in the exchangeable phase of sediments (Salamons and Forstner,1980; Padmalal and Seralathan, 1995; Padmalal et al.1997).

In the carbonate bound fraction of sediments, metals like Cd (8 to 11 %), Zn (5 to 8 %), Co (5 to 7 %), Cu (4 to 7 %), Ni (4 to 5 %), Cr (3 to 5 %), Mn (1 to 3 %), Pb (0.5 to 1.0 %) and Fe (0.5 to 1.0 %) showed a minor association. This minor association of metals like Fe, Mn, Co, Cu, Cr, Zn, Ni, Pb and Cd indicates a minor enrichment of these metals in carbonate minerals by co-precipitation reactions (Forstner and Wittmann, 1983). A similar minor association of metals like Fe, Mn, Co, Cu, Cr, Zn, Ni, Pb and Cd was also noted by Nair et al. (1991) and Nair and Balchand (1993) in the carbonate phase of sediments from the upper freshwater regions of the Cochin backwaters.

The association of metals to the organic fraction or to the Fe-Mn oxide fraction has great environmental relevance since it has been proposed by some authors as a primary source of anthropogenic metal contribution to bed sediments (Jain et al. 2007). In the organic/sulphide fraction of sediments, metals like Mn (30 to 35 %), Zn (20 to 30 %), Co (20 to 24 %), Cr (17 to 25 %), Cu (20 to 29 %), Pb (10 to 15 %), Cd (8 to 11 %) showed a moderate association indicating moderate enrichment whereas metals like Ni (6 to 8 %) and Fe (0.4 to 0.6 %) showed a minor association indicating minor enrichment. A similar moderate association of metals like Mn, Co, Cu, Cr, Zn, Ni, Pb and Cd was also noted by Nair et al. (1991) and Nair and Balchand (1993) in the organic/sulphide phase of sediments from the upper freshwater regions of the Cochin backwaters. Similarly, a minor association of the metal Fe was also noted by Nair and Balchand (1993) in the organic/sulphide phase of sediments from the upper freshwater regions of the Cochin backwaters. The

moderate association of metals like Mn, Zn, Cr, Co, Cu, Pb and Cd in sediments indicates a moderate enrichment of these metals in organic matter whereas the minor association of metals like Ni and Fe indicates a minor enrichment of these metals in organic matter. The moderate/minor enrichment of metals in the organic fraction showed the scavenging efficiency of metal-organic complexes as a carrier host phase in the Muvattupuzha River which is further sensitive to autochthonous/allochthonous and authigenic substances inputs from land run-off (Madhu et al. 2010).

The hydrous oxides of iron and manganese constitute significant sinks of heavy metals by adsorption and co-precipitation reactions in aquatic systems, particularly under oxidizing conditions (Sholkovitz and Copland, 1981; Chester, 1990). Metals like Mn (25 to 30 %), Cr (17 to 25 %), Co (10 to 14 %), Zn (10 to 15 %) showed a moderate association whereas metals like Cu (5 to 9 %), Fe (4 to 7 %), Ni (4 to 5 %), Pb (1 to 6 %) and Cd (2 to 4 %) showed a minor association in sedimentary fractions bound to Fe-Mn oxides or reducible fractions. A similar moderate association of metals like Mn, Cr, Co and Zn and minor association of metals like Cu, Fe, Ni, Pb and Cd were also noted by Nair et al. (1991) and Nair and Balchand (1993) in the Fe-Mn oxide phase of sediments from the upper freshwater regions of the Cochin backwaters. The moderate association of metals like Mn, Cr, Co and Zn in sediments indicates a moderate enrichment of these metals in ferromanganese minerals whereas the minor association of metals like Cu, Fe, Ni, Pb and Cd indicates a minor enrichment of these metals in ferromanganese minerals. The moderate/minor enrichment of metals in the reducible fraction showed the sinking efficiency of Fe-Mn oxide as a carrier host phase on the heavy metals released by anthropogenic activities into the Muvattupuzha River (Reimann and Caritat, 2005).

The residual fraction of metals in sediments is thought to be of terrestrial origin is usually composed of weathered detrital silicate minerals, resistant sulphides and refractory organics which is an important carrier sink of metals and is regarded as environmentally/chemically inert and hence biologically inactive (Tessier et. al. 1979). Metals bound within the silicate mineral lattices probably account for the bulk of metals in this phase which are not soluble under experimental conditions as they are tightly bound and provide a guide to the degree of contamination of fluvial fluxes and their concentrations are largely governed by the catchment geology (Salamons and Forstner, 1980). The metal Fe (90 to 95 %) showed a very high association/partition dynamics indicating a very high enrichment in residual form bound to sediments. In the residual fraction of sediments, metals like Ni (63 to 73 %), Cr (50 to 55 %), Co (45 to 53 %) and Zn (40 to 50 %) showed a high dynamic association/partition indicating high enrichment, metals like Mn (30 to 35 %) and Cu (24 to 35 %) showed a moderate association indicating moderate enrichment, metals like Cd (15 to 20 %) and Pb (9 to 18 %) showed a minor association indicating minor enrichment. A similar major association of metals like Fe, Ni, Cr, Co and Zn and moderate association of metals like Mn and Cu and minor association of metals like Cd and Pb were also noted by Nair et al. (1991) and Nair and Balchand (1993) in the residual phase of sediments from the upper freshwater regions of the Cochin backwaters. Similar to a high amount of Fe, a major amount of Ni, Cr, Co and Zn, a moderate amount of Mn and Cu, and a minor amount of Cd and Pb that were associated indicating that residual fraction is acting as an important carrier phase of metals. Similar to this a high amount of Fe in residual fraction which is represented as the metal associated with silicate minerals and refractory organic materials and a low amount of Fe in other labile fractions were

reported in sediments by Tessier et al. (1980) for Yamaska/ St. Francois (Quebes, Canada) Rivers and by Gibbs (1977) for Amazon (Brazil)/ Yukon (Alaska) Rivers respectively.

High concentrations of trace metals recorded during the monsoon months when compared to post-monsoon or pre-monsoon months from the exchangeable, carbonate, Fe-Mn oxide, organic/sulphide and residual fractions (or phases) of sediments suggesting that these fractions were associated with the suspended load derived from terrestrial sources under the influence of land run-off and erosion (Table 2.1.1). The higher amount of Fe, a major amount of Ni, Cr, Co and Zn, a moderate amount of Mn and Cu in the residual carrier phase points a lower pollution load of these metals. However the minor amount of Cd and Pb associated with the residual carrier phase indicate some pollution load of fluvial fluxes for these metals.

6.4. Factors controlling the distribution of trace metals in sediments

Grain-size distributions exert a major influence on the geochemical composition of riverine sediments. The silty-clay type of sediments present in rivers is rich in organic matter contents and thus has higher cation exchange capacity and large surface area (Fernandes et al. 2011). Fe-Mn oxides along with organic matter are generally considered as predominant metal sorbents due to their large surface area (Forstner and Wittmann, 1979). Thus, geochemical variations in metal distribution in rivers is associated with the extent to which the precipitation or dissolution of Fe and Mn oxides/hydroxides which act as specific ‘‘sink’’ or “source” of heavy metals (Lacuraj and Maria, 2006).

In particular, the presence of fine-grained sediments leads to the accumulation of trace metals because in contrast to coarser grains, the larger

surface area provided by finer sediments preferentially adsorb metal scavenging phases such as Fe/Mn hydrolysates and serve as potential traps for metals (Forstner, 1983; Dutta and Subramanian, 1997; Murray et al. 1999). Most of the heavy metal contaminants available in the water column of rivers are adsorbed onto suspended particulate matter (SPM) and gets deposited to bottom sediments by flocculation and sedimentation processes (Turner and Millward, 2002). Thus, heavy metals tend to accumulate in riverine sediments through complex physical and chemical adsorption mechanisms depending on the nature of sediment matrix and on properties of the adsorbed compounds (Leivouri, 1998). Several processes lead to the association of heavy metals with solid phases, such as the direct absorption by fine-grained inorganic particles of clays; adsorption of hydrous ferric and manganic oxides which may in turn be associated with clays; adsorption on or complexation with natural organic substances, which may also be associated with inorganic particles, and direct precipitation as new solid phases (Gibbs, 1973; Gibbs, 1977; Rubio et al. 2000). The adsorption process is influenced by several physical and chemical parameters such as: pH, oxidative–reductive potential, dissolved oxygen content, organic and inorganic carbon content, and the presence of water phase anions and cations that can bind or co-precipitate the water-dissolved or suspended pollutants (Calmano et al. 1993; Wen and Allen, 1999). Thus, measurement of trace metal contents in sediments and their distribution in the riverine environment leads to a better understanding of their behaviour and is important for detecting sources of pollution (Forstner and Wittman, 1979). The possible geochemical factors that affecting the spatial distribution of trace metals in sediments of the Muvattupuzha River are discussed below.

6.4.1. Geochemistry and inter-metal relationships

Pearson correlation coefficient (r) was calculated for the overall bimonthly data (n=108) on sediment geochemical parameters (sand, silt, clay & organic carbon) and various metals and the results are given in *Table 6.6.4*. Intermetallic relationship in sediments revealed a high degree of correlation among certain metals, indicating their identical behaviour during transport in the riverine environment (Sutherland, 2000). This matrix provided clues for the interaction of various carrier phases with trace metals and for their geochemical association which in turn led to their incorporation into the sediments (Chester, 1990; Song et al. 2011).

Table 6.6.4. Pearson product-moment correlation coefficients (r) between sediment trace metals, organic carbon, sand, silt & clay in the Muvattupuzha River (n= 108)

Sediment metal	Fe	Mn	Co	Cr	Cu	Ni	Zn	Cd	Pb	OC	Sand	Silt	Clay
Fe	1.000												
Mn	0.368	1.000											
Co	0.454	0.685	1.000										
Cr	0.379	0.368	0.449	1.000									
Cu	0.335	0.371	0.610	0.403	1.000								
Ni	0.243	0.611	0.718	0.316	0.640	1.000							
Zn	0.484	0.635	0.789	0.577	0.674	0.707	1.000						
Cd	0.517	0.266	0.543	0.288	0.338	0.381	0.497	1.000					
Pb	0.673	0.296	0.561	0.317	0.560	0.442	0.632	0.509	1.000				
OC	0.411	0.363	0.485	0.441	0.524	0.396	0.634	0.248	0.542	1.000			
Sand	-0.032	-0.016	-0.014	-0.033	0.011	-0.101	-0.192	-0.239	-0.006	-0.256	1.000		
Silt	-0.006	0.001	0.118	-0.066	-0.053	0.082	0.154	0.222	-0.030	0.205	-0.997	1.000	
Clay	0.467	0.188	0.362	0.388	0.489	0.275	0.528	0.294	0.443	0.716	-0.412	0.342	1.000

6.4.2. Metal-metal correlations

Trace metal enrichment in sediments is linked to scavenging mechanisms involving hydrous oxides (Wang and Chen, 2000). All the metals are significantly positively correlated with each other in sediments. Fe and Mn being the abundant

elements in the study region exert a major control on the distribution of other elements in the sediments. Fe and Mn have fairly close spatial distribution patterns and correlations in sediments indicating their strong association in the geochemical matrix. The strong Fe and Mn positive correlation ($r= 0.368$, significant at $p < 0.001$), observed in sediments revealed the formation of stable Fe–Mn oxyhydroxides. Except Cu and Ni ($r= 0.243$ to 0.335, significant at $p < 0.01$), Fe exhibits high positive correlation ($r= 0.379$ to 0.673, significant at $p < 0.001$) with Mn, Co, Cr, Zn, Cd and Pb. Similarly, except Cd and Pb ($r= 0.266$ to 0.296, significant at $p < 0.02$), Mn exhibits high positive correlation ($r= 0.368$ to 0.685, significant at $p < 0.001$) with Co, Cr, Ni, Cu and Zn. The strong positive correlation of these metals with Fe and Mn indicates adsorption of them onto Fe-Mn oxide geochemical phase. The moderate percentage of Cr (17 to 25 %), Zn (10 to 15 %) and Co (10 to 14 %) in the Fe-Mn oxide/reducible fractions of sediments further confirm the adsorption of these metals. The weakening of Cu and Ni correlation with Fe, weakening of Cd and Pb correlation with Mn indicated the co-precipitation of these metals with Fe-Mn hydroxides. The low percentage of Cu (5 to 9 %), Ni (4 to 5 %), Cd (2 to 4 %) and Pb (1 to 6 %) in the Fe-Mn oxide/reducible fractions of sediments further confirm the co-precipitation of these metals. Thus co-precipitation of Cu, Ni, Cd and Pb with Fe–Mn hydroxides along with scavenging of other metals could account for the net accumulation of trace metals in sediments of the Muvattupuzha River. The results of the correlation matrix thus indicated that a substantial fraction of the trace metal were co-precipitated with or adsorbed onto Fe and Mn geochemical phases in sediments.

6.4.3. Metal-sediment texture-organic carbon correlations

During the present study Fe, Co, Cr, Cu, Zn and Pb are well correlated with clay content (r= 0.362 to 0.528, significant at $p < 0.001$) in sediments whereas Mn, Cd and Ni are weakly correlated with clay content (r= 0.188, significant at $p < 0.10$; r= 0.275 to 0.294, significant at $p < 0.02$) in sediments. Similarly, the metals Fe, Mn, Ni, Co, Cr, Cu, Zn and Pb are well correlated with organic carbon content (r= 0.363 to 0.634, significant at $p < 0.001$) in sediments whereas Cd is weakly correlated (r= 0.248, significant at $p < 0.02$) with organic carbon content in sediments. Organic matter contents and grain size are important controlling factors influencing the abundance of trace metals in sediments (Liaghati et al. 2003). Furthermore adsorption of metal in sediments increases with order: sand < silt < clay, due to an increase in their superficial area and with respect to their mineral/organic matter contents (Padmalal and Seralathan, 1995; Padmalal et al.1997; Murray et al. 1999). The weak to strong positive correlations of metals with clay and organic carbon (OC) implies that these metals can be accumulated either by clay minerals that adsorb these trace metals directly or by organic matter, which is mounted on the clay surface and hence are interrelated to the fine grained fraction (Wang and Chen 2000). The strong correlation of Fe with organic carbon and clay in sediments suggests its presence as a constituent of clay minerals and on coatings on the surface of clay particles. This authenticates the effective relation of organic carbon with most of the elements and endorses the role of sediment organic matter as metal carrier and of complexation with organic matter playing an important role in defining their distribution patterns (Tessier et al. 1996; Li et al. 2000). This is further substantiated by the minor to moderate enrichment of these metals in organic/sulphide fractions of sediments. Thus clays and hydrous Fe-Mn oxides exert a major influence on

the adsorption properties of sediments on trace metals accumulation. The strong correlation of trace metals with clay indicates that they are concentrated to the fine-grained particles and are hosted by clay phases (Sobha and Anish, 2003). Thus metal accumulation in Muvattupuzha River sediments was most probably due to their adsorption onto clay minerals, their co-precipitation with iron oxides and to their association with organic matter content.

6.5. Ecological risk assessment of trace metal enrichment in sediments

It is important to determine whether the concentration of metals in sedimentary fractions found pose a threat to aquatic life. According to the Risk Assessment Code (*RAC*), the metals in sediments are bound with different strengths to the sedimentary fractions and can give an indication of sediment reactivity which assesses the risk connected with the presence of metals (Jain, 2004; Singh et al. 2005). Thus knowing the % values (relative concentrations) of metals in different sedimentary phases with respect to total metal concentrations in sediments of the river their bioavailability and toxicity can be ascertained. Hence RAC assesses the availability of metals in solution by applying a scale to the percentage of sediments that can reduce metals in the exchangeable and carbonate fractions. According to this classification criteria if a metal concentration in exchangeable and carbonate bound fractions is < 1 % it refers to no risk to environment or biota, if a metal concentration in exchangeable and carbonate bound fractions is 1-10 % it refers to low risk to environment or biota, if a metal concentration in exchangeable and carbonate bound fractions is 11-30 % it refers to medium risk to environment or biota, if a metal concentration in exchangeable and carbonate bound fractions is 31-50 % it refers to high risk to environment or biota, and if a metal concentration in

exchangeable and carbonate bound fractions is 75 % it refers to very high risk to environment or biota respectively (Perin et al. 1985; Singh et al. 2005). The risk assessment classification criteria are tabulated as given below.

Risk assessment code		
Risk	**Metal bound to exchangeable Phase (%)**	**Metal bound to carbonate Phase (%)**
No risk	< 1	< 1
Low risk	1-10	1-10
Medium risk	11-30	11-30
High risk	31-50	31-50
Very high risk	75	75

During the present study also RAC criteria are used to assess whether the concentrations of trace metals in exchangeable and carbonate bound sedimentary phases could have any adverse biological impacts. Concentrations of exchangeable and carbonate Fe at all sites are < 1 % posing no risk to the environment. Similarly, concentrations of exchangeable Cr are < 1 % posing no risk to the environment whereas concentrations of carbonate Cr are ~ 3-4 % posing a low risk to the environment. Concentrations of carbonate Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb at many sites are ~ 1- 10 % or ≤10 % posing low risk to the environment. Concentrations of exchangeable Mn, Co, Ni, Cr and Zn at many sites are ~ 1- 10 % or ≤10 % posing low risk to the environment. However, concentration of exchangeable Cu varies between ~ 30 to 35 % whereas concentration of exchangeable Cd varies between ~ 40 to 45 % posing medium risk to the environment. Concentrations of exchangeable Pb ranges from ~ 70 to 75 % posing a high risk to very high risk to the environment. This indicates that the existing concentrations of metals (Cu, Cd & Pb) in the exchangeable bound sedimentary phase derived from anthropogenic contamination are highly toxic to impose stress to river ecology and can easily enter the food chain to cause adverse biological effects. This

means that metal contamination in the Muvattupuzha River sediments is a cause for concern as these metals may diffuse into the overlying water column under the prevailing environmental conditions and can undergo bioaccumulation and affect the benthic organisms.

6.6. Concluding remarks

Sequential extraction of trace metals was performed during the bimonthly intervals of July 2005 to May 2006 from the Muvattupuzha River sediments in order to elucidate the most important sediment bearing fractions of various metals to investigate its geochemical behaviour, mobility, bioavailability and potential risk to aquatic organisms. Due to the neutral to alkaline nature of the river water, most of the heavy metals have precipitated and settled as carbonates, oxides and hydroxides to bearing sediments and elevated levels indicate higher exposure risks to the benthic biota of the river. The occurrence of heavy metals in river water and sediments is due to the discharge of effluents from various sources including untreated domestic sewage, municipal waste and agrochemical runoff from nearby towns and villages directly into the river. The toxicity and fate of water borne metal is dependent on its chemical form and therefore quantification of different forms of metal is more meaningful than the estimation of its total metal concentrations. The results of the fractionation studies reveal that the metals in sediments are bound to different fractions in different strengths. Amoung the various metals studied the risk assessment code reveals that about 70 to 75% of lead at most sites exist in exchangeable fraction posing a high risk to very high risk to the aquatic environment and can easily enter the food chain.

Table 6.6.5. Bimonthly mean concentrations and standard deviations of iron fractions in sediments of the Muvattupuzha River

Month	Fe_{exch} (ppm)	Fe_{carb} (ppm)	Fe_{redu} (ppm)	Fe_{org} (ppm)	Fe_{resid} (ppm)
July 2005	251.3±97.6	313.5±110.3	2240.2±851.5	180.1±68.5	33062.2±11356.8
Sep 2005	199.8±90.1	250.6±103.5	1811.4±782.5	144.4±65.5	27086.2±11342.5
Nov 2005	180.5±87.7	224.9±106.2	1638.1±770.5	131.2±63.4	24931.7±10433.5
Jan 2006	164.2±50.5	200.8±60.8	1476.2±441.8	117.8±36.8	22926.7±5947.5
March 2006	138.6±85.4	170.8±70.5	1259.0±755.4	100.3±61.7	19965.3±10250.7
May 2006	168.0±97.3	179.2±88.5	1557.2±758.5	124.3±85.7	22982.8±11450.5

Table 6.6.6. Bimonthly mean concentrations and standard deviations of manganese fractions in sediments of the Muvattupuzha River

Month	Mn_{exch} (ppm)	Mn_{carb} (ppm)	Mn_{redu} (ppm)	Mn_{org} (ppm)	Mn_{resid} (ppm)
July 2005	12.73±5.39	5.31±3.35	63.38±25.58	68.10±23.57	49.27±27.85
Sep 2005	17.19±6.65	7.15±3.38	85.26±28.68	92.20±25.57	74.02±33.55
Nov 2005	8.78±4.39	3.63±1.84	43.91±21.08	47.32±20.55	43.59±16.52
Jan 2006	7.28±2.13	3.01±0.91	36.14±10.47	39.14±11.35	38.21±8.35
March 2006	7.57±3.52	3.09±1.45	37.73±12.57	40.71±12.85	38.34±9.68
May 2006	9.36±4.85	3.88±2.61	46.53±12.85	50.31±18.87	42.87±15.65

Table 6.6.7. Bimonthly mean concentrations and standard deviations of cobalt fractions in sediments of the Muvattupuzha River

Month	Co_{exch} (ppm)	Co_{carb} (ppm)	Co_{redu} (ppm)	Co_{org} (ppm)	Co_{resid} (ppm)
July 2005	0.936±0.273	0.517±0.151	0.848±0.232	1.818±0.533	4.065±1.180
Sep 2005	1.153±0.427	0.629±0.257	1.042±0.405	2.221±0.929	4.999±2.045
Nov 2005	0.839±0.302	0.462±0.163	0.770±0.251	1.621±0.585	3.658±1.302
Jan 2006	0.922±0.387	0.501±0.165	0.833±0.305	1.781±0.752	4.025±1.605
March 2006	0.633±0.356	0.351±0.165	0.598±0.302	1.229±0.685	2.764±1.152
May 2006	0.625±0.325	0.346±0.151	0.587±0.308	1.210±0.856	2.728±1.857

Table 6.6.8. Bimonthly mean concentrations and standard deviations of nickel fractions in sediments of the Muvattupuzha River

Month	Ni_{exch} (ppm)	Ni_{carb} (ppm)	Ni_{redu} (ppm)	Ni_{org} (ppm)	Ni_{resid} (ppm)
July 2005	1.70±1.15	0.88±0.65	0.83±0.74	1.49±1.07	13.55±10.25
Sep 2005	4.45±2.08	2.31±1.30	2.16±1.22	3.95±2.24	35.58±20.01
Nov 2005	3.38±1.65	1.76±0.97	1.64±0.90	2.99±1.65	26.91±14.60
Jan 2006	1.86±0.75	0.97±0.40	0.91±0.33	1.64±0.67	14.82±5.94
March 2006	1.91±1.08	0.99±0.71	0.93±0.36	1.68±1.22	15.26±11.08
May 2006	1.15±0.85	0.59±0.35	0.56±0.28	1.00±0.85	9.14±5.65

Table 6.6.9. Bimonthly mean concentrations and standard deviations of copper fractions in sediments of the Muvattupuzha River

Month	Cu_{exch} (ppm)	Cu_{carb} (ppm)	Cu_{redu} (ppm)	Cu_{org} (ppm)	Cu_{resid} (ppm)
July 2005	4.43±1.38	0.83±0.30	0.75±0.21	3.58±1.23	3.34±0.88
Sep 2005	6.66±2.31	1.32±0.51	1.08±0.35	5.59±2.09	4.77±1.50
Nov 2005	4.59±3.31	0.87±0.55	0.77±0.53	3.73±1.85	3.44±1.85
Jan 2006	4.21±2.55	0.79±0.53	0.71±0.38	3.39±1.78	3.16±1.71
March 2006	2.98±1.48	0.51±0.31	0.52±0.23	2.27±1.36	2.39±0.98
May 2006	2.72±1.13	0.49±0.30	0.48±0.21	2.09±1.25	2.11±0.95

Table 6.7.0. Bimonthly mean concentrations and standard deviations of chromium fractions in sediments of the Muvattupuzha River

Month	Cr_{exch} (ppm)	Cr_{carb} (ppm)	Cr_{redu} (ppm)	Cr_{org} (ppm)	Cr_{resid} (ppm)
July 2005	0.260±0.048	1.78±0.39	9.06±1.78	9.15±2.01	19.03±3.60
Sep 2005	0.184±0.046	1.21±0.35	6.42±1.61	6.14±1.65	13.77±3.20
Nov 2005	0.112±0.021	0.67±0.14	3.86±0.67	3.38±0.68	8.48±1.28
Jan 2006	0.132±0.020	0.82±0.15	4.59±0.71	4.20±0.73	9.98±1.36
March 2006	0.117±0.074	0.71±0.53	4.00±0.78	3.05±0.75	8.84±1.35
May 2006	0.073±0.050	0.42±0.32	2.46±0.87	2.68±0.78	5.56±1.25

Table 6.7.1. Bimonthly mean concentrations and standard deviations of zinc fractions in sediments of the Muvattupuzha River

Month	Zn_{exch} (ppm)	Zn_{carb} (ppm)	Zn_{redu} (ppm)	Zn_{org} (ppm)	Zn_{resid} (ppm)
July 2005	5.01±2.01	3.43±1.38	6.77±2.72	12.94±5.19	19.98±6.01
Sep 2005	6.91±2.24	4.75±1.54	9.40±3.04	17.84±5.75	25.71±6.70
Nov 2005	3.46±1.34	2.37±0.92	4.66±1.80	8.96±3.45	15.31±3.98
Jan 2006	3.72±1.37	2.55±0.95	5.04±1.95	9.68±3.85	16.12±4.40
March 2006	3.70±1.65	2.53±0.98	5.00±1.88	9.71±3.44	16.09±4.22
May 2006	2.42±1.85	1.66±0.96	3.24±1.77	6.34±3.35	10.57±3.65

Table 6.7.2. Bimonthly mean concentrations and standard deviations of cadmium fractions in sediments of the Muvattupuzha River

Month	Cd_{exch} (ppm)	Cd_{carb} (ppm)	Cd_{redu} (ppm)	Cd_{org} (ppm)	Cd_{resid} (ppm)
July 2005	0.152±0.032	0.0372±0.0081	0.0114±0.0027	0.0360±0.0081	0.0685±0.0157
Sep 2005	0.126±0.037	0.0308±0.0088	0.0093±0.0031	0.0298±0.0097	0.0554±0.0183
Nov 2005	0.165±0.023	0.0402±0.0060	0.0122±0.0018	0.0392±0.0061	0.0745±0.0112
Jan 2006	0.182±0.037	0.0446±0.0096	0.0137±0.0030	0.0406±0.0110	0.0802±0.0192
March 2006	0.153±0.075	0.0371±0.0200	0.0114±0.0061	0.0341±0.0150	0.0684±0.0367
May 2006	0.117±0.084	0.0289±0.0200	0.0088±0.0064	0.0277±0.0200	0.0546±0.0360

Table 6.7.3. Bimonthly mean concentrations and standard deviations of lead fractions in sediments of the Muvattupuzha River

Month	Pb_{exch} (ppm)	Pb_{carb} (ppm)	Pb_{redu} (ppm)	Pb_{org} (ppm)	Pb_{resid} (ppm)
July 2005	7.27±2.17	0.105±0.038	0.49±0.15	1.36±0.50	1.21±0.31
Sep 2005	8.75±3.58	0.131±0.063	0.55±0.22	1.70±0.82	1.36±0.32
Nov 2005	7.61±2.44	0.110±0.043	0.45±0.22	1.43±0.56	1.26±0.21
Jan 2006	8.62±2.01	0.123±0.034	0.48±0.15	1.58±0.44	1.32±0.17
March 2006	6.68±2.45	0.092±0.045	0.42±0.16	1.20±0.62	1.17±0.24
May 2006	5.13±2.48	0.075±0.042	0.33±0.15	0.94±0.65	0.91±0.22

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Chapter 7

SUMMARY AND CONCLUSION

Heavy metal contamination in aquatic environments is of major environmental concern because of their potential toxicity and threat to ecosystems. In rivers, trace metals released from anthropogenic sources are transported to water, get predominantly associated with suspended particulate matter along with various carrier phases and becomes incorporated to bottom sediments, which makes them an important repository for metallic pollutants. Information on the dynamic metal interactions in and between the different compartments like water, suspended particulate matter and sediments from the upstream regions of the Muvattupuzha River is vital for addressing the environmental impacts of heavy metal pollution. The present study describes the spatial and seasonal variations of trace metals in the dissolved phase, particulate phase and trace metals that bound among various sedimentary geochemical phases from the upstream areas of the Muvattupuzha River.

The study area is predominantly surrounded by agricultural lands and municipal townships. Based on specific geographical features, water flow regimes and anthropogenic activities, 18 sampling locations were selected in the upper reaches of the Muvattupuzha River. Water and sediment samples were collected at bimonthly intervals (6 times) between July 2005 and May 2006. All stations are located at fresh water zones.

pH values in the water column ranges from 6.52 to 7.56 during the period of study. The bimonthly variation of pH values at most sites exceeds 7.00 indicating the slightly alkaline nature of the river which is due to the

discharge of domestic water effluents that containing high amount of alkaline detergents. The average pH values during the monsoon, post-monsoon and pre-monsoon months will not exhibit considerable seasonal trends.

Temperature in the water column ranges from 23.9 to 33.2°C during the period of study. The bimonthly average temperature values showed relatively colder waters persist during monsoon months and post-monsoon months whereas relatively warmer waters persist during pre-monsoon months in the river. The persistence of relatively colder waters during the monsoon and post-monsoon months is attributed to high rainfall in the region.

During the period of study a high amount of dissolved oxygen (5.07 to 11.57 mg l^{-1}) is present in the river which is attributed to photosynthetic activities of phytoplanktons and effective water circulation. Dissolved oxygen showed higher values during the monsoon season when compared to post-monsoon or pre-monsoon seasons which may be attributed to the lowering of temperature and turbulence produced by heavy rains and high local precipitation.

COD values in water during the period of study ranges from 1.61 to 240.26 mg l^{-1}. Seasonal average values of COD showed higher values during the monsoon and pre-monsoon periods when compared to post-monsoon periods. Higher values during the monsoon period are attributed to added load of organic matter brought down to river along with land drainage following the monsoonal showers.

Chloride content in water ranges from 6.12 to 56.48 mg l^{-1} during the period of study. Chloride ion concentration showed higher values during the pre-monsoon than post-monsoon or monsoon months. The monsoonal decrease in chloride is attributed to heavy rain and strong flushing. The pre-

monsoonal increase in chloride is due to high rate of evaporation by high air temperature.

Sand, silt and clay content in sediments during the period of study varies from 9.95 to 93.55 %, 3.65 to 87.81 % and 1.32 to 8.12 % respectively. Average sand and clay content showed the following seasonal pattern of accumulation: monsoon months > post-monsoon months > pre-monsoon months whereas average silt content showed another seasonal pattern of accumulation: pre-monsoon months > post-monsoon months > monsoon months. Sediment texture showed that sediments are medium to coarse grained. The coarseness of the sediments is due to the relative proximity of the weathering sources, high energy conditions existing in the river by high water currents and influx of sediments from the neighbouring tributaries.

Organic carbon content in sediments during the period of study varies between 0.32 to 6.99 %. Average organic carbon content showed the following seasonal pattern of accumulation: monsoon months > post-monsoon months > pre-monsoon months. The higher organic carbon values (> 5 %) encountered at stations S_3 to S_6 and at stations S_{15} to S_{16} during the monsoon months indicated the presence of organic pollutants derived by agricultural and domestic waste discharges to river. The progressive decrease of organic carbon from the monsoon to post-monsoon and to pre-monsoon periods is due to high energy non-depositional conditions such as the incessant stirring up of bottom sediments by water currents, high dissolved oxygen in the overlying waters and sandy nature of sediments in the river.

The distribution of dissolved and particulate Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb in water were investigated in the study. The concentration of dissolved metals varied from 16.24 to 69.70 ppb for Fe, 13.18 to 33.85 ppb

for Mn, 0.104 to 0.557 ppb for Co, 0.364 to 0.828 ppb for Ni, 0.685 to 1.857 ppb for Cu, 0.378 to 0.777 ppb for Cr, 7.89 to 19.85 ppb for Zn, 0.623 to 1.244 ppb for Cd and 0.254 to 0.945 ppb for Pb respectively. The concentration of particulate metals varied from 106.18 to 474.67 ppb for Fe, 65.67 to 149.25 ppb for Mn, 0.124 to 0.905 ppb for Co, 0.665 to 1.490 ppb for Ni, 0.655 to 1.625 ppb for Cu, 0.518 to 0.985 ppb for Cr, 18.91 to 41.69 ppb for Zn, 0.426 to 0.878 ppb for Cd and 0.585 to 2.766 ppb for Pb respectively.

The bimonthly average concentration of dissolved metals in water showed the respective orders of abundance:

Fe > Mn > Zn > Cu > Cd > Pb > Cr > Ni > Co (for July and September 2005)
Fe > Mn > Zn > Cu > Cd > Cr > Ni > Pb > Co (for November 2005 and January, March and May 2006)

The order of abundance of dissolved metals during all seasons showed that Fe was the most abundant metal which was followed by Mn and the least abundant metal was Co. Of the 9 metals studied the average concentrations of Cr, Ni, and Pb vary considerably between monsoon months and non-monsoon months.

Dissolved Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb concentrations during all months showed considerable spatial variations possibly due to varying inputs from anthropogenic sources like municipal effluents as well as agricultural runoff.

The seasonal trend of dissolved metals showed a decreasing order in concentrations which is as follows: monsoon > post-monsoon > pre-monsoon. The increase in concentration of dissolved metals in water during the monsoon months when compared to post-monsoon months or pre-monsoon months

indicates the influence of freshwater as a major source for trace metal input in the river. The high concentration of dissolved metals observed during monsoon season could be attributed to heavy rainfall and subsequent river runoff that bringing much of the land derived materials containing domestic, municipal and agricultural wastes with residues of heavy metals, pesticides as well as fertilizers and partly from remobilisation of metals from the bulk sedimentary phases by strong water currents. The low concentrations of dissolved metals during post-monsoon and pre-monsoon periods are possibly due to dilution effect and reduced re-suspension of sediments by weak water currents.

The bimonthly average concentration of particulate metals in water showed the respective decreasing orders of abundance:

Fe > Mn > Zn > Pb > Cu > Ni > Cr > Cd > Co (for July, September and November, 2005 and January 2006)
Fe > Mn > Zn > Cu > Ni > Pb > Cr > Cd > Co (for March 2006)
Fe > Mn > Zn > Cu > Pb > Ni > Cr > Cd > Co (for May 2006)

The order of abundance of particulate metals during different seasons showed that Fe was the most abundant metal which was followed by Mn and the least abundant metal was Co. Of the 9 metals studied the average concentrations of Fe, Mn, Zn, Cr, Cd and Co showed the same order of abundance between monsoon months and non-monsoon months.

Particulate Fe, Mn, Co, Ni, Cu, Cr, Zn, Cd and Pb concentrations during all months showed considerable spatial variations due to varying inputs of suspended particles which are possibly derived from anthropogenic sources like municipal effluents as well as agricultural runoff.

The seasonal trend of particulate metals showed a decreasing order of concentrations which is as follows: monsoon > post-monsoon > pre-monsoon. The increase in concentration of particulate metals in water during the monsoon months when compared to post-monsoon months or pre-monsoon months indicates the influence of freshwater as a major source for trace metal input in the river. The observed higher values for particulate trace metals during monsoon season than other seasons is due to significant inputs of agro-chemical residues from agricultural lands and municipal wastes through the land runoff washing process and partly from re-suspension of metal rich bulk sediments due to strong water currents. The strong adsorption of metal rich fine particles onto suspended particulate matter resulted in an increase in concentration of particulate metals during monsoon when compared to post-monsoon or pre-monsoon periods. The observed low concentrations of particulate metals during post-monsoon and pre-monsoon periods are possibly due to reduced re-suspension of sediments by weak water currents.

Quantification of contamination of dissolved trace metals by an enrichment ratio (ER) calculated lies in the following ranges: Cd (31.13 to 62.19), Mn (2.20 to 5.64), Pb (1.270 to 4.725), Ni (1.28 to 2.76), Zn (0.85 to 1.98), Co (0.60 to 2.79), Cu (0.76 to 1.86), Cr (0.85 to 1.50), Fe (0.30 to 1.27). During the period of study spatially all the metals in the river occasionally showed ER > 1 suggesting its enrichment and contribution from anthropogenic sources. The enrichment ratio for these metals during all seasons follows the decreasing order: Cd > Mn > Pb > Ni > Zn > Co > Cu > Cr > Fe. Cd showed the highest enrichment ratio whereas Fe showed the lowest enrichment ratio. The order of enrichment ratio of various metals indicates that Cd, Mn, Pb and Ni are sufficiently enriched in the Muvattupuzha River waters from anthropogenic sources at a higher rate than the other metals.

All the metals showed higher ER during monsoon months when compared to post-monsoon or pre-monsoon months suggesting the contribution from land runoff materials in the river. The anthropogenic sources in the area are agricultural runoff and domestic waste water discharges. Thus enrichment ratio data suggest that agricultural wastes and municipal wastes contribute to most of the metal enrichment in the river.

The results of the correlation matrix between dissolved and particulate trace metals with dissolved oxygen showed that a substantial fraction of trace metals in dissolved phase derived from anthropogenic sources were adsorbed onto Fe-Mn geochemical phases of suspended particulate matter which can contaminate the bottom sediments by sinking.

The ranges of partition coefficient values (Kd) obtained for various metals during the study period were as follows: Fe (3.76 to 10.87), Mn (3.28 to 6.74), Co (1.02 to 3.16), Ni (1.53 to 2.49), Cu (0.850 to 1.027), Cr (1.16 to 1.43), Zn (1.62 to 3.00), Cd (0.61 to 0.91), Pb (1.60 to 3.73). These ranges or spatial variations of partition coefficient values for various metals are a consequence of variations in the relative spatial enrichment or affinity of these metals in the particulates which are as follows: Fe (83.3 to 91.1 %), Mn (79.0 to 91.6 %), Co (50.3 to 75.4 %), Ni (60.5 to 71.3 %), Cu (45.9 to 50.7 %), Cr (53.6 to 58.9 %), Zn (61.8 to 75.0 %), Cd (38.4 to 45.5 %), Pb (61.5 to 78.9 %). This indicates that except Cd and Cu, a large fraction of other metals in the river is bounded to particulate phase. The averaged partition coefficient values for the metals in the water column during the study period demonstrate a similar ranking for the metals which were as follows: Fe > Mn > Pb > Zn > Ni > Co > Cr > Cu > Cd. This ranking is attributed to the different bio-geochemical behaviour of these elements in the river. For Fe, Mn and Pb its high affinity to particles may promote association with particulate matter

while the low affinity to particles and a stronger potential to form stable organic complexes allow Cd to remain in dissolved phase.

Total metal concentrations in sediments during the study period varies between 3584 to 59565 ppm for Fe, 18.81 to 498.45 ppm for Mn, 0.10 to 17.54 ppm for Co, 0.23 to 93.99 ppm for Ni, 1.76 to 48.04 ppm for Cu, 3.74 to 44.64 ppm for Cr, 5.96 to 77.77 ppm for Zn, 0.07 to 0.83 ppm for Cd and 1.79 to 23.59 ppm for Pb respectively.

The seasonal trend of all total metals (except Cd) in sediments showed a decreasing order of concentrations which is as follows: monsoon > post-monsoon > pre-monsoon. The increase in concentration of total metals in sediments during the monsoon months when compared to post-monsoon months or pre-monsoon months is due to the influence of land run-off materials in the trace metal accumulation in sediments of the river. The observed higher values for total trace metals in sediments during the monsoon season than other seasons is due to enrichment of trace metal residues from agro-chemicals used in agricultural lands and municipal wastes through the land runoff washing process by heavy rain and strong water currents. The observed low concentrations of total metals in sediments during post-monsoon and pre-monsoon periods are possibly due to dilution process.

The bimonthly average concentration of total metals in sediments showed the respective decreasing orders of abundance:

Fe > Mn > Zn > Cr > Ni > Cu > Pb > Co > Cd (for July 2005)
Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > Cd (for September 2005)
Fe > Mn > Ni > Zn > Cr > Cu > Pb > Co > Cd (for November 2005)
Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > Cd (for January 2006)
Fe > Mn > Zn > Ni > Cr > Pb > Cu > Co > Cd (for March 2006)
Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > Cd (for May 2006)

The order of abundance of metals in sediments during all seasons showed that Fe was the most abundant metal which was followed by Mn and the least abundant metal was Cd. Of the 9 metals studied the average concentrations of Zn, Cu, Cr, Ni and Pb vary considerably between months.

A comparison of total Mn, Cu, Co, Cr and Zn concentrations in sediment obtained during the present study with respect to shale standard average values indicating no enrichment for these metals in the sediments. However total Fe, Ni, Cd and Pb concentrations in sediments obtained during the present study at certain sites exceeded the respective shale standard average values indicating its enrichment due to the influence of land-based anthropogenic inputs in the sediments.

The total trace metals and pollution status in sediments of the Muvattupuzha River was assessed by means of geo-statistical tools like Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI) and Geo-accumulation Index (I geo).

The Enrichment Factor (EF) values during the period of study varies from 0.03 to 7.29 for Mn, 0.06 to 11.78 for Co, 0.04 to 17.64 for Ni, 0.08 to 8.26 for Cu, 0.05 to 4.06 for Cr, 0.11 to 9.11 for Zn, 0.78 to 11.23 for Cd and 0.38 to 5.29 for Pb respectively. Mn showed a spatial segregation with a minor (EF < 3) to moderately severe (EF > 5) enrichment in sediments indicating a marginal contribution of this element from the nearby urban areas. Co and Ni showed a spatial segregation with a minor (EF < 3) to moderate (EF = 3-5) to severe enrichment (EF = 10-25) in sediments indicating a marginal contribution of this element from the nearby municipal and agricultural areas. The metals Cu, Cr, Zn, Cd and Pb showed a spatial segregation with a minor

(EF < 3) to moderate enrichment (EF = 3-5) in sediments indicating a marginal contribution of these elements from the nearby urban and agricultural areas.

EF values (> 2) for all metals together with its minor to moderate enrichment in sediments showed a moderate anthropogenic impact on the trace metal concentration levels in sediments. The high EF values (>1.5) for all trace metals at certain locations indicating some terrestrial input of contaminated sediment through the river and their spatial segregation suggests anthropogenic sources in the study area that derived from human activities like sand/clay mining, agriculture as well as domestic waste discharges.

The contamination factor (CF) values during the period of study ranges from 0.08 to 1.26 for Fe, 0.02 to 0.59 for Mn, 0.01 to 0.92 for Co, 0.03 to 1.38 for Ni, 0.04 to 1.07 for Cu, 0.04 to 0.50 for Cr, 0.11 to 0.82 for Zn, 0.22 to 2.76 for Cd and 0.09 to 1.18 for Pb respectively. The contamination factors for the metals Fe, Mn, Co, Cu, Cr, Zn and Pb in sediments were ≤ 1 indicating a low level contamination and low level pollution load of these elements from the urban and agricultural areas whereas the contamination factors for metals like Ni and Cd were > 1 in sediments indicating a moderate level contamination and moderate level pollution load of these elements from the urban and agricultural areas. Thus the elevated value of contamination factor (CF) identified for some metals at certain locations suggests the influence of human impact on the riverine sediments.

The pollution load index (PLI) value ranges for trace metals during the months of July, September, November, January, March and May were 0.16 to 0.64, 0.24 to 0.74, 0.22 to 0.58, 0.23 to 0.58, 0.18 to 0.62 and 0.05 to 0.68 respectively. Since values of PLI for trace metals were found to be low (maximum value 0.74) during all months (i.e., PLI < 1) this indicates only a

minor metallic pollution or its mere presence and hence a major metallic pollution is quite insignificant in the river. Thus the pollution load index (PLI) indicates that this riverine ecosystem is not of a severe or major pollution concerns with respect to trace metal concentrations in sediments in the present scenario of human impacts.

Sediment quality based on the index of geo-accumulation (*I*geo) classifies all the sediments as unpolluted with Fe, Mn, Ni, Co, Zn, Cu, Cr and Pb (*I*geo < 0 for each trace metal) and unpolluted to somewhat moderately polluted with Cd (*I* geo value 0 to 1). Thus the index of geo-accumulation (*I*geo) reveals that sediments are not seriously polluted by heavy metals.

Fractionation of trace metals in sediments was attempted to identify the character of each of the metal in the riverine system. The percentage amount of metals that can be extractable from the exchangeable, carbonate, Fe-Mn oxide, organic/sulphide and residual fractions/phases of sediments were estimated by Tessier procedure and the respective orders of abundance are:

Pb > Cd > Cu > Zn > Ni > Co > Mn > Cr > Fe (exchangeable fraction)
Cd > Zn > Cu > Co > Ni > Cr > Mn > Pb > Fe (carbonate fraction)
Mn > Cr > Zn > Co > Cu > Fe > Pb > Ni > Cd (Fe-Mn oxide/reducible fraction)
Mn > Zn > Cu > Cr > Co > Pb > Cd > Ni > Fe (organic/sulphide fraction)
Fe > Ni > Cr > Co > Zn > Mn > Cu > Cd > Pb (residual fraction)

In the exchangeable fraction of sediments, metals like Pb (70 to 75 %), Cd (40 to 45 %) and Cu (30 to 35 %) showed a high dynamic association/partition indicating high enrichment, metals like Zn (7 to 12 %),

Co (10 to 12 %) and Ni (8 to 9 %) showed a moderate association indicating moderate enrichment, metals like Mn (4 to 6 %) showed a minor association indicating minor enrichment whereas metals like Cr (0.4 to 0.8 %) and Fe (0.3 to 0.7 %) showed a very low minor association indicating very low minor enrichment. A high percentage of light minerals and clay minerals and organics in the sediments may possibly act as an adsorbent, retaining metals through ion-exchange processes with a net result of enhancing metal levels in the exchangeable phase of sediments.

In the carbonate bound fraction of sediments, metals like Cd (8 to 11 %), Zn (5 to 8 %), Co (5 to 7 %), Cu (4 to 7 %), Ni (4 to 5 %), Cr (3 to 5 %), Mn (1 to 3 %), Pb (0.5 to 1.0 %) and Fe (0.5 to 1.0 %) showed minor associations indicating co-precipitation reactions.

In the organic/sulphide fraction of sediments, metals like Mn (30 to 35 %), Zn (20 to 30 %), Co (20 to 24 %), Cr (17 to 25 %), Cu (20 to 29 %), Pb (10 to 15 %), Cd (8 to 11 %) showed a moderate association indicating moderate enrichment in organic matter whereas metals like Ni (6 to 8 %) and Fe (0.4 to 0.6 %) showed only minor enrichment in organic matter.

Metals like Mn (25 to 30 %), Cr (17 to 25 %), Co (10 to 14 %), Zn (10 to 15 %) showed a moderate association whereas metals like Cu (5 to 9 %), Fe (4 to 7 %), Ni (4 to 5 %), Pb (1 to 6 %) and Cd (2 to 4 %) showed a minor association in sedimentary fractions bound to Fe-Mn oxides or reducible fractions. Mn, Cr, Co and Zn in sediments indicated a moderate enrichment of these metals in ferromanganese minerals whereas Cu, Fe, Ni, Pb and Cd indicated a minor enrichment of these metals in ferromanganese minerals. The moderate/minor enrichment of metals in the reducible fraction showed the

sinking efficiency of Fe-Mn oxide as a carrier host phase in the river which is further sensitive to anthropogenic inputs.

The metal Fe (90 to 95 %) showed a very high association/partition dynamics indicating a very high enrichment in residual form bound to sediments. In the residual fraction of sediments, metals like Ni (63 to 73 %), Cr (50 to 55 %), Co (45 to 53 %) and Zn (40 to 50 %) showed a high dynamic association/partition indicating high enrichment, metals like Mn (30 to 35 %) and Cu (24 to 35 %) showed moderate enrichment and Cd (15 to 20 %) and Pb (9 to 18 %) showed minor enrichment. Similar to a high amount of Fe, a major amount of Ni, Cr, Co and Zn, a moderate amount of Mn and Cu, and a minor amount of Cd and Pb were associated indicating that residual fraction is acting as an important carrier phase of metals.

High concentrations of trace metals recorded during the monsoon months when compared to post-monsoon or pre-monsoon months in the exchangeable, carbonate, Fe-Mn oxide, organic/sulphide and residual fractions (or phases) of sediments suggesting that these fractions were associated from the suspended load derived from terrestrial sources under the influence of land run-off and erosion.

A Risk Assessment Code (RAC) criterion is used to assess whether the concentrations of trace metals in exchangeable and carbonate bound sedimentary phases could have any adverse biological impacts in the aquatic environment. Concentrations of exchangeable and carbonate Fe at all sites are < 1 % posing no risk and hence safe to the environment. Similarly, concentrations of exchangeable Cr are < 1 % posing no risk and hence safe to the environment whereas concentrations of carbonate Cr are ~ 3-4 % posing a low risk to the environment. Concentrations of carbonate Mn, Co, Ni, Cu, Cr,

Zn, Cd and Pb at many sites are ~ 1- 10 % or ≤ 10 % posing low risk to the environment. Concentrations of exchangeable Mn, Co, Ni, Cr and Zn at many sites are ~ 1- 10 % or ≤10 % posing low risk to the environment. However, concentration of exchangeable Cu varies between ~ 30 to 35 % whereas concentration of exchangeable Cd varies between ~ 40 to 45 % posing medium risk to the environment. Concentrations of exchangeable Pb ranges from ~ 70 to 75 % posing a high risk to very high risk to the environment. This indicates that the existing concentrations of metals (Cu, Cd & Pb) in the exchangeable bound sedimentary phase derived from anthropogenic contamination are highly toxic to impose stress to river ecology and hence can easily enter the food chain to cause adverse biological effects. This means that metal enrichment in the Muvattupuzha River sediments is a cause for concern as these metals may diffuse into the overlying water column under the prevailing environmental conditions and can undergo bioaccumulation and harmfully affects the sediment-dwelling organisms which are expected to occur frequently.

The metal fractionation data presented here opens a new dimension in river water quality monitoring to determine the ecotoxic potential of metal ions. There is a considerable enrichment of metals in the Muvattupuzha River environment from domestic and agricultural wastes. This study demonstrates the high ecological risks and hence a need for further environmental monitoring programmes for supporting and developing effective management strategies/protocol to control the loading of contaminants in the riverine environment from industrial, urban and agricultural effluent discharges is highlighted.

Table A 3.1.0. Spatial variation of pH, Temperature, Dissolved Oxygen, Chloride and Chemical Oxygen Demand in the water column of the Muvattupuzha River during July 2005

Station position	p^H	Temperature (°C)	Dissolved Oxygen (mg/l)	Chloride (mg/l)	COD (mg/l)
S1	6.68	27.4	8.71	14.98	31.67
S2	6.67	27.0	8.82	13.60	37.54
S3	6.69	26.7	8.46	9.20	40.21
S4	7.02	26.7	8.54	8.05	44.92
S5	7.08	26.6	8.87	8.05	50.21
S6	7.11	26.4	9.43	12.10	33.01
S7	7.12	26.6	9.91	12.08	23.08
S8	7.13	26.4	9.73	12.04	20.06
S9	7.14	25.6	9.43	10.08	18.04
S10	7.14	25.2	8.57	9.07	22.04
S11	7.15	25.0	9.08	9.00	36.51
S12	7.13	24.9	9.35	8.20	28.54
S13	7.11	24.6	10.80	8.17	21.54
S14	7.12	24.4	10.76	8.14	22.08
S15	7.18	24.2	10.95	8.05	23.08
S16	7.21	24.0	11.20	8.06	23.08
S17	6.67	28.3	9.54	11.96	59.33
S18	6.68	28.2	9.45	12.00	62.04

Table A 3.1.1. Spatial variation of pH, Temperature, Dissolved Oxygen, Chloride and Chemical Oxygen Demand in the water column of the Muvattupuzha River during September 2005

Station position	pH	Temperature (°C)	Dissolved Oxygen (mg/l)	Chloride (mg/l)	COD (mg/l)
S1	7.33	27.0	8.10	7.72	74.32
S2	7.33	26.9	8.20	8.20	104.23
S3	7.34	26.9	8.24	10.00	164.24
S4	7.34	26.8	7.96	10.00	240.26
S5	7.36	26.4	8.85	9.50	223.71
S6	7.36	26.0	9.64	8.40	186.49
S7	7.44	25.8	10.56	6.18	76.67
S8	7.45	26.0	10.03	6.20	81.52
S9	7.46	25.2	10.53	6.18	85.35
S10	7.48	25.0	11.57	6.18	76.55
S11	7.50	24.8	11.02	6.18	68.56
S12	7.56	24.8	10.56	6.17	62.13
S13	7.54	24.5	10.43	6.17	64.66
S14	7.52	24.3	10.05	7.70	68.39
S15	7.35	24.1	9.05	7.72	98.36
S16	7.35	23.9	7.88	7.72	102.48
S17	6.89	28.0	9.62	6.12	213.42
S18	6.92	27.9	9.42	6.22	231.52

Table A 3.1.2. Spatial variation of pH, Temperature, Dissolved Oxygen, Chloride and Chemical Oxygen Demand in the water column of the Muvattupuzha River during November 2005

Station position	p^H	Temperature (°C)	Dissolved Oxygen (mg/l)	Chloride (mg/l)	COD (mg/l)
S1	6.72	27.5	7.29	15.69	6.36
S2	6.72	27.5	7.45	15.00	5.03
S3	6.74	27.4	7.80	11.00	7.26
S4	6.79	27.4	7.84	10.98	11.48
S5	6.79	27.3	8.88	10.90	8.42
S6	6.84	27.3	8.96	10.60	7.32
S7	6.79	27.2	9.01	9.40	7.83
S8	7.00	27.0	8.91	9.40	14.51
S9	7.08	25.2	9.10	9.40	13.56
S10	7.16	24.9	8.61	9.40	16.8
S11	7.14	24.8	7.21	10.00	30.28
S12	7.13	24.6	7.03	12.80	25.6
S13	7.15	24.3	8.23	13.00	18.13
S14	7.18	24.2	8.33	13.40	13.33
S15	7.19	24.0	7.62	13.32	15.76
S16	7.23	23.9	7.07	13.32	25.31
S17	6.76	28.5	8.96	9.42	26.4
S18	6.82	28.4	8.89	9.22	29.44

Table A 3.1.3. Spatial variation of pH, Temperature, Dissolved Oxygen, Chloride and Chemical Oxygen Demand in the water column of the Muvattupuzha River during January 2006

Station position	p^H	Temperature (°C)	Dissolved Oxygen (mg/l)	Chloride (mg/l)	COD (mg/l)
S1	6.96	30.6	6.65	40.36	20.55
S2	6.98	30.5	6.72	30.36	17.26
S3	7.04	30.4	6.12	20.22	15.47
S4	7.04	30.3	6.13	15.79	13.76
S5	7.08	30.1	6.25	12.80	8.89
S6	7.08	30.0	6.64	8.80	6.46
S7	7.11	28.9	6.94	7.86	4.04
S8	7.18	28.5	6.88	7.95	4.83
S9	7.20	28.0	7.07	7.90	5.23
S10	7.20	27.9	7.20	7.86	5.71
S11	7.24	27.3	6.89	7.84	5.47
S12	7.26	27.1	6.28	7.80	3.02
S13	7.30	26.9	6.35	9.77	1.61
S14	7.38	26.4	6.45	9.78	7.24
S15	7.40	26.3	6.15	9.79	10.06
S16	7.42	26.1	5.98	9.80	12.67
S17	6.62	29.2	6.32	8.00	9.51
S18	6.52	29.0	6.41	8.10	7.02

Table A 3.1.4. Spatial variation of pH, Temperature, Dissolved Oxygen, Chloride and Chemical Oxygen Demand in the water column of the Muvattupuzha River during March 2006

Station position	p^H	Temperature (°C)	Dissolved Oxygen (mg/l)	Chloride (mg/l)	COD (mg/l)
S1	6.88	32.2	5.64	23.86	48.28
S2	6.89	32.2	5.94	20.84	56.21
S3	7.02	32.1	5.63	10.26	62.42
S4	7.04	32.0	5.07	9.55	56.36
S5	7.02	32.0	5.32	9.50	54.27
S6	7.01	31.9	5.52	9.40	60.45
S7	7.02	31.8	5.74	9.34	56.23
S8	7.03	31.7	5.62	9.68	54.54
S9	7.04	31.5	5.92	9.70	60.04
S10	7.04	31.0	6.52	9.73	62.86
S11	7.05	29.5	6.32	9.70	64.28
S12	7.05	28.3	5.73	20.10	40.02
S13	7.06	28.0	5.54	21.47	72.21
S14	7.08	27.3	5.93	21.50	152.42
S15	7.08	27.2	6.03	21.50	16.37
S16	7.10	27.1	5.85	20.96	48.22
S17	6.88	32.0	5.80	10.20	60.22
S18	6.76	31.9	5.59	10.40	58.63

Table A 3.1.5. Spatial variation of pH, Temperature, Dissolved Oxygen, Chloride and Chemical Oxygen Demand in the water column of the Muvattupuzha River during May 2006

Station position	p^H	Temperature (°C)	Dissolved Oxygen (mg/l)	Chloride (mg/l)	COD (mg/l)
S1	6.90	32.8	6.48	28.16	91.31
S2	6.92	32.7	6.65	38.20	74.27
S3	6.95	33.2	6.06	50.54	40.11
S4	6.95	32.5	5.75	56.48	49.81
S5	7.10	32.4	6.21	48.20	26.40
S6	7.15	32.3	6.23	30.20	30.85
S7	7.25	32.0	6.64	20.53	21.69
S8	7.30	31.8	6.56	20.55	23.42
S9	7.32	31.0	6.66	20.54	17.42
S10	7.35	30.8	7.03	20.68	27.92
S11	7.20	30.8	6.99	20.60	22.67
S12	7.15	30.0	6.35	18.80	29.62
S13	7.10	29.9	5.85	11.27	18.78
S14	6.97	29.8	6.15	11.12	17.71
S15	6.95	29.5	6.08	8.60	14.37
S16	6.85	29.0	5.94	8.42	15.03
S17	6.69	32.4	6.21	22.00	32.55
S18	6.80	32.6	6.16	21.00	37.41

Table A 3.1.6. Spatial variation of Sand, Silt, Clay and Organic Carbon in sediments of the Muvattupuzha River during July 2005

Station position	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Nature of Sediment
S1	45.88	47.97	6.15	2.36	Silty-sand
S2	44.04	50.04	5.92	2.55	Silty-sand
S3	36.54	56.91	6.55	5.11	Silty-sand
S4	30.05	62.25	7.70	6.21	Silty-sand
S5	27.15	65.64	7.21	5.51	Silty-sand
S6	23.00	71.05	5.95	5.03	Silty-sand
S7	28.75	66.49	4.76	4.74	Silty-sand
S8	41.82	53.93	4.25	3.32	Silty-sand
S9	62.55	33.90	3.55	2.78	Sandy-silt
S10	81.01	16.29	2.70	1.77	Sandy-silt
S11	84.33	12.92	2.75	1.53	Sandy-silt
S12	87.42	9.78	2.80	1.45	Sandy-silt
S13	92.45	4.90	2.65	1.36	Sandy-silt
S14	40.57	54.20	5.23	2.86	Silty-sand
S15	29.82	62.34	7.84	4.37	Silty-sand
S16	30.93	61.09	7.98	5.02	Silty-sand
S17	44.55	52.30	3.15	3.89	Silty-sand
S18	43.27	53.48	3.25	3.01	Silty-sand

Table A 3.1.7. Spatial variation of Sand, Silt, Clay and Organic Carbon in sediments of the Muvattupuzha River during September 2005

Station position	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Nature of Sediment
S1	47.35	46.40	6.25	2.99	Sandy-silt
S2	45.65	48.50	5.85	3.18	Sandy-silt
S3	39.15	54.00	6.85	6.15	Silty-sand
S4	33.41	58.71	7.88	7.92	Silty-sand
S5	28.42	63.77	7.81	7.02	Silty-sand
S6	24.95	68.74	6.31	6.24	Silty-sand
S7	24.45	70.35	5.20	4.95	Silty-sand
S8	45.15	50.40	4.45	4.32	Silty-sand
S9	63.42	32.83	3.75	3.83	Sandy-silt
S10	82.20	14.82	2.98	1.54	Sandy-silt
S11	84.95	12.10	2.95	1.56	Sandy-silt
S12	89.31	7.77	2.92	1.63	Sandy-silt
S13	93.55	3.65	2.80	1.66	Sandy-silt
S14	44.84	49.51	5.65	4.88	Silty-sand
S15	35.55	56.47	7.98	6.12	Silty-sand
S16	37.35	54.53	8.12	6.48	Silty-sand
S17	47.51	49.14	3.35	4.12	Silty-sand
S18	44.48	52.02	3.50	4.01	Silty-sand

Table A 3.1.8. Spatial variation of Sand, Silt, Clay and Organic Carbon in sediments of the Muvattupuzha River during November 2005

Station position	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Nature of Sediment
S1	44.85	49.57	5.58	1.86	Silty-sand
S2	43.35	50.76	5.89	2.04	Silty-sand
S3	35.41	58.47	6.12	4.37	Silty-sand
S4	30.05	63.60	6.35	4.67	Silty-sand
S5	26.88	67.37	5.75	4.18	Silty-sand
S6	22.95	71.78	5.27	3.49	Silty-sand
S7	20.15	75.70	4.15	3.14	Silty-sand
S8	40.25	56.08	3.67	3.01	Silty-sand
S9	60.15	36.71	3.14	2.22	Sandy-silt
S10	78.05	19.40	2.55	1.56	Sandy-silt
S11	82.55	14.95	2.50	0.89	Sandy-silt
S12	86.05	11.47	2.48	0.57	Sandy-silt
S13	90.75	6.80	2.45	0.60	Sandy-silt
S14	40.05	57.57	2.38	1.79	Silty-sand
S15	27.88	65.17	6.95	4.95	Silty-sand
S16	29.50	63.65	6.85	5.02	Silty-sand
S17	44.05	53.01	2.94	3.02	Silty-sand
S18	43.00	54.17	2.83	3.00	Silty-sand

Table A 3.1.9. Spatial variation of Sand, Silt, Clay and Organic Carbon in sediments of the Muvattupuzha River during January 2006

Station position	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Nature of Sediment
S1	34.56	60.52	4.92	2.00	Silty-sand
S2	30.46	64.72	4.82	2.19	Silty-sand
S3	28.92	66.14	4.94	3.90	Silty-sand
S4	25.16	68.85	5.99	5.82	Silty-sand
S5	24.58	71.84	3.58	4.34	Silty-sand
S6	19.37	75.48	5.15	3.96	Silty-sand
S7	15.44	81.48	3.08	2.25	Silty-sand
S8	19.47	77.43	3.10	3.16	Silty-sand
S9	40.55	57.23	2.22	2.38	Silty-sand
S10	68.47	29.68	1.85	2.04	Sandy-silt
S11	74.43	23.69	1.88	0.90	Sandy-silt
S12	77.28	21.15	1.57	0.58	Sandy-silt
S13	84.44	14.12	1.44	1.06	Sandy-silt
S14	38.54	59.09	2.37	1.88	Silty-sand
S15	55.92	39.24	4.84	6.64	Sandy-silt
S16	56.33	38.70	4.97	6.99	Sandy-silt
S17	27.97	69.16	2.87	3.01	Silty-sand
S18	26.58	70.54	2.88	2.81	Silty-sand

Table A 3.2.0. Spatial variation of Sand, Silt, Clay and Organic Carbon in sediments of the Muvattupuzha River during March 2006

Station position	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Nature of Sediment
S1	24.36	71.72	3.92	1.02	Silty-sand
S2	22.49	73.49	4.02	1.13	Silty-sand
S3	15.87	80.21	3.92	1.82	Silty-sand
S4	10.15	85.96	3.89	1.92	Silty-sand
S5	10.25	86.17	3.58	1.99	Silty-sand
S6	10.05	86.91	3.04	0.99	Silty-sand
S7	9.95	87.81	2.24	1.00	Silty-sand
S8	20.47	77.47	2.06	1.48	Silty-sand
S9	38.98	59.24	1.78	0.61	Silty-sand
S10	55.32	43.08	1.60	0.76	Sandy-silt
S11	60.53	37.91	1.56	0.64	Sandy-silt
S12	69.27	29.27	1.46	0.55	Sandy-silt
S13	75.61	23.07	1.32	0.45	Sandy-silt
S14	35.49	62.23	2.28	0.93	Silty-sand
S15	47.13	49.35	3.52	3.53	Silty-sand
S16	49.72	46.43	3.85	3.82	Sandy-silt
S17	24.82	73.30	1.88	1.37	Silty-sand
S18	23.66	74.55	1.79	1.23	Silty-sand

Table A 3.2.1. Spatial variation of Sand, Silt, Clay and Organic Carbon in sediments of the Muvattupuzha River during May 2006

Station position	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	Nature of Sediment
S1	25.55	69.31	5.14	0.88	Silty-sand
S2	24.44	69.96	5.60	0.99	Silty-sand
S3	17.34	76.81	5.85	0.92	Silty-sand
S4	14.41	79.51	6.08	0.86	Silty-sand
S5	14.16	81.50	4.34	0.63	Silty-sand
S6	14.17	82.00	3.83	0.55	Silty-sand
S7	13.85	82.90	3.25	0.45	Silty-sand
S8	21.56	75.12	3.32	0.63	Silty-sand
S9	39.95	57.53	2.52	0.89	Silty-sand
S10	59.37	38.23	2.40	0.90	Sandy-silt
S11	68.17	29.51	2.32	0.75	Sandy-silt
S12	79.41	18.44	2.15	0.45	Sandy-silt
S13	80.51	17.54	1.95	0.32	Sandy-silt
S14	38.85	58.70	2.45	0.82	Silty-sand
S15	51.75	42.26	5.99	1.52	Sandy-silt
S16	51.28	42.67	6.05	0.96	Sandy-silt
S17	25.94	71.11	2.95	0.54	Silty-sand
S18	24.48	72.63	2.89	0.59	Silty-sand

Table A4.1.0. Dissolved trace metal concentrations in water column of the Muvattupuzha River during July 2005

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	53.55	25.65	0.398	0.818	1.548	15.95	1.135	0.755	0.938
S2	45.95	26.25	0.557	0.825	1.557	18.13	1.145	0.756	0.945
S3	38.85	24.82	0.264	0.568	1.298	17.03	1.013	0.661	0.788
S4	40.88	26.06	0.288	0.465	1.345	15.83	0.965	0.619	0.815
S5	43.35	27.55	0.284	0.457	1.448	14.27	0.985	0.595	0.858
S6	45.95	30.95	0.286	0.488	1.857	15.12	0.968	0.628	0.658
S7	48.45	30.95	0.333	0.548	1.556	15.16	0.978	0.645	0.667
S8	45.98	30.78	0.332	0.515	1.356	16.56	0.945	0.744	0.685
S9	43.35	27.56	0.384	0.485	1.298	16.14	0.986	0.726	0.788
S10	40.88	26.96	0.291	0.686	1.365	15.88	0.965	0.676	0.825
S11	38.25	33.07	0.344	0.458	1.788	15.85	0.968	0.626	0.588
S12	40.88	32.45	0.301	0.485	1.235	17.47	0.868	0.616	0.625
S13	41.85	33.15	0.189	0.658	1.857	17.98	0.945	0.512	0.658
S14	53.55	32.58	0.145	0.527	1.246	18.14	1.065	0.524	0.755
S15	65.85	33.85	0.229	0.656	1.684	18.25	1.015	0.666	0.648
S16	68.88	29.67	0.222	0.828	1.665	15.46	1.013	0.567	0.826
S17	48.45	30.55	0.306	0.565	1.395	15.96	1.145	0.657	0.845
S18	45.85	31.85	0.286	0.675	1.538	16.55	1.175	0.721	0.928

Table A4.1.1. Dissolved trace metal concentrations in water column of the Muvattupuzha River during September 2005

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	57.9	26.55	0.487	0.787	1.384	18.78	1.063	0.666	0.748
S2	58.8	32.57	0.453	0.789	1.448	18.87	1.220	0.676	0.784
S3	48.8	31.97	0.393	0.536	1.585	16.08	0.965	0.714	0.586
S4	53.8	32.65	0.387	0.442	1.698	18.94	0.946	0.628	0.594
S5	69.7	32.09	0.394	0.434	1.564	16.62	0.965	0.615	0.625
S6	65.6	33.34	0.341	0.464	1.345	17.57	0.948	0.577	0.727
S7	61.5	29.22	0.313	0.521	1.378	18.84	0.958	0.521	0.615
S8	53.3	30.09	0.307	0.589	1.452	19.85	0.926	0.777	0.785
S9	43.1	31.37	0.298	0.468	1.656	17.89	0.966	0.719	0.895
S10	44.8	25.27	0.285	0.652	1.661	19.41	0.946	0.663	0.898
S11	34.9	25.86	0.231	0.535	1.384	18.08	0.948	0.682	0.748
S12	42.8	24.45	0.255	0.561	1.434	19.28	0.850	0.684	0.775
S13	32.8	25.67	0.199	0.625	1.507	18.76	0.926	0.585	0.815
S14	44.9	27.17	0.189	0.581	1.356	17.54	1.244	0.521	0.625
S15	39.0	30.48	0.204	0.623	1.230	18.61	0.995	0.673	0.665
S16	36.9	30.48	0.205	0.787	1.216	17.97	1.123	0.661	0.658
S17	57.4	30.38	0.257	0.537	1.531	17.54	1.122	0.663	0.828
S18	51.5	27.15	0.245	0.641	1.637	19.23	0.968	0.658	0.885

Table A4.1.2. Dissolved trace metal concentrations in water column of the Muvattupuzha River during November 2005

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	40.59	21.27	0.271	0.717	1.146	15.23	0.984	0.534	0.536
S2	42.53	25.77	0.264	0.734	0.975	15.10	1.037	0.521	0.382
S3	36.54	25.35	0.228	0.530	0.869	12.94	0.856	0.531	0.416
S4	37.56	25.86	0.253	0.418	0.885	13.79	0.885	0.496	0.428
S5	35.56	25.45	0.203	0.414	0.975	13.42	0.865	0.497	0.498
S6	37.56	26.45	0.250	0.364	0.936	12.55	0.858	0.513	0.429
S7	35.53	23.16	0.265	0.421	1.047	15.14	0.874	0.517	0.537
S8	35.53	23.86	0.280	0.428	1.078	12.86	0.887	0.554	0.549
S9	36.54	24.86	0.189	0.461	1.226	13.43	0.828	0.562	0.629
S10	35.53	20.78	0.203	0.552	1.223	14.11	0.838	0.541	0.627
S11	33.53	20.48	0.154	0.435	1.198	15.50	0.858	0.536	0.614
S12	36.54	20.36	0.116	0.461	0.998	14.16	0.726	0.602	0.512
S13	35.53	20.35	0.114	0.525	1.028	11.89	0.787	0.584	0.525
S14	36.54	21.47	0.195	0.501	1.087	12.57	1.057	0.579	0.557
S15	37.56	24.15	0.177	0.623	0.985	13.48	1.055	0.546	0.428
S16	38.56	24.18	0.150	0.627	0.845	14.20	0.954	0.575	0.434
S17	36.54	24.85	0.251	0.537	0.987	14.55	0.954	0.528	0.445
S18	37.55	21.48	0.214	0.541	1.056	15.76	0.886	0.548	0.519

Table A4.1.3. Dissolved trace metal concentrations in water column of the Muvattupuzha River during January 2006

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	40.16	23.87	0.351	0.690	1.095	14.58	0.975	0.688	0.618
S2	34.46	19.95	0.399	0.686	1.158	14.78	0.978	0.629	0.628
S3	29.14	19.66	0.333	0.520	1.036	16.66	0.865	0.619	0.596
S4	30.66	18.59	0.308	0.419	0.866	13.53	0.828	0.565	0.497
S5	32.55	19.53	0.349	0.416	0.985	14.79	0.837	0.548	0.525
S6	34.46	20.61	0.187	0.424	1.098	14.79	0.875	0.526	0.541
S7	36.34	23.18	0.192	0.482	0.898	14.83	0.839	0.523	0.415
S8	34.49	23.21	0.190	0.453	0.978	15.25	0.836	0.536	0.421
S9	32.57	20.42	0.186	0.427	1.197	15.78	0.838	0.523	0.526
S10	30.66	24.74	0.120	0.517	0.838	14.76	0.825	0.498	0.375
S11	28.69	24.34	0.116	0.416	0.937	15.51	0.827	0.480	0.438
S12	30.66	24.82	0.180	0.427	0.995	16.68	0.778	0.438	0.415
S13	31.39	24.43	0.188	0.578	0.818	14.55	0.825	0.556	0.486
S14	40.16	25.39	0.171	0.468	0.987	13.75	0.905	0.543	0.416
S15	49.39	22.23	0.165	0.577	0.878	15.89	0.863	0.414	0.521
S16	51.66	22.90	0.155	0.729	0.898	15.12	0.861	0.569	0.533
S17	36.34	23.86	0.173	0.497	1.078	14.77	0.973	0.561	0.432
S18	34.39	20.62	0.189	0.594	1.088	16.15	0.822	0.546	0.525

Table A4.1.4. Dissolved trace metal concentrations in water column of the Muvattupuzha River during March 2006

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	22.33	14.65	0.203	0.520	1.058	10.42	0.895	0.445	0.385
S2	21.32	17.97	0.193	0.526	0.985	9.70	0.887	0.455	0.354
S3	16.24	17.58	0.123	0.484	1.028	9.72	0.775	0.434	0.371
S4	17.26	17.96	0.126	0.418	0.728	7.89	0.745	0.479	0.265
S5	22.33	17.65	0.130	0.416	0.773	8.16	0.758	0.469	0.281
S6	29.44	18.38	0.109	0.425	0.814	8.38	0.745	0.488	0.296
S7	23.50	16.77	0.109	0.482	0.934	8.65	0.757	0.474	0.340
S8	24.51	16.55	0.179	0.453	1.061	9.45	0.728	0.529	0.422
S9	25.53	17.25	0.157	0.427	1.065	9.21	0.758	0.518	0.425
S10	26.54	13.85	0.143	0.437	0.975	8.61	0.745	0.388	0.354
S11	25.53	14.28	0.118	0.403	1.086	9.05	0.745	0.378	0.367
S12	24.51	13.45	0.115	0.427	1.061	9.73	0.678	0.425	0.386
S13	23.50	14.57	0.109	0.475	0.814	10.22	0.728	0.518	0.296
S14	25.53	14.96	0.104	0.464	0.866	10.37	0.826	0.514	0.315
S15	28.58	16.77	0.107	0.477	0.801	10.39	0.786	0.414	0.291
S16	27.55	16.76	0.110	0.526	1.028	8.82	0.776	0.452	0.372
S17	23.50	16.77	0.119	0.457	1.046	8.61	0.887	0.513	0.380
S18	26.24	14.95	0.114	0.485	1.148	9.42	0.745	0.529	0.417

Table A4.1.5. Dissolved trace metal concentrations in water column of the Muvattupuzha River during May 2006

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	19.29	16.91	0.231	0.494	1.065	9.47	0.794	0.449	0.366
S2	25.38	13.57	0.208	0.517	0.948	10.27	0.785	0.446	0.345
S3	28.42	14.00	0.240	0.455	0.986	9.57	0.762	0.438	0.356
S4	24.51	13.18	0.209	0.397	0.685	10.26	0.764	0.429	0.254
S5	23.50	16.43	0.132	0.395	0.758	9.97	0.688	0.475	0.276
S6	22.48	14.65	0.126	0.414	0.787	9.28	0.723	0.424	0.284
S7	21.47	16.43	0.145	0.458	0.897	9.85	0.635	0.433	0.326
S8	23.50	16.43	0.173	0.431	1.045	9.59	0.644	0.445	0.405
S9	25.53	14.36	0.174	0.405	1.066	9.94	0.684	0.523	0.408
S10	26.54	17.61	0.124	0.415	0.936	9.96	0.687	0.475	0.340
S11	28.59	17.23	0.119	0.383	0.968	8.56	0.623	0.486	0.352
S12	22.63	17.60	0.141	0.415	1.019	10.29	0.627	0.493	0.370
S13	25.68	17.30	0.110	0.451	0.787	8.77	0.675	0.488	0.284
S14	21.32	18.01	0.115	0.441	0.894	9.39	0.767	0.516	0.325
S15	23.05	16.44	0.122	0.453	0.765	9.97	0.766	0.489	0.278
S16	23.05	16.22	0.123	0.500	0.986	10.58	0.693	0.425	0.357
S17	22.48	14.28	0.143	0.435	1.038	9.28	0.892	0.496	0.365
S18	21.47	14.66	0.129	0.468	1.087	10.18	0.843	0.523	0.468

Table A4.1.6. Enrichment ratio (ER) of dissolved trace metals of the Muvattupuzha River with respect to global background value during July 2005

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	0.97	4.28	1.99	2.727	1.55	1.60	56.75	1.511	4.690
S2	0.84	4.38	2.79	2.750	1.56	1.81	57.25	1.512	4.725
S3	0.71	4.14	1.32	1.893	1.30	1.70	50.63	1.321	3.938
S4	0.74	4.34	1.44	1.550	1.34	1.58	48.25	1.238	4.075
S5	0.79	4.59	1.42	1.523	1.45	1.43	49.25	1.190	4.288
S6	0.84	5.16	1.43	1.627	1.86	1.51	48.38	1.256	3.290
S7	0.88	5.16	1.66	1.827	1.56	1.52	48.88	1.290	3.335
S8	0.84	5.13	1.66	1.717	1.36	1.66	47.25	1.487	3.425
S9	0.79	4.59	1.92	1.617	1.30	1.61	49.28	1.452	3.938
S10	0.74	4.49	1.45	2.287	1.37	1.59	48.25	1.351	4.125
S11	0.70	5.51	1.72	1.527	1.79	1.59	48.38	1.252	2.940
S12	0.74	5.41	1.50	1.617	1.24	1.75	43.38	1.232	3.125
S13	0.76	5.53	0.94	2.193	1.86	1.80	47.25	1.024	3.290
S14	0.97	5.43	0.73	1.757	1.25	1.81	53.25	1.047	3.775
S15	1.20	5.64	1.14	2.187	1.68	1.83	50.75	1.332	3.238
S16	1.25	4.95	1.11	2.760	1.67	1.55	50.63	1.135	4.130
S17	0.88	5.09	1.53	1.883	1.40	1.60	57.25	1.314	4.225
S18	0.83	5.31	1.43	2.250	1.54	1.65	58.75	1.441	4.638
Average	**0.86**	**4.95**	**1.51**	**1.983**	**1.50**	**1.64**	**50.77**	**1.299**	**3.844**

Table A4.1.7. Enrichment ratio (ER) of dissolved trace metals of the Muvattupuzha River with respect to global background value during September 2005

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	1.05	4.43	2.44	2.624	1.38	1.88	53.17	1.331	3.741
S2	1.07	5.43	2.26	2.629	1.45	1.89	61.01	1.352	3.919
S3	0.89	5.33	1.96	1.785	1.59	1.61	48.27	1.428	2.930
S4	0.98	5.44	1.93	1.473	1.70	1.89	47.29	1.256	2.969
S5	1.27	5.35	1.97	1.447	1.56	1.66	48.27	1.231	3.126
S6	1.19	5.56	1.71	1.545	1.35	1.76	47.41	1.155	3.636
S7	1.12	4.87	1.56	1.735	1.38	1.88	47.90	1.041	3.076
S8	0.97	5.01	1.53	1.964	1.45	1.98	46.31	1.553	3.924
S9	0.78	5.23	1.49	1.558	1.66	1.79	48.29	1.437	4.475
S10	0.81	4.21	1.43	2.172	1.66	1.94	47.29	1.327	4.489
S11	0.63	4.31	1.16	1.784	1.38	1.81	47.41	1.363	3.741
S12	0.78	4.08	1.27	1.869	1.43	1.93	42.51	1.368	3.875
S13	0.60	4.28	0.99	2.084	1.51	1.88	46.31	1.169	4.073
S14	0.82	4.53	0.95	1.936	1.36	1.75	62.19	1.041	3.126
S15	0.71	5.08	1.02	2.077	1.23	1.86	49.74	1.347	3.325
S16	0.67	5.08	1.03	2.622	1.22	1.80	56.13	1.322	3.288
S17	1.04	5.06	1.28	1.789	1.53	1.75	56.11	1.327	4.138
S18	0.94	4.52	1.23	2.138	1.64	1.92	48.41	1.316	4.425
Average	**0.91**	**4.88**	**1.51**	**1.957**	**1.47**	**1.83**	**50.22**	**1.298**	**3.682**

Table A4.1.8. Enrichment ratio (ER) of dissolved trace metals of the Muvattupuzha River with respect to global background value during November 2005

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	0.74	3.55	1.36	2.390	1.15	1.52	49.19	1.067	2.681
S2	0.77	4.30	1.32	2.446	0.97	1.51	51.85	1.042	1.911
S3	0.66	4.22	1.14	1.765	0.87	1.29	42.80	1.062	2.081
S4	0.68	4.31	1.26	1.392	0.89	1.38	44.23	0.991	2.139
S5	0.65	4.24	1.01	1.381	0.98	1.34	43.25	0.995	2.488
S6	0.68	4.41	1.25	1.212	0.94	1.25	42.88	1.027	2.144
S7	0.65	3.86	1.33	1.402	1.05	1.51	43.71	1.033	2.685
S8	0.65	3.98	1.40	1.428	1.08	1.29	44.36	1.107	2.746
S9	0.66	4.14	0.94	1.536	1.23	1.34	41.41	1.125	3.144
S10	0.65	3.46	1.01	1.839	1.22	1.41	41.92	1.083	3.135
S11	0.61	3.41	0.77	1.450	1.20	1.55	42.88	1.073	3.071
S12	0.66	3.39	0.58	1.536	1.00	1.42	36.31	1.204	2.559
S13	0.65	3.39	0.57	1.750	1.03	1.19	39.36	1.168	2.625
S14	0.66	3.58	0.98	1.669	1.09	1.26	52.86	1.158	2.787
S15	0.68	4.03	0.89	2.077	0.99	1.35	52.75	1.092	2.139
S16	0.70	4.03	0.75	2.089	0.85	1.42	47.71	1.150	2.168
S17	0.66	4.14	1.25	1.789	0.99	1.45	47.69	1.055	2.226
S18	0.68	3.58	1.07	1.804	1.06	1.58	44.29	1.097	2.594
Average	**0.67**	**3.89**	**1.05**	**1.720**	**1.03**	**1.39**	**44.97**	**1.085**	**2.518**

Table A4.1.9. Enrichment ratio (ER) of dissolved trace metals of the Muvattupuzha River with respect to global background value during January 2006

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	0.73	3.98	1.75	2.299	1.10	1.46	48.75	1.376	3.090
S2	0.63	3.32	1.99	2.287	1.16	1.48	48.90	1.259	3.141
S3	0.53	3.28	1.67	1.733	1.04	1.67	43.25	1.238	2.979
S4	0.56	3.10	1.54	1.397	0.87	1.35	41.40	1.129	2.483
S5	0.59	3.26	1.74	1.387	0.98	1.48	41.86	1.097	2.625
S6	0.63	3.44	0.93	1.415	1.10	1.48	43.75	1.051	2.703
S7	0.66	3.86	0.96	1.607	0.90	1.48	41.94	1.046	2.074
S8	0.63	3.87	0.95	1.511	0.98	1.52	41.80	1.071	2.103
S9	0.59	3.40	0.93	1.423	1.20	1.58	41.88	1.046	2.631
S10	0.56	4.12	0.60	1.723	0.84	1.48	41.25	0.997	1.877
S11	0.52	4.06	0.58	1.387	0.94	1.55	41.35	0.959	2.188
S12	0.56	4.14	0.90	1.423	1.00	1.67	38.90	0.876	2.074
S13	0.57	4.07	0.94	1.927	0.82	1.46	41.25	1.112	2.429
S14	0.73	4.23	0.85	1.559	0.99	1.37	45.26	1.087	2.079
S15	0.90	3.71	0.83	1.924	0.88	1.59	43.14	0.828	2.604
S16	0.94	3.82	0.77	2.429	0.90	1.51	43.03	1.137	2.664
S17	0.66	3.98	0.86	1.657	1.08	1.48	48.66	1.122	2.159
S18	0.63	3.44	0.95	1.980	1.09	1.61	41.12	1.092	2.625
Average	**0.64**	**3.73**	**1.10**	**1.726**	**0.99**	**1.51**	**43.19**	**1.085**	**2.474**

Table A4.2.0. Enrichment ratio (ER) of dissolved trace metals of the Muvattupuzha River with respect to global background value during March 2006

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	0.41	2.44	1.02	1.733	1.06	1.04	44.75	0.891	1.925
S2	0.39	2.99	0.96	1.753	0.98	0.97	44.33	0.909	1.772
S3	0.30	2.93	0.62	1.613	1.03	0.97	38.75	0.868	1.856
S4	0.31	2.99	0.63	1.394	0.73	0.79	37.25	0.958	1.323
S5	0.41	2.94	0.65	1.387	0.77	0.82	37.92	0.938	1.406
S6	0.54	3.06	0.55	1.418	0.81	0.84	37.25	0.976	1.481
S7	0.43	2.80	0.55	1.607	0.93	0.86	37.84	0.948	1.699
S8	0.45	2.76	0.90	1.511	1.06	0.95	36.38	1.058	2.111
S9	0.46	2.88	0.79	1.423	1.07	0.92	37.92	1.037	2.126
S10	0.48	2.31	0.71	1.456	0.97	0.86	37.25	0.777	1.772
S11	0.46	2.38	0.59	1.343	1.09	0.90	37.25	0.756	1.834
S12	0.45	2.24	0.58	1.423	1.06	0.97	33.88	0.851	1.929
S13	0.43	2.43	0.55	1.583	0.81	1.02	36.38	1.036	1.481
S14	0.46	2.49	0.52	1.546	0.87	1.04	41.30	1.028	1.575
S15	0.52	2.79	0.53	1.591	0.80	1.04	39.28	0.828	1.457
S16	0.50	2.79	0.55	1.755	1.03	0.88	38.81	0.904	1.859
S17	0.43	2.79	0.60	1.524	1.05	0.86	44.33	1.026	1.901
S18	0.48	2.49	0.57	1.617	1.15	0.94	37.25	1.058	2.087
Average	**0.44**	**2.70**	**0.66**	**1.538**	**0.96**	**0.93**	**38.78**	**0.936**	**1.755**

Table A4.2.1. Enrichment ratio (ER) of dissolved trace metals of the Muvattupuzha River with respect to global background value during May 2006

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	0.35	2.82	1.16	1.646	1.07	0.95	39.71	0.898	1.830
S2	0.46	2.26	1.04	1.723	0.95	1.03	39.26	0.892	1.725
S3	0.52	2.33	1.20	1.517	0.99	0.96	38.11	0.875	1.782
S4	0.45	2.20	1.04	1.324	0.69	1.03	38.21	0.858	1.270
S5	0.43	2.74	0.66	1.317	0.76	1.00	34.40	0.951	1.380
S6	0.41	2.44	0.63	1.381	0.79	0.93	36.13	0.849	1.421
S7	0.39	2.74	0.72	1.527	0.90	0.99	31.74	0.866	1.631
S8	0.43	2.74	0.86	1.435	1.05	0.96	32.20	0.890	2.026
S9	0.46	2.39	0.87	1.352	1.07	0.99	34.20	1.046	2.041
S10	0.48	2.93	0.62	1.383	0.94	1.00	34.36	0.951	1.701
S11	0.52	2.87	0.60	1.276	0.97	0.86	31.13	0.972	1.760
S12	0.41	2.93	0.71	1.385	1.02	1.03	31.36	0.985	1.852
S13	0.47	2.88	0.55	1.504	0.79	0.88	33.75	0.977	1.421
S14	0.39	3.00	0.57	1.469	0.89	0.94	38.37	1.031	1.625
S15	0.42	2.74	0.61	1.511	0.76	1.00	38.29	0.978	1.390
S16	0.42	2.70	0.62	1.667	0.99	1.06	34.63	0.851	1.784
S17	0.41	2.38	0.71	1.451	1.04	0.93	44.62	0.992	1.825
S18	0.39	2.44	0.64	1.558	1.09	1.02	42.15	1.046	2.340
Average	**0.43**	**2.64**	**0.77**	**1.468**	**0.93**	**0.97**	**36.26**	**0.939**	**1.711**

Table A4.2.2. Particulate trace metal concentrations in water column of the Muvattupuzha River during July 2005

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	281.77	120.68	0.485	1.255	1.416	36.85	0.878	0.974	2.685
S2	268.17	114.88	0.804	1.485	1.325	35.06	0.865	0.975	2.576
S3	208.73	100.98	0.605	1.222	1.288	37.02	0.758	0.875	2.258
S4	192.12	105.88	0.505	1.157	1.148	30.07	0.765	0.886	2.289
S5	261.56	112.14	0.506	0.983	1.238	31.08	0.758	0.788	2.456
S6	244.62	124.75	0.607	0.898	1.578	32.87	0.748	0.885	1.885
S7	227.08	125.95	0.456	0.986	1.323	32.95	0.757	0.857	1.865
S8	264.04	125.24	0.405	0.977	1.153	36.01	0.728	0.985	1.875
S9	311.39	112.13	0.446	0.873	1.103	35.08	0.758	0.935	2.256
S10	334.37	109.68	0.305	1.235	1.125	32.80	0.745	0.895	2.358
S11	297.19	134.58	0.348	0.884	1.518	34.47	0.748	0.816	1.687
S12	331.09	149.25	0.306	0.873	1.048	37.06	0.675	0.816	1.756
S13	429.96	142.86	0.208	1.184	1.578	38.92	0.738	0.678	1.885
S14	397.61	145.87	0.205	0.986	1.058	39.44	0.825	0.667	2.156
S15	421.90	137.58	0.255	1.181	1.435	39.58	0.766	0.882	1.855
S16	474.67	147.97	0.287	1.490	1.415	33.61	0.746	0.778	2.367
S17	248.82	124.45	0.407	1.217	1.186	32.82	0.765	0.857	1.475
S18	228.18	128.98	0.408	1.225	1.307	35.88	0.745	0.928	2.658

Table A4.2.3. Particulate trace metal concentrations in water column of the Muvattupuzha River during September 2005

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	305.16	107.48	0.905	1.298	1.328	41.69	0.851	0.865	2.324
S2	327.68	131.88	0.806	1.351	1.368	38.81	0.859	0.885	2.429
S3	291.25	146.27	0.625	0.887	1.578	38.87	0.759	0.955	1.738
S4	324.47	140.28	0.525	0.829	1.625	31.57	0.724	0.815	1.809
S5	421.36	142.96	0.504	0.726	1.478	32.63	0.739	0.825	1.942
S6	389.66	134.88	0.625	0.765	1.275	33.51	0.726	0.775	2.221
S7	413.46	145.56	0.406	0.959	1.323	34.60	0.733	0.687	1.911
S8	465.18	121.96	0.408	0.972	1.379	37.81	0.719	0.985	2.438
S9	276.13	126.36	0.406	0.781	1.565	36.83	0.739	0.935	2.766
S10	262.81	118.27	0.305	1.175	1.569	34.45	0.724	0.875	2.653
S11	204.56	112.58	0.305	0.983	1.328	36.18	0.726	0.886	2.326
S12	188.28	118.96	0.315	0.925	1.355	38.91	0.651	0.876	2.358
S13	256.33	108.76	0.208	1.031	1.424	40.86	0.709	0.758	2.530
S14	239.73	112.90	0.225	0.988	1.282	41.48	0.799	0.687	1.942
S15	222.54	122.26	0.208	1.028	1.263	41.55	0.761	0.862	1.921
S16	258.76	123.45	0.225	1.298	1.249	35.29	0.759	0.885	1.931
S17	243.84	122.75	0.385	1.189	1.447	34.46	0.859	0.875	1.519
S18	223.62	109.87	0.428	1.158	1.547	37.67	0.761	0.868	2.738

Table A4.2.4. Particulate trace metal concentrations in water column of the Muvattupuzha River during November 2005

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	219.55	95.35	0.605	1.325	1.088	29.85	0.695	0.718	1.582
S2	217.95	93.29	0.608	1.257	0.958	31.35	0.797	0.728	1.427
S3	177.42	114.37	0.505	0.990	0.825	25.56	0.628	0.688	1.218
S4	163.35	126.87	0.504	0.877	0.841	31.47	0.615	0.648	1.262
S5	222.33	121.45	0.505	0.766	0.926	26.42	0.627	0.657	1.468
S6	207.93	123.98	0.405	0.777	0.895	27.94	0.616	0.665	1.265
S7	193.18	116.95	0.408	0.778	0.995	29.95	0.623	0.685	1.584
S8	224.43	125.77	0.306	0.792	1.024	31.56	0.602	0.718	1.620
S9	264.68	102.58	0.208	0.875	1.165	33.85	0.628	0.756	1.855
S10	284.25	98.65	0.206	1.021	1.162	33.56	0.615	0.715	1.847
S11	252.65	95.85	0.165	0.885	1.138	28.75	0.616	0.714	1.812
S12	281.43	93.98	0.175	0.852	0.948	30.65	0.553	0.795	1.556
S13	265.47	95.37	0.155	0.971	0.976	29.82	0.602	0.758	1.547
S14	237.97	106.04	0.205	0.986	1.033	27.88	0.808	0.765	1.644
S15	258.65	107.06	0.208	1.053	0.936	33.64	0.647	0.748	1.267
S16	263.47	106.45	0.225	1.159	0.832	28.57	0.730	0.786	1.279
S17	211.47	105.78	0.287	1.183	0.937	27.88	0.729	0.697	1.313
S18	193.95	109.68	0.257	1.101	1.034	30.58	0.629	0.715	1.530

Table A4.2.5. Particulate trace metal concentrations in water column of the Muvattupuzha River during January 2006

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	254.09	115.52	0.705	1.248	1.081	27.15	0.687	0.795	1.773
S2	272.88	128.13	0.708	1.132	1.143	28.38	0.724	0.815	1.746
S3	242.54	122.67	0.606	0.958	1.026	30.63	0.598	0.788	1.494
S4	270.17	125.22	0.505	0.792	0.855	29.84	0.617	0.756	1.485
S5	254.85	118.12	0.505	0.686	0.972	27.95	0.604	0.748	1.578
S6	228.45	96.31	0.408	0.726	1.084	33.77	0.599	0.718	1.216
S7	248.35	94.22	0.308	0.796	0.886	31.44	0.610	0.688	1.228
S8	252.93	127.03	0.208	0.778	0.965	31.49	0.619	0.718	1.265
S9	210.76	103.60	0.225	0.724	1.181	25.57	0.578	0.675	1.468
S10	209.25	99.64	0.208	0.853	0.827	26.43	0.585	0.648	1.318
S11	170.37	96.81	0.156	0.686	0.925	29.36	0.599	0.618	1.086
S12	156.86	94.92	0.228	0.742	0.982	31.52	0.507	0.576	1.178
S13	213.43	96.32	0.198	0.954	0.808	33.76	0.549	0.758	1.246
S14	199.68	107.10	0.228	0.782	0.974	33.46	0.738	0.715	1.478
S15	185.45	108.13	0.256	0.953	0.866	33.66	0.706	0.545	1.214
S16	215.46	107.52	0.235	1.252	0.886	28.58	0.666	0.735	1.525
S17	203.35	106.84	0.328	0.924	1.064	27.97	0.666	0.738	1.555
S18	186.15	110.78	0.355	0.985	1.074	30.56	0.618	0.745	1.786

Table A4.2.6. Particulate trace metal concentrations in water column of the Muvattupuzha River during March 2006

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	172.04	71.27	0.454	0.973	1.044	22.39	0.613	0.614	0.927
S2	184.76	87.48	0.436	0.984	0.972	23.55	0.617	0.613	0.934
S3	164.22	97.45	0.389	0.853	1.014	19.17	0.531	0.612	0.778
S4	182.93	92.86	0.378	0.726	0.718	23.65	0.513	0.658	0.885
S5	172.55	94.88	0.399	0.719	0.763	19.85	0.525	0.645	0.847
S6	154.68	89.47	0.324	0.725	0.804	20.95	0.515	0.657	0.656
S7	168.12	96.18	0.306	0.816	0.922	22.46	0.518	0.625	0.659
S8	171.26	80.85	0.230	0.764	1.047	23.67	0.498	0.685	0.677
S9	142.70	83.85	0.176	0.717	1.052	25.39	0.519	0.684	0.778
S10	141.67	78.45	0.155	0.734	0.962	25.17	0.512	0.518	0.815
S11	115.32	74.67	0.124	0.677	1.072	21.56	0.513	0.525	0.585
S12	106.18	65.67	0.131	0.737	1.047	22.99	0.464	0.548	0.618
S13	144.51	68.88	0.136	0.798	0.804	22.36	0.498	0.685	0.655
S14	135.15	72.85	0.154	0.779	0.855	20.96	0.566	0.678	0.746
S15	125.57	81.88	0.156	0.872	0.791	25.26	0.538	0.586	0.647
S16	145.88	81.87	0.169	0.884	1.014	21.45	0.532	0.596	0.816
S17	137.46	81.45	0.215	0.788	1.032	20.95	0.607	0.677	0.835
S18	126.07	72.88	0.193	0.848	1.133	22.95	0.510	0.685	0.916

Table A4.2.7. Particulate trace metal concentrations in water column of the Muvattupuzha River during May 2006

Station position	Fe (ppb)	Mn (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Cr (ppb)	Pb (ppb)
S1	144.54	82.37	0.399	0.877	1.028	21.05	0.538	0.585	0.696
S2	112.51	78.48	0.386	0.866	0.916	22.83	0.525	0.576	0.794
S3	123.55	68.95	0.294	0.768	0.943	21.28	0.497	0.578	0.835
S4	140.98	72.38	0.325	0.674	0.655	22.68	0.498	0.556	0.597
S5	131.85	76.45	0.303	0.665	0.725	22.07	0.449	0.628	0.625
S6	122.46	85.97	0.284	0.688	0.752	20.63	0.479	0.587	0.668
S7	142.32	85.96	0.271	0.767	0.857	21.89	0.514	0.585	0.769
S8	134.18	85.55	0.266	0.727	0.998	21.14	0.426	0.588	0.945
S9	122.99	76.56	0.227	0.781	1.019	22.09	0.446	0.678	0.952
S10	167.84	74.88	0.182	0.697	0.894	22.20	0.448	0.628	0.794
S11	180.23	91.85	0.189	0.743	0.926	18.91	0.516	0.655	0.928
S12	160.19	98.37	0.195	0.698	0.974	22.29	0.519	0.648	0.864
S13	178.46	97.55	0.184	0.758	0.752	19.55	0.448	0.645	0.669
S14	231.75	98.65	0.131	0.746	0.854	20.68	0.557	0.668	0.672
S15	214.31	93.95	0.163	0.762	0.731	22.16	0.499	0.646	0.665
S16	127.40	98.98	0.172	0.847	0.945	23.35	0.452	0.575	0.835
S17	155.85	84.85	0.256	0.757	0.995	20.63	0.582	0.655	0.856
S18	151.87	88.45	0.239	0.785	1.038	22.63	0.557	0.678	0.935

Table A4.2.8. Partition coefficient values of trace metals in water column of the Muvattupuzha River during July 2005

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	5.26	4.19	1.22	1.53	0.915	2.31	0.77	1.29	2.86
S2	5.84	5.02	2.08	1.80	0.851	1.93	0.76	1.29	2.73
S3	5.37	5.89	2.06	2.15	0.992	2.17	0.75	1.32	2.87
S4	4.70	5.38	1.55	2.49	0.853	1.90	0.79	1.43	2.81
S5	6.03	5.19	1.67	2.15	0.855	2.18	0.77	1.32	2.86
S6	5.32	4.36	2.14	1.84	0.850	2.17	0.77	1.41	2.86
S7	4.69	4.70	1.68	1.80	0.850	2.17	0.77	1.33	2.80
S8	5.74	3.96	1.52	1.90	0.850	2.17	0.77	1.32	2.74
S9	7.18	4.58	1.96	1.80	0.850	2.17	0.77	1.29	2.86
S10	8.18	4.39	1.68	1.80	0.824	2.06	0.77	1.32	2.86
S11	7.77	3.40	1.84	1.93	0.849	2.17	0.77	1.30	2.87
S12	8.10	3.67	1.57	1.80	0.848	2.12	0.78	1.32	2.81
S13	10.27	3.28	1.13	1.80	0.850	2.16	0.78	1.32	2.86
S14	7.43	3.47	1.56	1.87	0.849	2.17	0.77	1.27	2.86
S15	6.41	3.61	1.57	1.80	0.852	2.17	0.75	1.32	2.86
S16	6.89	4.16	1.67	1.80	0.850	2.17	0.74	1.37	2.87
S17	5.14	4.02	1.59	2.15	0.850	2.06	0.67	1.30	1.75
S18	4.98	3.45	1.71	1.81	0.850	2.17	0.63	1.29	2.87
Average	**6.41**	**4.26**	**1.68**	**1.90**	**0.861**	**2.14**	**0.76**	**1.32**	**2.78**

Table A4.2.9. Partition coefficient values of trace metals in water column of the Muvattupuzha River during September 2005

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	5.27	4.19	1.86	1.65	0.959	2.22	0.80	1.30	3.11
S2	5.58	5.02	1.78	1.71	0.945	2.06	0.70	1.31	3.10
S3	5.97	5.89	1.59	1.66	0.996	2.42	0.79	1.34	2.97
S4	6.03	5.38	1.36	1.88	0.957	1.67	0.77	1.30	3.05
S5	6.05	5.19	1.28	1.67	0.945	1.96	0.77	1.34	3.11
S6	5.94	4.36	1.83	1.65	0.948	1.91	0.77	1.34	3.05
S7	6.72	4.70	1.30	1.84	0.960	1.84	0.77	1.32	3.11
S8	8.73	3.96	1.33	1.65	0.950	1.90	0.78	1.27	3.11
S9	6.41	4.58	1.36	1.67	0.945	2.06	0.77	1.30	3.09
S10	5.87	4.39	1.07	1.80	0.945	1.78	0.77	1.32	2.96
S11	5.87	3.40	1.32	1.84	0.959	2.00	0.77	1.30	3.11
S12	4.40	3.67	1.24	1.65	0.945	2.02	0.77	1.28	3.04
S13	7.81	3.28	1.05	1.65	0.945	2.18	0.77	1.30	3.11
S14	5.35	3.47	1.19	1.70	0.945	2.37	0.64	1.32	3.11
S15	5.71	3.61	1.02	1.65	1.026	2.23	0.77	1.28	2.89
S16	7.01	4.16	1.10	1.65	1.027	1.96	0.68	1.34	2.94
S17	4.25	4.02	1.50	2.21	0.945	1.96	0.77	1.32	1.84
S18	4.34	3.45	1.74	1.81	0.945	1.96	0.79	1.32	3.09
Average	**5.96**	**4.26**	**1.38**	**1.74**	**0.960**	**2.03**	**0.76**	**1.31**	**2.99**

Table A4.3.0. Partition coefficient values of trace metals in water column of the Muvattupuzha River during November 2005

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	5.41	4.48	2.23	1.85	0.950	1.96	0.71	1.35	2.95
S2	5.13	3.62	2.31	1.71	0.983	2.08	0.77	1.40	3.73
S3	4.86	4.51	2.21	1.87	0.950	1.98	0.73	1.30	2.93
S4	4.35	4.91	1.99	2.10	0.950	2.28	0.69	1.31	2.95
S5	6.25	4.77	2.49	1.85	0.950	1.97	0.73	1.32	2.95
S6	5.54	4.69	1.62	2.14	0.956	2.23	0.72	1.30	2.95
S7	5.44	5.05	1.54	1.85	0.950	1.98	0.71	1.33	2.95
S8	6.32	5.27	1.09	1.85	0.950	2.45	0.68	1.30	2.95
S9	7.24	4.13	1.10	1.90	0.950	2.52	0.76	1.34	2.95
S10	8.00	4.75	1.02	1.85	0.950	2.38	0.73	1.32	2.94
S11	7.54	4.68	1.07	2.03	0.950	1.85	0.72	1.33	2.95
S12	7.70	4.62	1.51	1.85	0.950	2.16	0.76	1.32	3.04
S13	7.47	4.69	1.36	1.85	0.950	2.51	0.76	1.30	2.95
S14	6.51	4.94	1.05	1.97	0.950	2.22	0.76	1.32	2.95
S15	6.89	4.43	1.17	1.69	0.950	2.50	0.61	1.37	2.96
S16	6.83	4.40	1.50	1.85	0.984	2.01	0.76	1.37	2.95
S17	5.79	4.26	1.14	2.20	0.950	1.92	0.76	1.32	2.95
S18	5.17	5.11	1.20	2.03	0.979	1.94	0.71	1.30	2.95
Average	**6.25**	**4.63**	**1.57**	**1.91**	**0.956**	**2.16**	**0.73**	**1.33**	**3.00**

Table A4.3.1. Partition coefficient values of trace metals in water column of the Muvattupuzha River during January 2006

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	6.33	4.84	2.01	1.81	0.987	1.86	0.70	1.16	2.87
S2	7.92	6.42	1.78	1.65	0.987	1.92	0.74	1.29	2.78
S3	8.32	6.24	1.82	1.84	0.990	1.84	0.69	1.27	2.51
S4	8.81	6.74	1.64	1.89	0.987	2.20	0.75	1.34	2.99
S5	7.83	6.05	1.45	1.65	0.987	1.89	0.72	1.36	3.01
S6	6.63	4.67	2.19	1.71	0.987	2.28	0.68	1.37	2.25
S7	6.83	4.06	1.60	1.65	0.987	2.12	0.73	1.32	2.96
S8	7.33	5.47	1.10	1.72	0.987	2.07	0.74	1.34	3.01
S9	6.47	5.07	1.21	1.70	0.987	1.62	0.69	1.29	2.79
S10	6.82	4.03	1.73	1.65	0.987	1.79	0.71	1.30	3.51
S11	5.94	3.98	1.34	1.65	0.987	1.89	0.72	1.29	2.48
S12	5.12	3.82	1.27	1.74	0.987	1.89	0.65	1.32	2.84
S13	6.80	3.94	1.05	1.65	0.987	2.32	0.67	1.36	2.57
S14	4.97	4.22	1.33	1.67	0.987	2.43	0.82	1.32	3.55
S15	3.76	4.86	1.55	1.65	0.987	2.12	0.82	1.32	2.33
S16	4.17	4.69	1.52	1.72	0.987	1.89	0.77	1.29	2.86
S17	5.60	4.48	1.90	1.86	0.987	1.89	0.68	1.32	3.60
S18	5.41	5.37	1.87	1.66	0.987	1.89	0.75	1.36	3.40
Average	**6.39**	**4.94**	**1.61**	**1.71**	**0.987**	**2.00**	**0.72**	**1.31**	**2.91**

Table A4.3.2. Partition coefficient values of trace metals in water column of the Muvattupuzha River during March 2006

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	7.70	4.86	2.23	1.87	0.987	2.15	0.69	1.38	2.41
S2	8.67	4.87	2.26	1.87	0.987	2.43	0.70	1.35	2.63
S3	10.11	5.54	3.16	1.76	0.987	1.97	0.69	1.41	2.10
S4	10.60	5.17	3.00	1.74	0.987	3.00	0.69	1.37	3.35
S5	7.73	5.38	3.06	1.73	0.987	2.43	0.69	1.38	3.01
S6	5.25	4.87	2.97	1.70	0.987	2.50	0.69	1.35	2.22
S7	7.16	5.73	2.80	1.69	0.987	2.60	0.69	1.32	1.94
S8	6.99	4.89	1.28	1.69	0.987	2.50	0.69	1.29	1.60
S9	5.59	4.86	1.12	1.68	0.987	2.76	0.69	1.32	1.83
S10	5.34	5.66	1.08	1.68	0.987	2.92	0.69	1.33	2.30
S11	4.52	5.23	1.05	1.68	0.987	2.38	0.69	1.39	1.60
S12	4.33	4.88	1.14	1.73	0.987	2.36	0.69	1.29	1.60
S13	6.15	4.73	1.25	1.68	0.987	2.19	0.69	1.32	2.21
S14	5.29	4.87	1.48	1.68	0.987	2.02	0.69	1.32	2.37
S15	4.39	4.88	1.46	1.83	0.987	2.43	0.69	1.41	2.22
S16	5.30	4.88	1.54	1.68	0.987	2.43	0.69	1.32	2.20
S17	5.85	4.86	1.80	1.72	0.987	2.43	0.69	1.32	2.20
S18	4.80	4.88	1.69	1.75	0.987	2.44	0.69	1.29	2.20
Average	**6.43**	**5.06**	**1.91**	**1.73**	**0.987**	**2.44**	**0.69**	**1.34**	**2.22**

Table A4.3.3. Partition coefficient values of trace metals in water column of the Muvattupuzha River during May 2006

Station position	Fe	Mn	Co	Ni	Cu	Zn	Cd	Cr	Pb
S1	7.50	4.87	1.73	1.78	0.965	2.22	0.68	1.30	1.90
S2	4.43	5.78	1.86	1.67	0.967	2.22	0.67	1.29	2.30
S3	4.35	4.93	1.22	1.69	0.956	2.22	0.65	1.32	2.34
S4	5.75	5.49	1.56	1.70	0.956	2.21	0.65	1.30	2.35
S5	5.61	4.65	2.29	1.68	0.956	2.21	0.65	1.32	2.26
S6	5.45	5.87	2.25	1.66	0.956	2.22	0.66	1.38	2.35
S7	6.63	5.23	1.87	1.67	0.956	2.22	0.81	1.35	2.36
S8	5.71	5.21	1.54	1.69	0.955	2.20	0.66	1.32	2.33
S9	4.82	5.33	1.31	1.93	0.956	2.22	0.65	1.30	2.33
S10	6.32	4.25	1.47	1.68	0.956	2.23	0.65	1.32	2.33
S11	6.30	5.33	1.59	1.94	0.956	2.21	0.83	1.35	2.64
S12	7.08	5.59	1.38	1.68	0.956	2.17	0.83	1.32	2.33
S13	6.95	5.64	1.68	1.68	0.956	2.23	0.66	1.32	2.35
S14	10.87	5.48	1.14	1.69	0.956	2.20	0.73	1.30	2.07
S15	9.30	5.72	1.33	1.68	0.956	2.22	0.65	1.32	2.39
S16	5.53	6.10	1.40	1.69	0.959	2.21	0.65	1.35	2.34
S17	6.93	5.94	1.79	1.74	0.959	2.22	0.65	1.32	2.34
S18	7.08	6.03	1.86	1.68	0.955	2.22	0.66	1.30	2.00
Average	**6.48**	**5.41**	**1.63**	**1.72**	**0.957**	**2.22**	**0.69**	**1.32**	**2.30**

Table A4.3.4. Percentage of particulate trace metals in water column of the Muvattupuzha River during July 2005

Station position	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Cd (%)	Cr (%)	Pb (%)
S1	84.0	82.5	55.0	60.5	47.8	69.8	43.9	56.3	74.1
S2	85.4	81.4	59.1	64.3	46.0	65.9	45.5	56.3	73.2
S3	84.3	80.3	69.6	68.3	49.8	68.5	42.6	57.0	74.1
S4	82.5	80.2	63.7	71.3	46.0	65.5	44.4	58.9	73.7
S5	85.8	80.3	64.1	68.3	46.1	68.5	43.8	57.0	74.1
S6	84.2	80.1	68.0	64.8	45.9	68.5	43.4	58.5	74.1
S7	82.4	80.3	57.8	64.3	45.9	68.5	44.4	57.1	73.7
S8	85.2	80.3	54.9	65.5	45.9	68.5	42.7	57.0	73.2
S9	87.8	80.3	53.7	64.3	45.9	68.5	43.8	56.3	74.1
S10	89.1	80.3	51.2	64.3	45.2	67.4	43.5	57.0	74.1
S11	88.6	80.3	50.3	65.9	45.9	68.5	45.5	56.6	74.2
S12	89.0	82.1	50.4	64.3	45.9	68.0	42.1	57.0	73.8
S13	91.1	81.2	52.4	64.3	45.9	68.4	41.7	57.0	74.1
S14	88.1	81.7	58.5	65.2	45.9	68.5	45.1	56.0	74.1
S15	86.5	80.3	52.7	64.3	46.0	68.4	43.5	57.0	74.1
S16	87.3	83.3	56.3	64.3	45.9	68.5	42.0	57.8	74.1
S17	83.7	80.3	57.1	68.3	45.9	67.3	40.5	56.6	63.6
S18	83.3	80.2	58.8	64.5	45.9	68.4	38.4	56.3	74.1
Average	**86.0**	**80.8**	**57.4**	**65.4**	46.2	**68.1**	**43.1**	**57.0**	**73.4**

Table A4.3.5. Percentage of particulate trace metals in water column of the Muvattupuzha River during September 2005

Station position	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Cd (%)	Cr (%)	Pb (%)
S1	84.1	80.2	65.0	62.3	49.0	68.9	44.5	56.5	75.6
S2	84.8	80.2	64.0	63.1	48.6	67.3	41.3	56.7	75.6
S3	85.7	82.1	61.4	62.4	49.9	70.7	44.0	57.2	74.8
S4	85.8	81.1	57.6	65.2	48.9	62.5	43.4	56.5	75.3
S5	85.8	81.7	56.1	62.6	48.6	66.3	43.4	57.3	75.6
S6	85.6	80.2	64.7	62.3	48.7	65.6	43.4	57.3	75.3
S7	87.1	83.3	56.5	64.8	49.0	64.7	43.4	56.9	75.6
S8	89.7	80.2	57.1	62.3	48.7	65.6	43.7	55.9	75.7
S9	86.5	80.1	57.7	62.6	48.6	67.3	43.4	56.5	75.6
S10	85.4	82.4	51.7	64.3	48.6	64.0	43.4	56.9	74.7
S11	85.4	81.3	56.9	64.8	49.0	66.7	43.4	56.5	75.7
S12	81.5	83.0	55.3	62.3	48.6	66.9	43.4	56.2	75.3
S13	88.7	80.9	51.2	62.3	48.6	68.5	43.4	56.5	75.6
S14	84.2	80.6	54.3	63.0	48.6	70.3	39.1	56.9	75.6
S15	85.1	80.0	50.5	62.3	50.6	69.1	43.4	56.1	74.3
S16	87.5	80.2	52.3	62.3	50.7	66.3	40.4	57.3	74.6
S17	80.9	80.2	60.0	68.9	48.6	66.3	43.4	56.9	64.7
S18	81.3	80.2	63.5	64.4	48.6	66.2	44.0	56.9	75.6
Average	**85.3**	**81.0**	**57.5**	**63.4**	49.0	**66.8**	**43.0**	**56.7**	**74.7**

Table A4.3.6. Percentage of particulate trace metals in water column of the Muvattupuzha River during November 2005

Station position	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Cd (%)	Cr (%)	Pb (%)
S1	84.4	81.8	69.1	64.9	48.7	66.2	41.4	57.4	74.7
S2	83.7	78.4	69.8	63.2	49.6	67.5	43.4	58.3	78.9
S3	82.9	81.9	68.9	65.1	48.7	66.4	42.3	56.4	74.5
S4	81.3	83.1	66.6	67.8	48.7	69.5	41.0	56.7	74.7
S5	86.2	82.7	71.4	64.9	48.7	66.3	42.0	56.9	74.7
S6	84.7	82.4	61.8	68.1	48.9	69.0	41.8	56.4	74.7
S7	84.5	83.5	60.6	64.9	48.7	66.4	41.6	57.0	74.7
S8	86.3	84.1	52.3	64.9	48.7	71.1	40.4	56.5	74.7
S9	87.9	80.5	52.4	65.5	48.7	71.6	43.1	57.3	74.7
S10	88.9	82.6	50.4	64.9	48.7	70.4	42.3	56.9	74.7
S11	88.3	82.4	51.8	67.0	48.7	65.0	41.8	57.1	74.7
S12	88.5	82.2	60.2	64.9	48.7	68.4	43.2	56.9	75.2
S13	88.2	82.4	57.6	64.9	48.7	71.5	43.3	56.5	74.7
S14	86.7	83.2	51.2	66.3	48.7	68.9	43.3	56.9	74.7
S15	87.3	81.6	54.0	62.8	48.7	71.4	38.0	57.8	74.8
S16	87.2	81.5	60.0	64.9	49.6	66.8	43.3	57.8	74.7
S17	85.3	81.0	53.4	68.8	48.7	65.7	43.3	56.9	74.7
S18	83.8	83.6	54.5	67.0	49.5	66.0	41.5	56.6	74.7
Average	86.1	**82.1**	**59.2**	**65.6**	**48.9**	**68.3**	**42.1**	**57.0**	74.9

Table A4.3.7. Percentage of particulate trace metals in water column of the Muvattupuzha River during January 2006

Station position	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Cd (%)	Cr (%)	Pb (%)
S1	86.4	82.9	66.8	64.4	49.7	65.1	41.3	53.6	74.1
S2	88.8	86.5	64.0	62.3	49.7	65.8	42.5	56.4	73.5
S3	89.3	86.2	64.5	64.8	49.8	64.8	40.9	56.0	71.5
S4	89.8	87.1	62.2	65.4	49.7	68.8	42.7	57.2	74.9
S5	88.7	85.8	59.2	62.3	49.7	65.4	41.9	57.7	75.0
S6	86.9	82.4	68.6	63.1	49.7	69.5	40.6	57.7	69.2
S7	87.2	80.3	61.6	62.3	49.7	68.0	42.1	56.8	74.7
S8	88.0	84.6	52.3	63.2	49.7	67.4	42.6	57.3	75.0
S9	86.6	83.5	54.8	62.9	49.7	61.8	40.8	56.3	73.6
S10	87.2	80.1	63.4	62.3	49.7	64.2	41.5	56.5	77.8
S11	85.6	79.9	57.3	62.3	49.7	65.4	42.0	56.3	71.3
S12	83.6	79.3	55.9	63.5	49.7	65.4	39.5	56.8	74.0
S13	87.2	79.8	51.2	62.3	49.7	69.9	40.0	57.7	72.0
S14	83.3	80.8	57.2	62.6	49.7	70.9	44.9	56.8	78.0
S15	79.0	82.9	60.8	62.3	49.7	67.9	45.0	56.8	70.0
S16	80.7	82.4	60.3	63.2	49.7	65.4	43.6	56.4	74.1
S17	84.8	81.7	65.5	65.0	49.7	65.4	40.6	56.8	78.3
S18	84.4	84.3	65.2	62.4	49.7	65.4	42.9	57.7	77.3
Average	86.2	**82.8**	**60.6**	**63.1**	49.7	**66.6**	**42.0**	**56.7**	**74.1**

Table A4.3.8. Percentage of particulate trace metals in water column of the Muvattupuzha River during March 2006

Station position	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Cd (%)	Cr (%)	Pb (%)
S1	88.5	82.9	69.1	65.2	49.7	68.2	40.7	58.0	70.6
S2	89.7	83.0	69.3	65.2	49.7	70.8	41.0	57.4	72.5
S3	91.0	84.7	76.0	63.8	49.7	66.4	40.7	58.5	67.7
S4	91.4	83.8	75.0	63.4	49.7	75.0	40.8	57.9	77.0
S5	88.5	84.3	75.4	63.3	49.7	70.9	40.9	57.9	75.1
S6	84.0	83.0	74.8	63.0	49.7	71.4	40.9	57.4	68.9
S7	87.7	85.2	73.7	62.9	49.7	72.2	40.7	56.9	66.0
S8	87.5	83.0	56.1	62.8	49.7	71.5	40.7	56.4	61.6
S9	84.8	82.9	52.8	62.7	49.7	73.4	40.7	56.9	64.7
S10	84.2	85.0	51.9	62.7	49.7	74.5	40.7	57.2	69.7
S11	81.9	83.9	51.1	62.7	49.7	70.4	40.8	58.1	61.5
S12	81.2	83.0	53.2	63.3	49.7	70.3	40.7	56.3	61.5
S13	86.0	82.5	55.6	62.7	49.7	68.6	40.7	56.9	68.9
S14	84.1	83.0	59.7	62.7	49.7	66.9	40.7	56.9	70.3
S15	81.5	83.0	59.4	64.6	49.7	70.9	40.7	58.6	69.0
S16	84.1	83.0	60.6	62.7	49.7	70.9	40.7	56.9	68.7
S17	85.4	82.9	64.3	63.3	49.7	70.9	40.7	56.9	68.7
S18	82.8	83.0	62.8	63.6	49.7	70.9	40.7	56.4	68.7
Average	86.1	**83.5**	**63.4**	**63.4**	49.7	**70.8**	**40.7**	**57.3**	**68.4**

Table A4.3.9. Percentage of particulate trace metals in water column of the Muvattupuzha River during May 2006

Station position	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Cd (%)	Cr (%)	Pb (%)
S1	88.2	83.0	63.3	64.0	49.1	69.0	40.4	56.6	65.5
S2	81.6	85.3	65.0	62.6	49.1	69.0	40.1	56.4	69.7
S3	81.3	83.1	55.0	62.8	48.9	69.0	39.5	56.9	70.1
S4	85.2	84.6	60.9	62.9	48.9	68.8	39.5	56.5	70.1
S5	84.9	82.3	69.6	62.7	48.9	68.9	39.5	56.9	69.4
S6	84.5	85.4	69.3	62.4	48.9	69.0	39.9	58.0	70.2
S7	86.9	84.0	65.2	62.6	48.9	69.0	44.7	57.5	70.2
S8	85.1	83.9	60.6	62.8	48.9	68.8	39.8	56.9	70.0
S9	82.8	84.2	56.7	65.8	48.9	69.0	39.5	56.4	70.0
S10	86.3	81.0	59.5	62.7	48.9	69.0	39.5	56.9	70.0
S11	86.3	84.2	61.4	66.0	48.9	68.8	45.3	57.4	72.5
S12	87.6	84.8	58.0	62.7	48.9	68.4	45.3	56.8	70.0
S13	87.4	84.9	62.6	62.7	48.9	69.0	39.9	56.9	70.2
S14	91.6	84.6	53.3	62.9	48.9	68.8	42.1	56.4	67.4
S15	90.3	85.1	57.1	62.7	48.9	69.0	39.5	56.9	70.5
S16	84.7	85.9	58.3	62.9	48.9	68.8	39.5	57.5	70.1
S17	87.4	85.6	64.1	63.5	49.0	69.0	39.5	56.9	70.1
S18	87.6	85.8	65.0	62.7	48.9	69.0	39.8	56.4	66.6
Average	**86.5**	**84.3**	**61.4**	**63.2**	**48.9**	**68.9**	**40.7**	**56.9**	**69.6**

A5.1.0. Total trace metal concentrations and pollution load index (PLI) in sediments of the Muvattupuzha River during July 2005

Station position	Fe (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	PLI
S1	6209	42.70	2.70	4.28	7.17	14.56	0.18	40.77	3.34	0.16
S2	10815	82.84	5.16	8.17	10.87	31.19	0.28	42.44	4.62	0.26
S3	33115	19.55	7.71	12.98	12.74	47.39	0.33	44.02	8.47	0.32
S4	45199	133.12	9.15	14.16	13.64	50.16	0.38	44.64	11.68	0.46
S5	41487	151.84	9.34	11.58	14.55	55.09	0.38	42.62	10.80	0.45
S6	39985	396.19	9.80	9.06	14.85	59.47	0.40	37.76	10.02	0.49
S7	38699	408.83	9.76	8.78	15.00	62.77	0.41	36.26	9.47	0.49
S8	37518	391.26	10.31	81.13	15.08	59.28	0.42	40.74	10.89	0.64
S9	36581	361.15	12.67	42.32	17.56	58.20	0.43	41.81	11.24	0.61
S10	44332	288.87	8.72	19.41	12.58	38.04	0.44	38.85	12.97	0.50
S11	59565	84.28	6.23	16.36	10.09	27.47	0.35	31.40	12.84	0.38
S12	45807	127.65	5.99	12.50	8.69	24.81	0.30	29.40	12.66	0.35
S13	27916	149.36	5.26	8.95	7.97	21.12	0.30	24.84	8.51	0.30
S14	22315	157.43	7.32	13.17	7.62	35.77	0.32	25.56	7.94	0.33
S15	39624	163.45	8.80	19.75	15.44	49.18	0.33	26.96	10.63	0.44
S16	40856	162.68	8.90	21.61	23.25	51.33	0.34	26.03	16.78	0.50
S17	39011	300.83	9.31	25.32	13.39	60.02	0.41	39.39	9.96	0.52
S18	38952	281.99	9.91	24.88	14.00	61.83	0.42	39.48	9.51	0.53

Table A5.1.1. Total trace metal concentrations and pollution load index (PLI) in sediments of the Muvattupuzha River during September 2005

Station position	Fe (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	PLI
S1	32618	153.94	10.18	80.10	21.67	71.59	0.33	36.06	15.23	0.56
S2	38584	138.38	8.36	60.23	21.26	69.29	0.30	34.52	16.74	0.51
S3	39906	130.92	6.15	47.46	21.04	66.16	0.28	25.39	17.56	0.45
S4	42136	126.12	5.47	18.24	20.93	64.88	0.27	22.69	18.90	0.52
S5	41892	121.22	8.39	39.39	20.82	66.33	0.33	24.42	17.24	0.68
S6	40994	408.47	12.81	55.32	23.86	69.73	0.40	27.76	16.19	0.74
S7	38764	498.45	14.76	83.75	25.38	70.65	0.38	30.09	16.21	0.55
S8	11055	489.16	15.81	89.12	26.91	68.01	0.29	29.56	4.71	0.53
S9	3699	485.70	17.54	93.99	29.12	67.84	0.26	28.60	8.28	0.39
S10	8516	88.65	8.45	58.48	31.33	39.26	0.19	24.15	12.67	0.29
S11	19116	69.88	5.09	12.56	19.14	31.20	0.16	21.09	9.80	0.24
S12	21445	102.82	4.97	11.41	6.97	26.45	0.14	16.85	6.91	0.26
S13	29118	126.43	4.82	7.29	8.45	22.36	0.28	11.38	7.20	0.40
S14	32459	229.34	7.66	19.13	9.90	51.98	0.35	19.32	8.10	0.55
S15	38123	282.43	9.82	41.45	14.12	70.51	0.38	25.59	12.19	0.68
S16	38428	491.20	11.47	51.93	18.34	77.77	0.42	29.13	18.93	0.60
S17	25882	498.07	14.02	82.55	16.67	69.28	0.32	30.13	7.08	0.58
S18	27663	487.16	14.88	81.61	15.94	69.80	0.32	29.18	5.18	0.54

Table A5.1.2.Total trace metal concentrations and pollution load index (PLI) in sediments of the Muvattupuzha River during November 2005

Station position	Fe (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	PLI
S1	22558	79.61	6.90	52.19	48.04	41.39	0.44	21.64	8.98	0.46
S2	20716	83.94	6.22	45.19	27.13	37.23	0.39	19.89	7.89	0.40
S3	14339	94.16	2.10	26.74	16.64	28.32	0.36	17.36	7.02	0.29
S4	15563	98.63	5.60	11.13	11.35	22.55	0.35	11.37	6.72	0.26
S5	19716	148.67	8.92	31.62	6.16	35.20	0.34	13.35	8.82	0.34
S6	23118	218.12	9.02	47.53	9.00	39.85	0.39	17.05	11.56	0.43
S7	25994	231.69	11.00	63.61	10.57	44.85	0.44	17.61	15.47	0.50
S8	23419	216.87	9.01	59.99	12.08	38.42	0.43	14.69	12.43	0.46
S9	20946	160.81	8.35	52.77	11.00	36.10	0.41	15.15	10.75	0.41
S10	20339	66.87	5.55	41.28	10.70	34.77	0.37	14.45	9.42	0.33
S11	20098	48.03	3.73	7.30	7.75	15.76	0.34	13.88	8.93	0.22
S12	26198	88.01	4.12	7.01	5.98	14.01	0.31	16.82	7.01	0.23
S13	30821	103.64	4.89	6.79	4.29	12.79	0.28	18.17	7.60	0.23
S14	39445	189.40	7.64	16.61	6.11	26.00	0.35	17.07	9.97	0.35
S15	48903	206.87	8.44	51.45	13.89	39.79	0.38	14.38	15.18	0.49
S16	56952	221.22	11.48	61.16	21.02	43.00	0.41	13.62	19.66	0.58
S17	24551	218.64	9.34	62.22	10.86	40.13	0.44	15.15	12.00	0.46
S18	36842	204.24	9.74	64.04	11.04	42.10	0.43	16.00	12.01	0.49

Table A5.1.3. Total trace metal concentrations and pollution load index (PLI) in sediments of the Muvattupuzha River during January 2006

Station position	Fe (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	PLI
S1	15439	71.21	6.56	21.30	10.31	35.88	0.50	23.83	11.03	0.34
S2	17519	80.00	7.00	19.49	10.86	34.93	0.50	22.13	10.54	0.35
S3	18781	87.64	7.46	17.73	11.02	33.95	0.47	20.92	10.68	0.35
S4	20646	104.23	8.77	16.69	11.44	33.43	0.46	19.46	10.73	0.36
S5	23617	118.19	9.81	22.82	14.05	38.81	0.49	18.15	12.82	0.41
S6	25625	129.33	11.33	26.90	15.38	42.04	0.50	20.28	13.17	0.45
S7	27426	139.37	12.10	29.81	16.70	44.40	0.47	21.64	13.43	0.47
S8	22516	142.45	10.21	24.19	9.20	37.62	0.42	19.32	11.43	0.39
S9	19626	159.68	0.46	15.48	5.44	27.68	0.37	15.69	10.33	0.23
S10	23336	150.59	5.33	13.27	1.76	27.47	0.36	14.45	9.86	0.26
S11	26046	146.00	4.53	11.57	5.95	27.09	0.35	16.16	9.99	0.29
S12	24109	120.03	4.01	9.39	8.08	18.17	0.37	16.12	8.11	0.27
S13	20168	82.81	3.92	8.81	10.23	9.99	0.30	16.18	7.15	0.23
S14	31663	168.34	8.97	18.63	10.21	27.40	0.23	16.98	10.02	0.35
S15	39021	184.34	9.76	29.90	23.32	40.00	0.36	17.17	16.39	0.49
S16	39196	138.27	10.78	40.56	35.97	61.98	0.48	18.76	18.69	0.58
S17	25840	130.45	11.82	31.07	11.73	45.62	0.42	21.22	12.12	0.44
S18	26616	130.29	12.02	33.81	10.57	44.98	0.43	20.35	12.32	0.44

Table A5.1.4. Total trace metal concentrations and pollution load index (PLI) in sediments of the Muvattupuzha River during March 2006

Station position	Fe (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	PLI
S1	33358	174.99	10.82	53.80	16.38	76.74	0.83	37.12	11.66	0.62
S2	34812	169.33	8.36	55.31	13.08	58.02	0.57	35.85	11.04	0.54
S3	35431	131.12	6.51	38.39	11.45	39.07	0.45	34.14	11.57	0.45
S4	37519	109.28	5.70	22.37	9.89	33.64	0.40	33.07	11.85	0.39
S5	27015	115.86	5.13	18.68	7.34	29.44	0.36	19.96	9.57	0.32
S6	19337	88.45	4.91	15.38	6.15	20.51	0.30	12.18	6.24	0.24
S7	11417	64.05	4.27	9.50	4.90	12.85	0.24	8.76	5.00	0.18
S8	11915	115.84	4.78	13.07	5.50	29.46	0.26	9.02	5.68	0.23
S9	12187	130.97	5.10	15.95	4.57	30.46	0.28	9.13	6.90	0.24
S10	12448	127.54	4.62	12.16	5.02	31.42	0.47	9.43	8.98	0.26
S11	12664	119.44	3.47	8.81	5.54	51.50	0.20	9.98	12.01	0.24
S12	12415	113.50	2.02	7.80	6.98	22.33	0.18	9.99	9.00	0.20
S13	11075	110.09	2.70	6.44	6.67	20.66	0.30	10.18	4.86	0.19
S14	25445	217.01	9.13	18.34	11.77	33.03	0.33	13.13	9.18	0.37
S15	35816	286.18	1.25	38.20	14.87	41.55	0.35	14.02	14.42	0.38
S16	36234	93.40	13.23	42.83	18.03	56.69	0.41	14.94	19.12	0.50
S17	10108	98.87	4.01	11.40	5.02	20.67	0.25	9.99	4.90	0.20
S18	10991	95.33	4.00	12.00	4.98	24.89	0.24	9.31	4.78	0.20

Table A5.1.5. Total trace metal concentrations and pollution load index (PLI) in sediments of the Muvattupuzha River during May 2006

Station position	Fe (ppm)	Mn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	PLI
S1	41839	218.01	14.06	45.18	20.11	71.58	0.55	3.74	8.95	0.48
S2	42998	200.11	9.14	37.91	12.81	55.46	0.52	8.28	7.91	0.44
S3	45841	172.81	7.31	17.85	7.79	15.61	0.50	5.96	7.81	0.31
S4	46079	162.32	3.90	8.84	5.69	10.30	0.49	4.69	7.39	0.23
S5	32081	167.43	2.78	5.76	3.69	12.90	0.31	5.51	5.76	0.19
S6	13554	55.89	2.00	2.61	2.86	13.02	0.18	5.99	2.31	0.11
S7	3584	18.81	1.11	0.23	2.45	14.81	0.07	6.94	1.89	0.05
S8	4457	26.32	1.12	1.80	2.24	9.47	0.08	8.16	1.92	0.07
S9	5571	28.09	1.20	2.91	2.20	5.96	0.09	10.22	2.21	0.08
S10	19861	206.34	3.52	6.30	4.80	13.21	0.10	10.99	4.98	0.19
S11	27521	267.54	5.15	8.64	6.09	14.02	0.20	11.77	7.01	0.25
S12	24382	181.58	4.34	8.46	6.79	13.18	0.23	13.35	6.34	0.24
S13	19959	164.93	3.94	8.01	7.13	10.27	0.28	15.66	7.64	0.23
S14	28991	185.83	8.42	18.39	14.44	34.00	0.29	19.21	11.42	0.39
S15	44701	304.19	14.58	29.03	18.10	63.58	0.41	22.12	18.92	0.60
S16	44801	344.72	14.78	34.38	21.70	65.28	0.52	26.87	23.59	0.68
S17	3914	24.61	0.10	1.56	2.01	12.09	0.07	7.81	1.79	0.05
S18	3735	24.02	1.22	1.99	2.12	13.19	0.07	8.02	1.82	0.07

Table A6.1.0. Fractionation of iron concentrations and its percentage from the total iron in sediments of the Muvattupuzha River during July 2005

Station position	Fe_{exch} (ppm)	$\%Fe_{exch}$	Fe_{carb} (ppm)	$\%Fe_{carb}$	Fe_{redu} (ppm)	$\%Fe_{redu}$	Fe_{org} (ppm)	$\%Fe_{org}$	Fe_{resid} (ppm)	$\%Fe_{resid}$
S1	20.5	0.33	45.0	0.72	270.9	4.36	24.7	0.40	5935.9	95.6
S2	56.3	0.52	68.8	0.64	518.1	4.79	40.2	0.37	10124.6	93.6
S3	229.5	0.69	281.1	0.85	2050.6	6.19	163.6	0.49	30404.3	91.8
S4	323.4	0.72	396.2	0.88	2889.3	6.39	230.5	0.51	41582.4	92.0
S5	294.6	0.71	360.8	0.87	2609.3	6.29	209.9	0.51	38360.6	92.5
S6	282.9	0.71	346.5	0.87	2544.0	6.36	201.6	0.50	36486.3	91.3
S7	272.9	0.71	334.3	0.86	2384.1	6.16	194.5	0.50	36320.8	93.9
S8	263.7	0.70	323.1	0.86	2339.7	6.24	188.0	0.50	34099.8	90.9
S9	256.5	0.70	314.1	0.86	2298.1	6.28	182.8	0.50	34099.8	93.2
S10	316.7	0.71	387.9	0.88	2743.7	6.19	225.7	0.51	40419.7	91.2
S11	432.8	0.73	546.4	0.92	3856.4	6.47	310.0	0.52	54004.3	90.7
S12	326.5	0.71	412.1	0.90	2917.1	6.37	233.8	0.51	41256.3	90.1
S13	188.2	0.67	237.5	0.85	1659.8	5.95	134.8	0.48	25870.9	92.7
S14	144.9	0.65	182.8	0.82	1313.7	5.89	103.8	0.47	20686.6	92.7
S15	278.7	0.70	351.8	0.89	2481.9	6.26	199.6	0.50	36330.7	91.7
S16	288.2	0.71	363.8	0.89	2539.1	6.21	206.4	0.51	37615.3	92.1
S17	274.0	0.70	345.8	0.89	2450.5	6.28	196.2	0.50	35946.7	92.1
S18	273.5	0.70	345.2	0.89	2457.4	6.31	195.9	0.50	35574.4	91.3
Average	**251.3**	**0.67**	**313.5**	**0.85**	**2240.2**	**6.06**	**180.1**	**0.49**	**33062.2**	**92.2**

Table A6.1.1. Fractionation of iron concentrations and its percentage from the total iron in sediments of the Muvattupuzha River during September 2005

Station position	Fe_{exch} (ppm)	$\%Fe_{exch}$	Fe_{carb} (ppm)	$\%Fe_{carb}$	Fe_{redu} (ppm)	$\%Fe_{redu}$	Fe_{org} (ppm)	$\%Fe_{org}$	Fe_{resid} (ppm)	$\%Fe_{resid}$
S1	222.4	0.68	279.2	0.86	1936.9	5.94	160.9	0.49	29952.3	91.8
S2	268.0	0.69	336.6	0.87	2375.5	6.16	193.9	0.50	35377.8	91.7
S3	278.2	0.70	349.3	0.88	2514.2	6.30	201.2	0.50	36580.0	91.7
S4	295.2	0.70	370.7	0.88	2679.2	6.36	213.5	0.51	38782.9	92.0
S5	293.4	0.70	368.4	0.88	2636.8	6.29	212.2	0.51	38732.5	92.5
S6	286.5	0.70	359.7	0.88	2613.6	6.38	207.2	0.51	37399.3	91.2
S7	269.4	0.70	338.3	0.87	2388.5	6.16	194.9	0.50	37229.2	96.0
S8	57.3	0.52	71.8	0.65	641.9	5.81	41.5	0.38	10274.9	92.9
S9	28.6	0.77	32.5	0.88	242.3	6.55	18.6	0.50	3450.9	93.3
S10	37.9	0.44	47.4	0.56	485.4	5.70	27.5	0.32	8011.4	94.1
S11	119.0	0.62	149.4	0.78	1094.8	5.73	86.1	0.45	17547.7	91.8
S12	136.8	0.64	171.8	0.80	1253.8	5.85	99.0	0.46	17617.6	82.2
S13	195.6	0.67	245.5	0.84	1740.0	5.98	141.5	0.49	26973.6	92.6
S14	221.2	0.68	277.7	0.86	2006.5	6.18	160.0	0.49	29967.9	92.3
S15	264.5	0.69	332.1	0.87	2379.9	6.24	191.3	0.50	34965.4	91.7
S16	266.8	0.69	335.1	0.87	2375.9	6.18	193.0	0.50	35396.1	92.1
S17	170.8	0.66	214.4	0.83	1555.1	6.01	123.6	0.48	23940.2	92.5
S18	184.4	0.67	231.5	0.84	1684.1	6.09	133.4	0.48	25352.2	91.6
Average	**199.8**	**0.66**	**250.6**	**0.83**	**1811.4**	**6.11**	**144.4**	**0.48**	**27086.2**	**91.9**

Table A6.1.2. Fractionation of iron concentrations and its percentage from the total iron in sediments of the Muvattupuzha River during November 2005

Station position	Fe_{exch} (ppm)	$\%Fe_{exch}$	Fe_{carb} (ppm)	$\%Fe_{carb}$	Fe_{redu} (ppm)	$\%Fe_{redu}$	Fe_{org} (ppm)	$\%Fe_{org}$	Fe_{resid} (ppm)	$\%Fe_{resid}$
S1	143.9	0.64	181.6	0.81	1310.4	5.81	105.2	0.47	20803.7	92.2
S2	130.0	0.63	164.0	0.79	1180.3	5.70	95.0	0.46	19128.6	92.3
S3	81.6	0.57	102.9	0.72	768.7	5.36	59.7	0.42	13329.3	93.0
S4	90.9	0.58	114.7	0.74	856.2	5.50	66.5	0.43	14496.5	93.1
S5	122.4	0.62	154.4	0.78	1130.3	5.73	89.5	0.45	18365.1	93.1
S6	148.2	0.64	187.0	0.81	1381.1	5.97	108.3	0.47	21224.1	91.8
S7	170.0	0.65	214.5	0.83	1534.0	5.90	124.2	0.48	21135.3	81.3
S8	150.4	0.64	189.8	0.81	1381.9	5.90	109.9	0.47	21406.3	91.4
S9	131.7	0.63	166.2	0.79	1225.5	5.85	96.3	0.46	20406.3	97.4
S10	127.1	0.62	160.4	0.79	1130.1	5.56	92.9	0.46	18709.5	92.0
S11	125.3	0.62	158.1	0.79	1161.9	5.78	91.6	0.46	18491.5	92.0
S12	173.2	0.66	216.4	0.83	1578.3	6.02	125.3	0.48	22807.1	87.1
S13	208.6	0.68	255.5	0.83	1853.8	6.01	150.9	0.49	28535.9	92.6
S14	274.6	0.70	336.4	0.85	2483.7	6.30	198.6	0.50	36447.6	92.4
S15	347.0	0.71	425.1	0.87	3111.9	6.36	251.0	0.51	44770.9	91.6
S16	408.6	0.72	500.6	0.88	3620.7	6.36	295.5	0.52	52327.0	91.9
S17	160.6	0.65	201.6	0.82	1464.3	5.96	116.2	0.47	22723.0	92.6
S18	254.7	0.69	319.8	0.87	2312.9	6.28	184.2	0.50	33663.8	91.4
Average	**180.5**	**0.65**	**224.9**	**0.81**	**1638.1**	**5.91**	**131.2**	**0.47**	**24931.7**	**91.6**

Table A6.1.3. Fractionation of iron concentrations and its percentage from the total iron in sediments of the Muvattupuzha River during January 2006

Station position	Fe_{exch} (ppm)	$\%Fe_{exch}$	Fe_{carb} (ppm)	$\%Fe_{carb}$	Fe_{redu} (ppm)	$\%Fe_{redu}$	Fe_{org} (ppm)	$\%Fe_{org}$	Fe_{resid} (ppm)	$\%Fe_{resid}$
S1	91.8	0.59	111.7	0.72	831.6	5.39	65.8	0.43	14329.7	92.8
S2	107.8	0.62	131.4	0.75	966.5	5.52	77.3	0.44	16221.2	92.6
S3	117.6	0.63	143.2	0.76	1071.9	5.71	84.3	0.45	17368.9	92.5
S4	132.0	0.64	160.8	0.78	1204.9	5.84	94.6	0.46	19142.1	92.7
S5	155.0	0.66	188.8	0.80	1395.3	5.91	111.0	0.47	21947.9	92.9
S6	170.5	0.67	207.8	0.81	1554.0	6.06	122.2	0.48	23492.6	91.7
S7	184.4	0.67	224.7	0.82	1629.8	5.94	132.1	0.48	24392.4	88.9
S8	146.5	0.65	178.5	0.79	1320.5	5.86	104.9	0.47	20593.3	91.5
S9	121.7	0.62	153.5	0.78	1134.9	5.78	89.0	0.45	17893.3	91.2
S10	149.8	0.64	186.2	0.80	1331.9	5.71	109.5	0.47	21421.4	91.8
S11	173.8	0.67	211.7	0.81	1567.9	6.02	124.5	0.48	23793.7	91.4
S12	158.8	0.66	193.5	0.80	1435.7	5.96	113.8	0.47	23894.7	99.1
S13	128.3	0.64	156.3	0.78	1142.2	5.66	92.0	0.46	18762.8	93.0
S14	217.2	0.69	263.4	0.83	1952.2	6.17	155.6	0.49	29239.6	92.3
S15	274.1	0.70	332.4	0.85	2440.9	6.26	196.3	0.50	35782.2	91.7
S16	275.4	0.70	334.1	0.85	2427.5	6.19	197.3	0.50	36098.0	92.1
S17	172.2	0.67	214.0	0.83	1552.2	6.01	123.3	0.48	23901.8	92.5
S18	178.2	0.67	221.5	0.83	1612.4	6.06	127.6	0.48	24404.2	91.7
Average	**164.2**	**0.65**	**200.8**	**0.80**	**1476.2**	**5.89**	**117.8**	**0.47**	**22926.7**	**92.4**

Table A6.1.4. Fractionation of iron concentrations and its percentage from the total iron in sediments of the Muvattupuzha River during March 2006

Station position	Fe_{exch} (ppm)	$\%Fe_{exch}$	Fe_{carb} (ppm)	$\%Fe_{carb}$	Fe_{redu} (ppm)	$\%Fe_{redu}$	Fe_{org} (ppm)	$\%Fe_{org}$	Fe_{resid} (ppm)	$\%Fe_{resid}$
S1	226.9	0.68	282.0	0.85	2036.7	6.11	164.9	0.49	30625.3	91.8
S2	238.0	0.68	295.8	0.85	2123.2	6.10	173.0	0.50	31947.5	91.8
S3	242.7	0.68	301.6	0.85	2164.6	6.11	176.4	0.50	32510.4	91.8
S4	258.6	0.69	321.4	0.86	2362.5	6.30	188.0	0.50	34409.3	91.7
S5	178.6	0.66	221.9	0.82	1626.2	6.02	129.8	0.48	25068.8	92.8
S6	120.1	0.62	149.2	0.77	1120.5	5.79	87.4	0.45	18017.0	93.2
S7	59.8	0.52	74.2	0.65	558.5	4.89	43.5	0.38	10031.2	87.9
S8	63.6	0.53	78.9	0.66	600.3	5.04	46.3	0.39	11049.1	92.7
S9	65.6	0.54	81.5	0.67	624.6	5.12	47.8	0.39	11049.1	90.7
S10	67.6	0.54	84.0	0.67	599.9	4.82	49.2	0.40	11569.3	92.9
S11	69.3	0.55	85.6	0.68	654.3	5.17	50.4	0.40	11732.5	92.6
S12	67.4	0.54	83.2	0.67	637.3	5.13	49.0	0.40	11773.3	94.8
S13	58.0	0.52	70.6	0.64	534.8	4.83	41.6	0.38	9947.8	89.8
S14	169.1	0.66	205.1	0.81	1527.5	6.00	121.2	0.48	23550.4	92.6
S15	249.3	0.70	302.4	0.84	2223.3	6.21	178.6	0.50	32867.0	91.8
S16	252.5	0.70	306.3	0.85	2251.7	6.21	180.9	0.50	33390.8	92.2
S17	50.6	0.50	61.2	0.61	477.7	4.73	36.3	0.36	9514.9	94.1
S18	57.4	0.52	69.5	0.63	537.7	4.89	41.2	0.37	10322.4	93.9
Average	**138.6**	**0.60**	**170.8**	**0.74**	**1259.0**	**5.53**	**100.3**	**0.44**	**19965.3**	**92.2**

Table A6.1.5. Fractionation of iron concentrations and its percentage from the total iron in sediments of the Muvattupuzha River during May 2006

Station position	Fe_{exch} (ppm)	$\%Fe_{exch}$	Fe_{carb} (ppm)	$\%Fe_{carb}$	Fe_{redu} (ppm)	$\%Fe_{redu}$	Fe_{org} (ppm)	$\%Fe_{org}$	Fe_{resid} (ppm)	$\%Fe_{resid}$
S1	287.3	0.69	266.1	0.80	2607.0	6.23	211.9	0.51	38337.9	91.6
S2	296.0	0.69	277.2	0.80	2685.0	6.24	218.3	0.51	39391.9	91.6
S3	317.3	0.69	304.4	0.86	2876.2	6.27	234.0	0.51	41977.3	91.6
S4	319.1	0.69	302.5	0.81	2949.7	6.40	235.3	0.51	42193.8	91.6
S5	214.1	0.67	172.7	0.64	1970.3	6.14	157.9	0.49	29721.7	92.6
S6	75.2	0.55	165.4	0.86	711.7	5.25	55.4	0.41	12705.6	93.7
S7	18.8	0.53	100.6	0.88	234.4	6.54	16.2	0.45	3548.7	99.0
S8	22.9	0.51	88.4	0.74	293.7	6.59	18.0	0.40	3934.6	88.3
S9	28.3	0.51	98.8	0.81	320.7	5.76	24.2	0.43	5094.6	91.4
S10	122.5	0.62	105.8	0.85	1151.0	5.80	90.3	0.45	17837.6	89.8
S11	179.9	0.65	109.1	0.86	1676.5	6.09	132.6	0.48	25123.1	91.3
S12	156.4	0.64	109.1	0.88	1461.2	5.99	115.3	0.47	21230.8	87.1
S13	123.2	0.62	106.7	0.96	1128.2	5.65	90.8	0.45	18387.5	92.1
S14	190.9	0.66	243.2	0.96	1769.7	6.10	140.8	0.49	25381.1	87.5
S15	308.8	0.69	293.5	0.82	2842.7	6.36	227.7	0.51	40948.8	91.6
S16	309.5	0.69	294.5	0.81	2849.5	6.36	228.3	0.51	41039.7	91.6
S17	28.6	0.73	93.2	0.92	256.9	6.56	20.0	0.51	3448.9	88.1
S18	25.2	0.67	94.5	0.86	244.7	6.55	21.0	0.56	3386.1	90.7
Average	**168.0**	**0.64**	**179.2**	**0.84**	**1557.2**	**6.16**	**124.3**	**0.48**	**22982.8**	**91.2**

Table A6.1.6. Fractionation of manganese concentrations and its percentage from the total manganese in sediments of the Muvattupuzha River during July 2005

Station position	Mn_{exch} (ppm)	$\%Mn_{exc}$	Mn_{carb} (ppm)	$\%Mn_{carb}$	Mn_{redu} (ppm)	$\%Mn_{redu}$	Mn_{org} (ppm)	$\%Mn_{org}$	Mn_{resid} (ppm)	$\%Mn_{resid}$
S1	2.61	6	1.07	2.50	12.95	30	11.66	27	15.31	18
S2	4.29	5	1.92	2.31	24.62	30	23.12	28	6.08	31
S3	1.20	6	0.53	2.71	6.25	32	6.12	31	22.46	17
S4	7.70	6	3.31	2.49	38.59	29	41.36	31	32.51	21
S5	8.89	6	3.58	2.36	44.23	29	48.22	32	68.18	17
S6	25.51	6	10.17	2.57	124.72	31	136.80	35	104.50	26
S7	26.21	6	12.07	2.95	130.89	32	140.80	34	107.42	27
S8	25.33	6	9.65	2.47	123.84	32	135.01	35	97.40	27
S9	22.94	6	9.93	2.75	115.57	32	123.31	34	65.67	23
S10	18.31	6	7.53	2.61	89.80	31	97.71	34	18.14	22
S11	4.41	5	1.83	2.17	24.10	29	23.63	28	27.36	21
S12	7.30	6	3.25	2.55	35.97	28	39.54	31	28.43	19
S13	8.84	6	3.38	2.26	44.33	30	47.23	32	33.57	21
S14	9.41	6	4.14	2.63	45.95	29	50.25	32	35.45	22
S15	9.68	6	3.89	2.38	48.67	30	52.22	32	36.99	23
S16	9.65	6	3.58	2.20	48.28	30	52.05	32	56.50	19
S17	19.12	6	8.43	2.80	94.06	31	101.59	34	67.62	24
S18	17.77	6	7.34	2.60	88.04	31	95.22	34	63.28	22
Average	**12.73**	**6**	**5.31**	**2.52**	**63.38**	**30**	**68.10**	**32**	**49.27**	**22**

Table A6.1.7. Fractionation of manganese concentrations and its percentage from the total manganese in sediments of the Muvattupuzha River during September 2005

Station position	Mn_{exch} (ppm)	$\%Mn_{exch}$	Mn_{carb} (ppm)	$\%Mn_{carb}$	Mn_{redu} (ppm)	$\%Mn_{redu}$	Mn_{org} (ppm)	$\%Mn_{org}$	Mn_{resid} (ppm)	$\%Mn_{resid}$
S1	9.11	6	3.78	2.45	44.95	29	48.99	32	38.06	25
S2	8.01	6	3.58	2.59	40.37	29	43.17	31	40.80	29
S3	7.60	6	2.91	2.22	37.06	28	40.73	31	38.91	30
S4	7.23	6	3.11	2.46	36.23	29	38.83	31	37.79	30
S5	6.84	6	2.76	2.28	34.05	28	37.12	31	36.61	30
S6	26.34	6	10.50	2.57	128.78	32	141.25	35	107.53	26
S7	32.23	6	14.84	2.98	160.97	32	173.15	35	129.51	26
S8	31.98	7	12.18	2.49	156.39	32	170.50	35	127.62	26
S9	31.28	6	13.54	2.79	157.62	32	168.18	35	126.37	26
S10	4.74	5	1.95	2.20	23.22	26	25.27	29	28.57	32
S11	3.44	5	1.67	2.39	17.24	25	18.44	26	23.82	34
S12	5.64	5	2.51	2.44	27.76	27	30.52	30	35.21	34
S13	7.29	6	2.79	2.20	36.55	29	38.94	31	37.90	30
S14	14.29	6	6.29	2.74	69.79	30	76.32	33	63.17	28
S15	17.64	6	7.09	2.51	88.71	31	95.17	34	76.37	27
S16	31.70	6	11.76	2.39	158.53	32	170.91	35	126.92	26
S17	32.49	7	14.33	2.88	159.83	32	172.63	35	129.76	26
S18	31.61	6	13.07	2.68	156.66	32	169.45	35	127.46	26
Average	**17.19**	**6**	**7.15**	**2.52**	**85.26**	**30**	**92.20**	**32**	**74.02**	**28**

Table A6.1.8. Fractionation of manganese concentrations and its percentage from the total manganese in sediments of the Muvattupuzha River during November 2005

Station position	Mn_{exch} (ppm)	$\%Mn_{exch}$	Mn_{carb} (ppm)	$\%Mn_{carb}$	Mn_{redu} (ppm)	$\%Mn_{redu}$	Mn_{org} (ppm)	$\%Mn_{org}$	Mn_{resid} (ppm)	$\%Mn_{resid}$
S1	4.10	5	1.70	2.13	22.22	28	22.04	28	21.53	27
S2	4.36	5	1.95	2.32	21.99	26	23.51	28	27.35	33
S3	5.11	5	1.95	2.08	24.91	26	27.38	29	29.85	32
S4	5.38	5	2.31	2.34	26.95	27	28.88	29	31.00	31
S5	8.67	6	3.50	2.35	43.18	29	47.08	32	43.40	29
S6	13.47	6	5.37	2.46	65.87	30	72.25	33	60.51	28
S7	14.31	6	6.59	2.84	71.44	31	76.85	33	63.76	28
S8	13.47	6	5.13	2.37	65.86	30	71.80	33	60.27	28
S9	9.66	6	4.12	2.56	47.94	30	51.15	32	46.28	29
S10	3.26	5	1.34	2.01	18.98	28	18.39	28	23.18	35
S11	1.97	4	0.73	1.51	12.86	27	14.55	30	18.45	38
S12	4.64	5	2.07	2.35	22.87	26	25.14	29	30.91	35
S13	5.74	6	2.20	2.12	28.81	28	30.69	30	32.26	31
S14	11.58	6	5.10	2.69	56.55	30	61.84	33	53.33	28
S15	12.58	6	5.06	2.45	63.28	31	67.89	33	57.72	28
S16	13.58	6	5.04	2.28	67.93	31	73.23	33	60.83	27
S17	13.55	6	5.97	2.73	66.64	30	71.98	33	63.86	29
S18	12.52	6	5.17	2.53	62.03	30	67.09	33	60.20	29
Average	**8.78**	**6**	**3.63**	**2.34**	**43.91**	**29**	**47.32**	**31**	**43.59**	**30**

Table A6.1.9. Fractionation of manganese concentrations and its percentage from the total manganese in sediments of the Muvattupuzha River during January 2006

Station position	Mn_{exch} (ppm)	$\%Mn_{exch}$	Mn_{carb} (ppm)	$\%Mn_{carb}$	Mn_{redu} (ppm)	$\%Mn_{redu}$	Mn_{org} (ppm)	$\%Mn_{org}$	Mn_{resid} (ppm)	$\%Mn_{resid}$
S1	3.53	5	1.46	2.06	18.43	26	20.16	28	20.11	28
S2	4.10	5	1.83	2.29	20.66	26	22.09	28	26.38	33
S3	4.67	5	1.79	2.04	22.76	26	25.01	29	28.25	32
S4	5.76	6	2.47	2.37	28.84	28	30.91	30	32.38	31
S5	6.64	6	2.68	2.27	33.04	28	36.03	30	35.86	30
S6	7.47	6	2.98	2.30	36.53	28	40.06	31	38.58	30
S7	8.10	6	3.73	2.68	40.46	29	43.52	31	41.00	29
S8	8.31	6	3.20	2.25	41.11	29	44.82	31	41.86	29
S9	9.47	6	4.09	2.56	47.56	30	50.74	32	46.00	29
S10	8.93	6	3.68	2.44	43.82	29	47.68	32	43.90	29
S11	8.56	6	3.17	2.17	42.29	29	45.91	31	42.51	29
S12	6.79	6	3.03	2.52	33.45	28	36.77	31	40.22	34
S13	4.33	5	1.66	2.00	21.74	26	23.16	28	27.11	33
S14	10.15	6	4.47	2.66	49.57	29	54.21	32	48.14	29
S15	11.07	6	4.45	2.42	55.70	30	59.76	32	52.15	28
S16	8.02	6	2.97	2.15	40.09	29	43.22	31	40.52	29
S17	7.57	6	3.34	2.56	37.23	29	40.21	31	41.06	31
S18	7.53	6	3.11	2.39	37.29	29	40.34	31	41.82	32
Average	**7.28**	**6**	**3.01**	**2.34**	**36.14**	**28**	**39.14**	**31**	**38.21**	**30**

Table A6.2.0. Fractionation of manganese concentrations and its percentage from the total manganese in sediments of the Muvattupuzha River during March 2006

Station position	Mn_{exch} (ppm)	$\%Mn_{exch}$	Mn_{carb} (ppm)	$\%Mn_{carb}$	Mn_{redu} (ppm)	$\%Mn_{redu}$	Mn_{org} (ppm)	$\%Mn_{org}$	Mn_{resid} (ppm)	$\%Mn_{resid}$
S1	10.53	6	4.36	2.49	51.95	30	56.63	32	37.60	21
S2	10.08	6	4.51	2.66	50.82	30	54.34	32	48.44	29
S3	7.61	6	3.36	2.56	37.13	28	40.80	31	38.96	30
S4	6.10	6	2.62	2.40	30.54	28	32.73	30	33.63	31
S5	6.48	6	2.61	2.26	32.77	28	35.18	30	35.29	30
S6	4.71	5	1.88	2.12	23.02	26	25.24	29	28.48	32
S7	3.06	5	1.40	2.19	18.18	28	17.33	27	22.43	35
S8	6.56	6	2.51	2.17	32.26	28	35.17	30	35.28	30
S9	7.58	6	3.25	2.48	37.86	29	40.40	31	38.93	30
S10	7.37	6	3.03	2.38	36.71	29	39.34	31	38.20	30
S11	6.77	6	2.51	2.10	33.97	28	36.33	30	35.99	30
S12	6.35	6	2.36	2.08	31.29	28	34.40	30	38.32	34
S13	6.18	6	2.36	2.15	31.00	28	33.03	30	33.86	31
S14	13.46	6	5.93	2.73	65.70	30	71.85	33	60.14	28
S15	17.89	6	7.19	2.51	88.63	31	96.52	34	77.30	27
S16	5.00	5	1.86	1.99	25.03	27	26.99	29	29.54	32
S17	5.43	5	1.99	2.02	26.70	27	28.84	29	22.45	23
S18	5.17	5	1.91	2.00	25.52	27	27.69	29	35.25	37
Average	**7.57**	**6**	**3.09**	**2.29**	**37.73**	**28**	**40.71**	**30**	**38.34**	**30**

Table A6.2.1. Fractionation of manganese concentrations and its percentage from the total manganese in sediments of the Muvattupuzha River during May 2006

Station position	Mn_{exch} (ppm)	$\%Mn_{exch}$	Mn_{carb} (ppm)	$\%Mn_{carb}$	Mn_{redu} (ppm)	$\%Mn_{redu}$	Mn_{org} (ppm)	$\%Mn_{org}$	Mn_{resid} (ppm)	$\%Mn_{resid}$
S1	13.43	6	5.57	2.55	66.25	30	72.22	33	44.85	21
S2	12.22	6	5.07	2.53	61.21	31	65.45	33	56.05	28
S3	10.38	6	4.30	2.49	50.91	29	55.95	32	49.24	28
S4	9.67	6	4.15	2.56	47.45	29	51.92	32	46.73	29
S5	9.93	6	4.00	2.39	49.14	29	53.88	32	48.04	29
S6	2.88	5	1.55	2.77	16.25	29	15.44	28	17.44	31
S7	1.13	6	0.55	2.92	5.52	29	5.55	30	6.28	33
S8	1.50	6	0.59	2.26	7.50	28	8.72	33	8.14	31
S9	1.62	6	0.65	2.32	8.09	29	8.35	30	8.57	30
S10	12.71	6	5.23	2.54	62.35	30	67.85	33	57.70	28
S11	16.74	6	6.94	2.59	82.70	31	89.79	34	72.36	27
S12	10.92	6	4.54	2.50	53.80	30	59.14	33	68.10	38
S13	9.80	6	3.78	2.29	49.62	30	52.87	32	47.42	29
S14	11.34	6	4.99	2.69	56.72	31	60.54	33	52.45	28
S15	19.38	6	8.53	2.81	96.91	32	103.02	34	81.75	27
S16	22.13	6	8.12	2.35	109.38	32	117.91	34	91.06	26
S17	1.39	6	0.68	2.78	6.95	28	8.09	33	7.28	30
S18	1.35	6	0.67	2.78	6.75	28	8.88	37	8.13	34
Average	**9.36**	**6**	**3.88**	**2.56**	**46.53**	**30**	**50.31**	**32**	**42.87**	**29**

Table A6.2.2. Fractionation of cobalt concentrations and its percentage from the total cobalt in sediments of the Muvattupuzha River during July 2005

Station position	Co_{exch} (ppm)	$\%Co_{exch}$	Co_{carb} (ppm)	$\%Co_{carb}$	Co_{redu} (ppm)	$\%Co_{redu}$	Co_{org} (ppm)	$\%Co_{org}$	Co_{resid} (ppm)	$\%Co_{resid}$
S1	0.314	12	0.168	6	0.308	11	0.585	22	1.342	50
S2	0.580	11	0.330	6	0.580	11	1.132	22	2.535	49
S3	0.876	11	0.566	7	0.803	10	1.703	22	3.801	49
S4	1.050	11	0.585	6	0.939	10	2.034	22	4.588	50
S5	1.084	12	0.591	6	0.958	10	2.079	22	4.697	50
S6	1.119	11	0.579	6	1.010	10	2.173	22	4.821	49
S7	1.120	11	0.627	6	1.011	10	2.164	22	4.906	50
S8	1.178	11	0.660	6	1.054	10	2.297	22	5.079	49
S9	1.458	12	0.818	6	1.299	10	2.827	22	6.291	50
S10	1.012	12	0.554	6	0.902	10	2.051	24	4.303	49
S11	0.711	11	0.393	6	0.650	10	1.370	22	3.079	49
S12	0.677	11	0.384	6	0.639	11	1.327	22	3.028	51
S13	0.598	11	0.333	6	0.557	11	1.161	22	2.671	51
S14	0.831	11	0.469	6	0.741	10	1.616	22	3.480	48
S15	1.022	12	0.559	6	0.905	10	1.956	22	4.432	50
S16	1.014	11	0.575	6	0.926	10	1.971	22	4.390	49
S17	1.062	11	0.485	5	0.961	10	2.066	22	4.830	52
S18	1.138	11	0.635	6	1.020	10	2.202	22	4.895	49
Average	**0.936**	**11**	**0.517**	**6**	**0.848**	**10**	**1.818**	**22**	**4.065**	**50**

Table A6.2.3. Fractionation of cobalt concentrations and its percentage from the total cobalt in sediments of the Muvattupuzha River during September 2005

Station position	Co_{exch} (ppm)	$\%Co_{exch}$	Co_{carb} (ppm)	$\%Co_{carb}$	Co_{redu} (ppm)	$\%Co_{redu}$	Co_{org} (ppm)	$\%Co_{org}$	Co_{resid} (ppm)	$\%Co_{resid}$
S1	1.182	12	0.651	6	1.047	10	2.265	22	5.066	50
S2	0.951	11	0.537	6	1.002	12	1.851	22	4.124	49
S3	0.695	11	0.409	7	0.649	11	1.354	22	3.026	49
S4	0.623	11	0.347	6	0.576	11	1.208	22	2.701	49
S5	0.974	12	0.529	6	0.864	10	1.865	22	4.227	50
S6	1.468	11	0.729	6	1.307	10	2.848	22	6.308	49
S7	1.701	12	0.951	6	1.505	10	3.288	22	7.401	50
S8	1.816	11	1.015	6	1.597	10	3.531	22	7.799	49
S9	2.023	12	1.133	6	1.780	10	3.920	22	8.710	50
S10	0.981	12	0.536	6	0.875	10	1.703	20	4.168	49
S11	0.579	11	0.319	6	0.538	11	1.114	22	2.513	49
S12	0.558	11	0.318	6	0.538	11	1.098	22	2.521	51
S13	0.547	11	0.305	6	0.512	11	1.061	22	2.445	51
S14	0.871	11	0.492	6	0.831	11	1.695	22	3.831	50
S15	1.139	12	0.624	6	1.015	10	2.183	22	4.934	50
S16	1.313	11	0.741	6	1.180	10	2.550	22	5.669	49
S17	1.609	11	0.737	5	1.426	10	3.124	22	7.171	51
S18	1.715	12	0.956	6	1.511	10	3.318	22	7.362	49
Average	**1.153**	**11**	**0.629**	**6**	**1.042**	**10**	**2.221**	**22**	**4.999**	**50**

Table A6.2.4. Fractionation of cobalt concentrations and its percentage from the total cobalt in sediments of the Muvattupuzha River during November 2005

Station position	Co_{exch} (ppm)	$\%Co_{exch}$	Co_{carb} (ppm)	$\%Co_{carb}$	Co_{redu} (ppm)	$\%Co_{redu}$	Co_{org} (ppm)	$\%Co_{org}$	Co_{resid} (ppm)	$\%Co_{resid}$
S1	0.801	12	0.439	6	0.722	10	1.527	22	3.424	50
S2	0.704	11	0.399	6	0.712	11	1.371	22	3.064	49
S3	0.225	11	0.148	7	0.249	12	0.445	21	1.018	48
S4	0.638	11	0.355	6	0.589	11	1.236	22	2.827	51
S5	1.035	12	0.563	6	0.916	10	1.983	22	4.489	50
S6	1.028	11	0.554	6	0.934	10	1.997	22	4.427	49
S7	1.264	11	0.707	6	1.133	10	2.443	22	5.520	50
S8	1.027	11	0.575	6	0.925	10	2.003	22	4.419	49
S9	0.957	11	0.539	6	0.873	10	1.857	22	4.148	50
S10	0.645	12	0.349	6	0.590	11	1.166	21	2.732	49
S11	0.421	11	0.231	6	0.403	11	0.809	22	1.828	49
S12	0.460	11	0.263	6	0.454	11	0.907	22	2.099	51
S13	0.555	11	0.309	6	0.517	11	1.077	22	2.479	51
S14	0.868	11	0.491	6	0.829	11	1.690	22	3.790	50
S15	0.980	12	0.536	6	0.869	10	1.875	22	4.252	50
S16	1.314	11	0.742	6	1.181	10	2.552	22	5.674	49
S17	1.065	11	0.487	5	0.964	10	2.073	22	4.847	52
S18	1.118	11	0.624	6	1.003	10	2.163	22	4.809	49
Average	**0.839**	**11**	**0.462**	**6**	**0.770**	**11**	**1.621**	**22**	**3.658**	**50**

Table A6.2.5. Fractionation of cobalt concentrations and its percentage from the total cobalt in sediments of the Muvattupuzha River during January 2006

Station position	Co_{exch} (ppm)	$\%Co_{exch}$	Co_{carb} (ppm)	$\%Co_{carb}$	Co_{redu} (ppm)	$\%Co_{redu}$	Co_{org} (ppm)	$\%Co_{org}$	Co_{resid} (ppm)	$\%Co_{resid}$
S1	0.761	12	0.417	6	0.689	11	1.451	22	3.251	50
S2	0.794	11	0.449	6	0.756	11	1.545	22	3.449	49
S3	0.847	11	0.483	6	0.778	10	1.647	22	3.661	49
S4	1.006	11	0.560	6	0.901	10	1.948	22	4.400	50
S5	1.139	12	0.621	6	1.005	10	2.186	22	4.934	50
S6	1.297	11	0.625	6	1.161	10	2.516	22	5.574	49
S7	1.392	12	0.779	6	1.243	10	2.689	22	6.059	50
S8	1.166	11	0.653	6	1.044	10	2.273	22	5.015	49
S9	0.051	11	0.029	6	0.055	12	0.084	18	0.221	48
S10	0.619	12	0.335	6	0.568	11	1.118	21	2.622	49
S11	0.514	11	0.283	6	0.482	11	0.987	22	2.223	49
S12	0.447	11	0.256	6	0.443	11	0.883	22	2.044	51
S13	0.442	11	0.246	6	0.423	11	0.860	22	1.997	51
S14	1.023	11	0.577	6	0.902	10	1.988	22	4.743	53
S15	1.133	12	0.621	6	0.998	10	2.173	22	4.908	50
S16	1.233	11	0.697	6	1.112	10	2.395	22	5.327	49
S17	1.354	11	0.620	5	1.209	10	2.632	22	6.079	51
S18	1.383	12	0.771	6	1.228	10	2.676	22	5.942	49
Average	**0.922**	**11**	**0.501**	**6**	**0.833**	**11**	**1.781**	**22**	**4.025**	**50**

Table A6.2.6. Fractionation of cobalt concentrations and its percentage from the total cobalt in sediments of the Muvattupuzha River during March 2006

Station position	Co_{exch} (ppm)	$\%Co_{exch}$	Co_{carb} (ppm)	$\%Co_{carb}$	Co_{redu} (ppm)	$\%Co_{redu}$	Co_{org} (ppm)	$\%Co_{org}$	Co_{resid} (ppm)	$\%Co_{resid}$
S1	1.256	12	0.693	6	1.110	10	2.409	22	5.375	50
S2	0.951	11	0.536	6	1.002	12	1.850	22	4.123	49
S3	0.737	11	0.422	6	0.685	11	1.436	22	3.207	49
S4	0.649	11	0.362	6	0.599	11	1.259	22	2.877	50
S5	0.595	12	0.319	6	0.542	11	1.133	22	2.607	51
S6	0.552	11	0.311	6	0.527	11	1.075	22	2.387	49
S7	0.484	11	0.273	6	0.469	11	0.934	22	2.182	51
S8	0.536	11	0.302	6	0.506	11	1.053	22	2.319	49
S9	0.580	11	0.329	6	0.552	11	1.126	22	2.532	50
S10	0.536	12	0.288	6	0.496	11	1.100	24	2.266	49
S11	0.390	11	0.214	6	0.377	11	0.749	22	1.696	49
S12	0.216	11	0.127	6	0.247	12	0.436	22	1.056	52
S13	0.301	11	0.168	6	0.302	11	0.585	22	1.392	52
S14	1.041	11	0.587	6	0.954	10	2.024	22	4.557	50
S15	0.145	12	0.071	6	0.159	13	0.260	21	0.680	55
S16	1.517	11	0.855	6	1.354	10	2.945	22	6.543	49
S17	0.447	11	0.202	5	0.438	11	0.877	22	2.001	50
S18	0.452	11	0.253	6	0.436	11	0.874	22	1.959	49
Average	**0.633**	**11**	**0.351**	**6**	**0.598**	**11**	**1.229**	**22**	**2.764**	**50**

Table A6.2.7. Fractionation of cobalt concentrations and its percentage from the total cobalt in sediments of the Muvattupuzha River during May 2006

Station position	Co_{exch} (ppm)	$\%Co_{exch}$	Co_{carb} (ppm)	$\%Co_{carb}$	Co_{redu} (ppm)	$\%Co_{redu}$	Co_{org} (ppm)	$\%Co_{org}$	Co_{resid} (ppm)	$\%Co_{resid}$
S1	1.632	12	0.902	6	1.430	10	3.136	22	6.982	50
S2	1.042	11	0.587	6	1.010	11	2.026	22	4.512	49
S3	0.830	11	0.423	6	0.764	10	1.616	22	3.605	49
S4	0.440	11	0.245	6	0.421	11	0.854	22	1.983	51
S5	0.323	12	0.167	6	0.311	11	0.606	22	1.443	52
S6	0.213	11	0.122	6	0.239	12	0.420	21	0.940	47
S7	0.117	11	0.069	6	0.157	14	0.224	20	0.614	55
S8	0.111	10	0.065	6	0.146	13	0.232	21	0.502	45
S9	0.127	11	0.077	6	0.166	14	0.250	21	0.594	50
S10	0.409	12	0.217	6	0.388	11	0.789	22	1.721	49
S11	0.585	11	0.323	6	0.543	11	1.127	22	2.530	49
S12	0.486	11	0.277	6	0.476	11	0.957	22	2.210	51
S13	0.445	11	0.248	6	0.425	11	0.864	22	2.009	51
S14	0.958	11	0.541	6	0.973	12	1.863	22	4.210	50
S15	1.692	12	0.933	6	1.476	10	3.253	22	7.301	50
S16	1.697	11	0.955	6	1.507	10	3.293	22	7.313	49
S17	0.012	12	0.007	6	0.011	11	0.021	20	0.052	50
S18	0.129	11	0.073	6	0.126	10	0.249	21	0.578	48
Average	**0.625**	**11**	**0.346**	**6**	**0.587**	**11**	**1.210**	**22**	**2.728**	**50**

Table A6.2.8. Fractionation of nickel concentrations and its percentage from the total nickel in sediments of the Muvattupuzha River during July 2005

Station position	Ni_{exch} (ppm)	$\%Ni_{exch}$	Ni_{carb} (ppm)	$\%Ni_{carb}$	Ni_{redu} (ppm)	$\%Ni_{redu}$	Ni_{org} (ppm)	$\%Ni_{org}$	Ni_{resid} (ppm)	$\%Ni_{resid}$
S1	0.38	9	0.18	4	0.19	4	0.31	7	3.11	73
S2	0.70	9	0.36	4	0.34	4	0.60	7	5.60	69
S3	1.14	9	0.57	4	0.54	4	0.98	8	9.02	69
S4	1.22	9	0.63	4	0.60	4	1.06	7	9.73	69
S5	1.01	9	0.51	4	0.49	4	0.88	8	7.96	69
S6	0.78	9	0.40	4	0.39	4	0.68	7	6.33	70
S7	0.77	9	0.39	4	0.38	4	0.65	7	6.07	69
S8	7.02	9	3.67	5	3.40	4	6.25	8	56.55	70
S9	3.67	9	1.90	4	1.76	4	3.21	8	29.03	69
S10	1.67	9	0.87	5	0.81	4	1.48	8	13.48	69
S11	1.41	9	0.73	4	0.68	4	1.23	8	11.25	69
S12	1.09	9	0.55	4	0.52	4	0.93	7	8.64	69
S13	0.77	9	0.39	4	0.38	4	0.66	7	6.01	67
S14	1.15	9	0.58	4	0.55	4	0.98	7	9.10	69
S15	1.68	9	0.87	4	0.82	4	1.49	8	13.52	68
S16	1.84	9	0.95	4	0.90	4	1.62	7	15.01	69
S17	2.17	9	1.12	4	1.05	4	1.92	8	16.09	64
S18	2.09	8	1.11	4	1.04	4	1.88	8	17.37	70
Average	**1.70**	**9**	**0.88**	**4**	**0.83**	**4**	**1.49**	**7**	**13.55**	**69**

Table A6.2.9. Fractionation of nickel concentrations and its percentage from the total nickel in sediments of the Muvattupuzha River during September 2005

Station position	Ni_{exch} (ppm)	$\%Ni_{exch}$	Ni_{carb} (ppm)	$\%Ni_{carb}$	Ni_{redu} (ppm)	$\%Ni_{redu}$	Ni_{org} (ppm)	$\%Ni_{org}$	Ni_{resid} (ppm)	$\%Ni_{resid}$
S1	6.86	9	3.60	4	3.33	4	6.14	8	55.37	69
S2	5.10	8	2.69	4	2.48	4	4.52	8	41.19	68
S3	4.13	9	2.11	4	1.97	4	3.63	8	32.93	69
S4	1.57	9	0.82	4	0.76	4	1.37	7	12.52	69
S5	3.40	9	1.77	4	1.63	4	3.03	8	27.02	69
S6	4.70	8	2.50	5	2.32	4	4.21	8	38.57	70
S7	7.28	9	3.38	4	3.53	4	6.33	8	57.74	69
S8	7.71	9	4.03	5	3.74	4	6.87	8	62.12	70
S9	8.16	9	4.24	5	3.90	4	7.14	8	64.44	69
S10	5.01	9	2.65	5	2.42	4	4.48	8	40.57	69
S11	1.08	9	0.55	4	0.52	4	0.94	7	8.64	69
S12	0.99	9	0.50	4	0.48	4	0.84	7	7.88	69
S13	0.63	9	0.32	4	0.31	4	0.54	7	4.90	67
S14	1.67	9	0.84	4	0.80	4	1.42	7	13.20	69
S15	3.51	8	1.84	4	1.72	4	3.14	8	28.35	68
S16	4.40	8	2.31	4	2.15	4	3.92	8	36.03	69
S17	7.04	9	3.69	4	3.41	4	6.30	8	52.37	63
S18	6.89	8	3.66	4	3.39	4	6.20	8	56.60	69
Average	**4.45**	**9**	**2.31**	**4**	**2.16**	**4**	**3.95**	**8**	**35.58**	**69**

Table A6.3.0. Fractionation of nickel concentrations and its percentage from the total nickel in sediments of the Muvattupuzha River during November 2005

Station position	Ni_{exch} (ppm)	$\%Ni_{exch}$	Ni_{carb} (ppm)	$\%Ni_{carb}$	Ni_{redu} (ppm)	$\%Ni_{redu}$	Ni_{org} (ppm)	$\%Ni_{org}$	Ni_{resid} (ppm)	$\%Ni_{resid}$
S1	4.48	9	2.34	4	2.17	4	4.00	8	36.13	69
S2	3.83	8	2.01	4	1.86	4	3.39	8	30.91	68
S3	2.33	9	1.18	4	1.11	4	2.04	8	18.56	69
S4	0.96	9	0.50	4	0.47	4	0.83	7	7.65	69
S5	2.73	9	1.42	4	1.31	4	2.43	8	21.69	69
S6	4.04	8	2.15	5	2.00	4	3.62	8	33.14	70
S7	5.53	9	2.90	5	2.68	4	4.80	8	43.86	69
S8	5.19	9	2.71	5	2.52	4	4.62	8	41.83	70
S9	4.58	9	2.38	5	2.20	4	4.00	8	36.19	69
S10	3.54	9	1.87	5	1.71	4	3.16	8	28.65	69
S11	0.63	9	0.32	4	0.31	4	0.54	7	5.03	69
S12	0.61	9	0.31	4	0.30	4	0.51	7	4.85	69
S13	0.59	9	0.29	4	0.29	4	0.50	7	4.56	67
S14	1.45	9	0.73	4	0.70	4	1.24	7	11.47	69
S15	4.36	8	2.29	4	2.13	4	3.90	8	35.19	68
S16	5.18	8	2.72	4	2.53	4	4.62	8	42.43	69
S17	5.31	9	2.78	4	2.57	4	4.74	8	39.49	63
S18	5.40	8	2.87	4	2.66	4	4.86	8	42.67	67
Average	**3.38**	**9**	**1.76**	**4**	**1.64**	**4**	**2.99**	**8**	**26.91**	**69**

Table A6.3.1. Fractionation of nickel concentrations and its percentage from the total nickel in sediments of the Muvattupuzha River during January 2006

Station position	Ni_{exch} (ppm)	$\%Ni_{exch}$	Ni_{carb} (ppm)	$\%Ni_{carb}$	Ni_{redu} (ppm)	$\%Ni_{redu}$	Ni_{org} (ppm)	$\%Ni_{org}$	Ni_{resid} (ppm)	$\%Ni_{resid}$
S1	1.84	9	0.95	4	0.89	4	1.62	8	14.85	70
S2	1.66	9	0.86	4	0.81	4	1.45	7	13.34	68
S3	1.55	9	0.78	4	0.74	4	1.35	8	12.32	69
S4	1.43	9	0.75	4	0.70	4	1.25	7	11.46	69
S5	1.97	9	1.02	4	0.95	4	1.75	8	15.66	69
S6	2.29	9	1.21	4	1.13	4	2.04	8	18.77	70
S7	2.54	9	1.35	5	1.26	4	2.24	8	20.79	70
S8	2.10	9	1.09	4	1.02	4	1.85	8	16.87	70
S9	1.34	9	0.69	4	0.65	4	1.16	8	10.63	69
S10	1.15	9	0.59	4	0.56	4	1.00	8	9.22	69
S11	1.00	9	0.51	4	0.48	4	0.87	8	7.96	69
S12	0.82	9	0.41	4	0.39	4	0.72	8	6.49	69
S13	0.76	9	0.38	4	0.37	4	0.65	7	5.91	67
S14	1.62	9	0.82	4	0.78	4	1.39	7	12.86	69
S15	2.54	8	1.33	4	1.24	4	2.26	8	20.46	68
S16	3.44	8	1.80	4	1.68	4	3.06	8	28.15	69
S17	2.66	9	1.38	4	1.29	4	2.36	8	19.73	64
S18	2.84	8	1.51	4	1.41	4	2.56	8	21.31	63
Average	**1.86**	**9**	**0.97**	**4**	**0.91**	**4**	**1.64**	**8**	**14.82**	**68**

Table A6.3.2. Fractionation of nickel concentrations and its percentage from the total nickel in sediments of the Muvattupuzha River during March 2006

Station position	Ni_{exch} (ppm)	$\%Ni_{exch}$	Ni_{carb} (ppm)	$\%Ni_{carb}$	Ni_{redu} (ppm)	$\%Ni_{redu}$	Ni_{org} (ppm)	$\%Ni_{org}$	Ni_{resid} (ppm)	$\%Ni_{resid}$
S1	4.61	9	2.41	4	2.24	4	4.12	8	37.24	69
S2	4.69	8	2.47	4	2.28	4	4.15	8	37.83	68
S3	3.35	9	1.71	4	1.59	4	2.94	8	26.64	69
S4	1.92	9	1.01	5	0.94	4	1.68	7	15.35	69
S5	1.62	9	0.83	4	0.78	4	1.43	8	12.82	69
S6	1.33	9	0.68	4	0.65	4	1.17	8	10.56	69
S7	0.83	9	0.44	5	0.41	4	0.70	7	6.53	69
S8	1.14	9	0.58	4	0.56	4	0.99	8	9.13	70
S9	1.39	9	0.71	4	0.67	4	1.20	8	10.95	69
S10	1.05	9	0.54	4	0.51	4	0.92	8	8.45	70
S11	0.76	9	0.39	4	0.37	4	0.65	7	6.07	69
S12	0.68	9	0.34	4	0.33	4	0.58	7	5.38	69
S13	0.56	9	0.28	4	0.27	4	0.47	7	4.33	67
S14	1.60	9	0.81	4	0.77	4	1.37	7	12.66	69
S15	3.24	8	1.70	4	1.58	4	2.86	7	26.13	68
S16	3.63	8	1.90	4	1.78	4	3.23	8	29.72	69
S17	0.98	9	0.50	4	0.48	4	0.85	7	7.26	64
S18	1.03	9	0.53	4	0.51	4	0.90	7	7.64	64
Average	**1.91**	**9**	**0.99**	**4**	**0.93**	**4**	**1.68**	**8**	**15.26**	**68**

Table A6.3.3. Fractionation of nickel concentrations and its percentage from the total nickel in sediments of the Muvattupuzha River during May 2006

Station position	Ni_{exch} (ppm)	$\%Ni_{exch}$	Ni_{carb} (ppm)	$\%Ni_{carb}$	Ni_{redu} (ppm)	$\%Ni_{redu}$	Ni_{org} (ppm)	$\%Ni_{org}$	Ni_{resid} (ppm)	$\%Ni_{resid}$
S1	3.88	9	2.02	4	1.88	4	3.46	8	31.30	69
S2	3.26	9	1.70	4	1.56	4	2.84	7	25.93	68
S3	1.56	9	0.79	4	0.75	4	1.36	8	12.40	69
S4	0.77	9	0.39	4	0.37	4	0.66	8	6.08	69
S5	0.50	9	0.25	4	0.25	4	0.43	7	3.97	69
S6	0.24	9	0.11	4	0.12	5	0.18	7	1.81	69
S7	0.02	8	0.01	5	0.01	5	0.02	7	0.16	69
S8	0.17	9	0.08	5	0.08	5	0.12	7	1.26	70
S9	0.26	9	0.12	4	0.13	4	0.20	7	2.02	69
S10	0.55	9	0.27	4	0.27	4	0.46	7	4.34	69
S11	0.75	9	0.38	4	0.37	4	0.64	7	5.94	69
S12	0.73	9	0.37	4	0.36	4	0.63	7	5.82	69
S13	0.69	9	0.35	4	0.34	4	0.59	7	5.38	67
S14	1.60	9	0.81	4	0.77	4	1.38	8	12.32	67
S15	2.46	8	1.29	4	1.21	4	2.19	8	19.43	67
S16	2.91	8	1.53	4	1.43	4	2.59	8	23.86	69
S17	0.14	9	0.07	4	0.07	5	0.10	6	1.10	71
S18	0.18	9	0.09	4	0.09	5	0.13	7	1.40	70
Average	**1.15**	**9**	**0.59**	**4**	**0.56**	**4**	**1.00**	**7**	**9.14**	**69**

Table A6.3.4. Fractionation of copper concentrations and its percentage from the total copper in sediments of the Muvattupuzha River during July 2005

Station position	Cu_{exch} (ppm)	$\%Cu_{exch}$	Cu_{carb} (ppm)	$\%Cu_{carb}$	Cu_{redu} (ppm)	$\%Cu_{redu}$	Cu_{org} (ppm)	$\%Cu_{org}$	Cu_{resid} (ppm)	$\%Cu_{resid}$
S1	2.50	35	0.38	5	0.44	6	1.76	25	2.04	28
S2	3.67	34	0.66	6	0.64	6	2.92	27	2.85	26
S3	4.39	34	0.81	6	0.72	6	3.50	27	3.28	26
S4	4.69	34	0.88	6	0.77	6	3.77	28	3.46	25
S5	5.11	35	0.95	7	0.84	6	4.05	28	3.69	25
S6	5.21	35	0.97	7	0.82	6	4.13	28	3.75	25
S7	5.16	34	0.98	7	0.86	6	4.20	28	3.77	25
S8	5.20	34	0.99	7	0.85	6	4.22	28	3.80	25
S9	6.01	34	1.18	7	0.97	6	4.98	28	4.35	25
S10	4.35	35	0.80	6	0.72	6	3.45	27	3.33	26
S11	3.46	34	0.61	6	0.60	6	2.67	26	2.68	27
S12	2.85	33	0.51	6	0.52	6	2.25	26	2.38	27
S13	2.71	34	0.45	6	0.50	6	2.01	25	2.22	28
S14	2.55	33	0.42	6	0.46	6	1.91	25	2.13	28
S15	5.23	34	1.02	7	0.86	6	4.32	28	3.88	25
S16	7.99	34	1.61	7	1.29	6	6.73	29	5.60	24
S17	4.26	32	0.86	6	0.76	6	3.70	28	3.43	26
S18	4.32	31	0.91	6	0.81	6	3.88	28	3.54	25
Average	**4.43**	**34**	**0.83**	**6**	**0.75**	**6**	**3.58**	**27**	**3.34**	**26**

Table A6.3.5. Fractionation of copper concentrations and its percentage from the total copper in sediments of the Muvattupuzha River during September 2005

Station position	Cu_{exch} (ppm)	$\%Cu_{exch}$	Cu_{carb} (ppm)	$\%Cu_{carb}$	Cu_{redu} (ppm)	$\%Cu_{redu}$	Cu_{org} (ppm)	$\%Cu_{org}$	Cu_{resid} (ppm)	$\%Cu_{resid}$
S1	7.46	34	1.49	7	1.21	6	6.26	29	4.88	23
S2	7.21	34	1.45	7	1.15	5	6.11	29	5.18	24
S3	7.24	34	1.44	7	1.17	6	6.06	29	5.10	24
S4	6.97	33	1.42	7	1.15	5	6.02	29	5.11	24
S5	7.12	34	1.42	7	1.14	5	5.97	29	5.06	24
S6	8.12	34	1.64	7	1.31	5	6.94	29	5.76	24
S7	8.37	33	1.77	7	1.39	5	7.40	29	6.08	24
S8	9.27	34	1.87	7	1.46	5	7.84	29	6.44	24
S9	10.05	35	2.05	7	1.59	5	8.56	29	6.91	24
S10	10.76	34	2.21	7	1.69	5	9.23	29	7.40	24
S11	6.56	34	1.30	7	1.08	6	5.47	29	4.71	25
S12	2.41	35	0.37	5	0.43	6	1.71	25	1.99	29
S13	2.92	35	0.49	6	0.51	6	2.17	26	2.31	27
S14	3.41	34	0.59	6	0.59	6	2.60	26	2.65	27
S15	4.77	34	0.92	6	0.81	6	3.92	28	3.57	25
S16	6.08	33	1.25	7	1.01	6	5.23	29	4.53	25
S17	5.72	34	1.11	7	0.95	6	4.70	28	4.14	25
S18	5.49	34	1.05	7	0.89	6	4.49	28	3.99	25
Average	**6.66**	**34**	**1.32**	**7**	**1.08**	**6**	**5.59**	**28**	**4.77**	**25**

Table A6.3.6. Fractionation of copper concentrations and its percentage from the total copper in sediments of the Muvattupuzha River during November 2005

Station position	Cu_{exch} (ppm)	$\%Cu_{exch}$	Cu_{carb} (ppm)	$\%Cu_{carb}$	Cu_{redu} (ppm)	$\%Cu_{redu}$	Cu_{org} (ppm)	$\%Cu_{org}$	Cu_{resid} (ppm)	$\%Cu_{resid}$
S1	15.50	32	3.47	7	2.53	5	14.33	30	11.04	23
S2	9.20	34	1.90	7	1.49	5	7.95	29	6.49	24
S3	5.64	34	1.10	7	0.94	6	4.70	28	4.05	24
S4	3.82	34	0.71	6	0.65	6	3.05	27	2.97	26
S5	2.13	35	0.30	5	0.39	6	1.47	24	1.82	30
S6	3.12	35	0.53	6	0.55	6	2.34	26	2.45	27
S7	3.57	34	0.63	6	0.60	6	2.81	27	2.80	26
S8	4.17	35	0.76	6	0.71	6	3.28	27	3.14	26
S9	3.70	34	0.67	6	0.64	6	2.96	27	2.90	26
S10	3.67	34	0.66	6	0.62	6	2.85	27	2.82	26
S11	2.80	36	0.42	5	0.47	6	1.95	25	2.17	28
S12	2.08	35	0.30	5	0.39	7	1.41	24	1.76	29
S13	1.49	35	0.16	4	0.29	7	0.87	20	1.40	33
S14	2.11	34	0.31	5	0.40	7	1.45	24	1.80	29
S15	4.73	34	0.89	6	0.78	6	3.86	28	3.54	25
S16	7.24	34	1.44	7	1.15	5	6.04	29	5.11	24
S17	3.76	35	0.66	6	0.63	6	2.92	27	2.86	26
S18	3.82	35	0.68	6	0.65	6	2.96	27	2.90	26
Average	**4.59**	**34**	**0.87**	**6**	**0.77**	**6**	**3.73**	**26**	**3.44**	**27**

Table A6.3.7. Fractionation of copper concentrations and its percentage from the total copper in sediments of the Muvattupuzha River during January 2006

Station position	Cu_{exch} (ppm)	$\%Cu_{exch}$	Cu_{carb} (ppm)	$\%Cu_{carb}$	Cu_{redu} (ppm)	$\%Cu_{redu}$	Cu_{org} (ppm)	$\%Cu_{org}$	Cu_{resid} (ppm)	$\%Cu_{resid}$
S1	3.37	33	0.63	6	0.62	6	2.73	26	2.74	27
S2	3.75	35	0.66	6	0.63	6	2.92	27	2.84	26
S3	3.81	35	0.68	6	0.63	6	2.95	27	2.90	26
S4	3.95	35	0.70	6	0.67	6	3.10	27	2.99	26
S5	4.85	35	0.91	6	0.81	6	3.89	28	3.56	25
S6	5.31	34	1.00	7	0.84	5	4.30	28	3.87	25
S7	5.58	33	1.11	7	0.95	6	4.73	28	4.17	25
S8	3.11	34	0.53	6	0.54	6	2.40	26	2.45	27
S9	1.90	35	0.26	5	0.35	7	1.22	22	1.66	30
S10	0.61	35	0.10	6	0.16	9	0.38	22	0.44	25
S11	2.07	35	0.29	5	0.39	7	1.40	24	1.67	28
S12	2.70	33	0.46	6	0.48	6	2.05	25	2.25	28
S13	3.54	35	0.61	6	0.61	6	2.73	27	2.72	27
S14	3.53	35	0.62	6	0.60	6	2.72	27	2.72	27
S15	8.03	34	1.61	7	1.27	5	6.75	29	5.62	24
S16	12.16	34	2.57	7	1.93	5	10.67	30	8.45	24
S17	4.01	34	0.74	6	0.69	6	3.17	27	3.05	26
S18	3.57	34	0.65	6	0.61	6	2.83	27	2.80	26
Average	**4.21**	**34**	**0.79**	**6**	**0.71**	**6**	**3.39**	**26**	**3.16**	**26**

Table A6.3.8. Fractionation of copper concentrations and its percentage from the total copper in sediments of the Muvattupuzha River during March 2006

Station position	Cu_{exch} (ppm)	$\%Cu_{exch}$	Cu_{carb} (ppm)	$\%Cu_{carb}$	Cu_{redu} (ppm)	$\%Cu_{redu}$	Cu_{org} (ppm)	$\%Cu_{org}$	Cu_{resid} (ppm)	$\%Cu_{resid}$
S1	5.51	34	1.09	7	0.91	6	4.62	28	4.08	25
S2	4.49	34	0.83	6	0.75	6	3.59	27	3.36	26
S3	3.76	33	0.71	6	0.66	6	3.10	27	2.99	26
S4	3.42	35	0.59	6	0.59	6	2.61	26	2.65	27
S5	2.45	33	0.40	5	0.43	6	1.81	25	2.06	28
S6	2.12	34	0.30	5	0.40	7	1.46	24	1.82	30
S7	1.71	35	0.22	4	0.32	6	1.08	22	1.54	31
S8	1.82	33	0.25	5	0.35	6	1.24	23	1.64	30
S9	1.60	35	0.19	4	0.31	7	0.98	21	1.47	32
S10	1.70	34	0.22	4	0.34	7	1.11	22	1.54	31
S11	1.93	35	0.27	5	0.34	6	1.26	23	1.68	30
S12	2.18	31	0.37	5	0.44	6	1.72	25	2.00	29
S13	2.23	33	0.35	5	0.42	6	1.62	24	1.92	29
S14	4.04	34	0.73	6	0.67	6	3.18	27	3.06	26
S15	5.03	34	0.97	7	0.83	6	4.16	28	3.76	25
S16	6.12	34	1.21	7	1.02	6	5.14	28	4.44	25
S17	1.75	35	0.23	5	0.31	6	1.11	22	1.56	31
S18	1.74	35	0.22	5	0.34	7	1.10	22	1.54	31
Average	**2.98**	**34**	**0.51**	**5**	**0.52**	**6**	**2.27**	**25**	**2.39**	**28**

Table A6.3.9. Fractionation of copper concentrations and its percentage from the total copper in sediments of the Muvattupuzha River during May 2006

Station position	Cu_{exch} (ppm)	$\%Cu_{exch}$	Cu_{carb} (ppm)	$\%Cu_{carb}$	Cu_{redu} (ppm)	$\%Cu_{redu}$	Cu_{org} (ppm)	$\%Cu_{org}$	Cu_{resid} (ppm)	$\%Cu_{resid}$
S1	6.71	33	1.55	8	1.10	5	5.77	29	4.90	24
S2	4.41	34	0.82	6	0.74	6	3.50	27	3.30	26
S3	2.70	35	0.43	5	0.47	6	1.97	25	2.17	28
S4	1.93	34	0.28	5	0.36	6	1.31	23	1.71	30
S5	1.27	34	0.12	3	0.25	7	0.75	20	1.25	34
S6	1.01	35	0.16	6	0.22	8	0.56	20	0.98	34
S7	0.86	35	0.12	5	0.19	8	0.54	22	0.85	35
S8	0.80	36	0.12	5	0.19	8	0.50	22	0.59	26
S9	0.79	36	0.11	5	0.20	9	0.44	20	0.63	28
S10	1.58	33	0.20	4	0.30	6	1.05	22	1.31	27
S11	2.11	35	0.31	5	0.40	7	1.45	24	1.78	29
S12	2.26	33	0.35	5	0.41	6	1.65	24	1.96	29
S13	2.39	33	0.39	5	0.43	6	1.76	25	2.03	28
S14	4.95	34	0.93	6	0.82	6	4.02	28	3.66	25
S15	6.22	34	1.22	7	1.02	6	5.11	28	4.46	25
S16	7.43	34	1.47	7	1.17	5	6.26	29	5.28	24
S17	0.72	36	0.12	6	0.19	9	0.49	24	0.58	29
S18	0.76	36	0.13	6	0.18	9	0.46	22	0.52	24
Average	**2.72**	**35**	**0.49**	**6**	**0.48**	**7**	**2.09**	26	**2.11**	**28**

Table A6.4.0. Fractionation of chromium concentrations and its percentage from the total chromium in sediments of the Muvattupuzha River during July 2005

Station position	Cr_{exch} (ppm)	$\%Cr_{exch}$	Cr_{carb} (ppm)	$\%Cr_{carb}$	Cr_{redu} (ppm)	$\%Cr_{redu}$	Cr_{org} (ppm)	$\%Cr_{org}$	Cr_{resid} (ppm)	$\%Cr_{resid}$
S1	0.297	0.73	2.09	5	10.44	26	10.36	25	21.36	52
S2	0.308	0.73	2.14	5	10.76	25	10.82	25	22.22	52
S3	0.293	0.66	2.15	5	11.23	26	11.30	26	23.05	52
S4	0.325	0.73	2.21	5	11.34	25	11.45	26	23.37	52
S5	0.283	0.66	2.17	5	10.75	25	10.90	26	22.32	52
S6	0.274	0.72	1.83	5	8.89	24	9.48	25	19.80	52
S7	0.261	0.72	1.80	5	9.15	25	9.05	25	19.02	52
S8	0.296	0.73	2.07	5	9.12	22	10.35	25	21.34	52
S9	0.302	0.72	2.12	5	10.66	25	11.66	28	21.89	52
S10	0.280	0.72	1.89	5	9.77	25	9.80	25	20.37	52
S11	0.227	0.72	1.48	5	7.88	25	7.72	25	16.50	53
S12	0.211	0.72	1.39	5	7.36	25	7.13	24	15.45	53
S13	0.180	0.72	1.12	5	6.18	25	5.89	24	13.08	53
S14	0.184	0.72	1.20	5	6.33	25	6.10	24	13.45	53
S15	0.195	0.72	1.24	5	6.77	25	6.50	24	14.20	53
S16	0.188	0.72	1.24	5	6.48	25	6.24	24	13.71	53
S17	0.284	0.72	1.89	5	9.94	25	9.96	25	20.64	52
S18	0.285	0.72	1.98	5	9.99	25	9.98	25	20.69	52
Average	**0.260**	**0.72**	**1.78**	**5**	**9.06**	**25**	**9.15**	**25**	**19.03**	**52**

Table A6.4.1. Fractionation of chromium concentrations and its percentage from the total chromium in sediments of the Muvattupuzha River during September 2005

Station position	Cr_{exch} (ppm)	$\%Cr_{exch}$	Cr_{carb} (ppm)	$\%Cr_{carb}$	Cr_{redu} (ppm)	$\%Cr_{redu}$	Cr_{org} (ppm)	$\%Cr_{org}$	Cr_{resid} (ppm)	$\%Cr_{resid}$
S1	0.263	0.73	1.83	5	9.20	26	8.87	25	19.10	53
S2	0.250	0.72	1.70	5	8.69	25	8.62	25	18.29	53
S3	0.157	0.62	1.16	5	6.34	25	5.95	23	13.51	53
S4	0.164	0.72	1.02	5	5.60	25	5.35	24	12.10	53
S5	0.151	0.62	1.15	5	6.02	25	5.77	24	13.00	53
S6	0.200	0.72	1.29	5	6.27	23	6.75	24	14.75	53
S7	0.216	0.72	1.46	5	7.54	25	7.14	24	15.97	53
S8	0.214	0.73	1.45	5	7.52	25	6.99	24	15.70	53
S9	0.206	0.72	1.38	5	7.19	25	6.69	23	15.19	53
S10	0.173	0.72	1.10	5	5.95	25	5.49	23	12.86	53
S11	0.152	0.72	0.93	4	5.19	25	4.70	22	11.26	53
S12	0.120	0.71	0.71	4	4.08	24	3.70	22	9.03	54
S13	0.081	0.71	0.41	4	2.65	23	2.14	19	6.15	54
S14	0.138	0.72	0.86	4	4.71	24	4.37	23	10.31	53
S15	0.185	0.72	1.17	5	6.41	25	6.12	24	13.62	53
S16	0.210	0.72	1.41	5	7.29	25	7.42	25	15.47	53
S17	0.217	0.72	1.40	5	7.53	25	7.40	25	16.00	53
S18	0.210	0.72	1.41	5	7.30	25	7.10	24	15.49	53
Average	**0.184**	**0.71**	**1.21**	**5**	**6.42**	**25**	**6.14**	**23**	**13.77**	**53**

Table A6.4.2. Fractionation of chromium concentrations and its percentage from the total chromium in sediments of the Muvattupuzha River during November 2005

Station position	Cr_{exch} (ppm)	$\%Cr_{exch}$	Cr_{carb} (ppm)	$\%Cr_{carb}$	Cr_{redu} (ppm)	$\%Cr_{redu}$	Cr_{org} (ppm)	$\%Cr_{org}$	Cr_{resid} (ppm)	$\%Cr_{resid}$
S1	0.157	0.72	1.02	5	5.39	25	4.99	23	11.42	53
S2	0.143	0.72	0.89	4	4.87	24	4.51	23	10.51	53
S3	0.099	0.57	0.73	4	4.22	24	3.80	22	9.20	53
S4	0.081	0.71	0.41	4	2.65	23	2.11	19	6.10	54
S5	0.070	0.52	0.54	4	3.15	24	2.71	20	7.13	53
S6	0.122	0.72	0.71	4	3.48	20	3.78	22	9.04	53
S7	0.126	0.71	0.77	4	4.28	24	3.87	22	9.33	53
S8	0.105	0.72	0.61	4	4.26	29	3.05	21	7.82	53
S9	0.108	0.71	0.64	4	3.65	24	3.12	21	8.05	53
S10	0.103	0.71	0.57	4	3.43	24	3.00	21	7.69	53
S11	0.099	0.71	0.54	4	3.30	24	2.87	21	7.40	53
S12	0.120	0.71	0.71	4	4.07	24	3.71	22	8.92	53
S13	0.131	0.72	0.77	4	4.43	24	3.22	18	9.60	53
S14	0.122	0.72	0.73	4	4.12	24	3.78	22	9.03	53
S15	0.103	0.71	0.57	4	3.46	24	3.01	21	7.66	53
S16	0.097	0.71	0.55	4	3.23	24	2.78	20	7.26	53
S17	0.108	0.71	0.60	4	3.62	24	3.25	21	8.06	53
S18	0.114	0.71	0.68	4	3.85	24	3.38	21	8.49	53
Average	**0.112**	**0.70**	**0.67**	**4**	**3.86**	**24**	**3.38**	**21**	**8.48**	**53**

Table A6.4.3. Fractionation of chromium concentrations and its percentage from the total chromium in sediments of the Muvattupuzha River during January 2006

Station position	Cr_{exch} (ppm)	$\%Cr_{exch}$	Cr_{carb} (ppm)	$\%Cr_{carb}$	Cr_{redu} (ppm)	$\%Cr_{redu}$	Cr_{org} (ppm)	$\%Cr_{org}$	Cr_{resid} (ppm)	$\%Cr_{resid}$
S1	0.173	0.72	1.14	5	5.96	25	5.66	24	12.58	53
S2	0.159	0.72	1.02	5	5.46	25	5.04	23	11.70	53
S3	0.125	0.60	0.92	4	5.16	25	4.81	23	11.07	53
S4	0.140	0.72	0.85	4	4.76	24	4.40	23	10.32	53
S5	0.105	0.58	0.80	4	4.39	24	4.01	22	9.63	53
S6	0.146	0.72	0.89	4	4.32	21	4.56	23	10.74	53
S7	0.155	0.72	0.99	5	5.33	25	4.99	23	11.45	53
S8	0.139	0.72	0.87	5	5.32	28	4.35	23	10.24	53
S9	0.112	0.71	0.67	4	3.79	24	3.38	22	8.35	53
S10	0.103	0.71	0.58	4	3.43	24	3.00	21	7.71	53
S11	0.116	0.72	0.66	4	3.90	24	3.51	22	8.60	53
S12	0.115	0.71	0.67	4	3.89	24	3.67	23	8.57	53
S13	0.116	0.72	0.66	4	3.91	24	3.49	22	8.59	53
S14	0.121	0.72	0.73	4	4.10	24	3.34	20	9.00	53
S15	0.123	0.72	0.72	4	4.19	24	3.70	22	9.13	53
S16	0.135	0.72	0.83	4	4.58	24	4.18	22	9.95	53
S17	0.152	0.72	0.93	4	5.21	25	4.88	23	11.23	53
S18	0.146	0.72	0.92	5	4.99	25	4.63	23	10.77	53
Average	**0.132**	**0.70**	**0.82**	**4**	**4.59**	**24**	**4.20**	**22**	**9.98**	**53**

Table A6.4.4. Fractionation of chromium concentrations and its percentage from the total chromium in sediments of the Muvattupuzha River during March 2006

Station position	Cr_{exch} (ppm)	$\%Cr_{exch}$	Cr_{carb} (ppm)	$\%Cr_{carb}$	Cr_{redu} (ppm)	$\%Cr_{redu}$	Cr_{org} (ppm)	$\%Cr_{org}$	Cr_{resid} (ppm)	$\%Cr_{resid}$
S1	0.270	0.73	1.89	5	9.48	26	6.35	17	19.42	52
S2	0.260	0.72	1.78	5	9.04	25	7.09	20	18.77	52
S3	0.221	0.65	1.62	5	8.64	25	6.45	19	17.88	52
S4	0.240	0.73	1.58	5	8.31	25	6.16	19	17.33	52
S5	0.118	0.59	0.90	5	4.86	24	3.53	18	10.54	53
S6	0.087	0.71	0.45	4	2.20	18	2.37	19	6.51	53
S7	0.061	0.70	0.28	3	1.96	22	1.43	16	4.74	54
S8	0.064	0.71	0.30	3	1.96	22	1.50	17	4.87	54
S9	0.064	0.70	0.30	3	2.07	23	1.46	16	4.92	54
S10	0.066	0.70	0.31	3	2.13	23	1.60	17	5.09	54
S11	0.070	0.71	0.33	3	2.28	23	1.75	18	5.37	54
S12	0.070	0.70	0.34	3	2.28	23	1.76	18	5.37	54
S13	0.072	0.71	0.34	3	2.34	23	1.83	18	5.46	54
S14	0.093	0.71	0.52	4	3.10	24	2.54	19	6.98	53
S15	0.100	0.71	0.55	4	3.36	24	2.88	21	7.47	53
S16	0.107	0.71	0.62	4	3.58	24	3.04	20	7.94	53
S17	0.070	0.71	0.33	3	2.28	23	1.71	17	5.37	54
S18	0.066	0.70	0.31	3	2.11	23	1.54	17	5.02	54
Average	**0.117**	**0.70**	**0.71**	**4**	**4.00**	**23**	**3.05**	**18**	**8.84**	**53**

Table A6.4.5. Fractionation of chromium concentrations and its percentage from the total chromium in sediments of the Muvattupuzha River during May 2006

Station position	Cr_{exch} (ppm)	$\%Cr_{exch}$	Cr_{carb} (ppm)	$\%Cr_{carb}$	Cr_{redu} (ppm)	$\%Cr_{redu}$	Cr_{org} (ppm)	$\%Cr_{org}$	Cr_{resid} (ppm)	$\%Cr_{resid}$
S1	0.015	0.40	0.13	3	0.65	17	3.85	10	1.26	34
S2	0.038	0.46	0.25	3	1.44	17	3.84	11	2.80	34
S3	0.026	0.44	0.18	3	1.03	17	4.63	14	2.30	39
S4	0.032	0.68	0.21	4	0.80	17	5.24	16	2.14	46
S5	0.013	0.23	0.20	4	1.11	20	2.82	14	2.63	48
S6	0.041	0.69	0.18	3	1.29	21	2.63	22	2.91	49
S7	0.048	0.69	0.20	3	1.49	21	1.89	22	3.81	55
S8	0.057	0.70	0.25	3	1.49	18	1.76	19	4.44	54
S9	0.072	0.71	0.36	4	2.36	23	1.71	19	5.50	54
S10	0.078	0.71	0.39	4	2.53	23	2.05	22	5.91	54
S11	0.084	0.71	0.43	4	2.75	23	2.24	22	6.31	54
S12	0.095	0.71	0.52	4	3.16	24	2.20	22	7.13	53
S13	0.112	0.72	0.63	4	3.78	24	2.25	22	8.32	53
S14	0.138	0.72	0.85	4	4.68	24	2.32	18	10.15	53
S15	0.159	0.72	0.98	4	5.50	25	2.37	17	11.69	53
S16	0.194	0.72	1.29	5	6.70	25	2.73	18	14.15	53
S17	0.055	0.70	0.25	3	1.71	22	1.85	19	4.26	54
S18	0.056	0.70	0.24	3	1.77	22	1.89	20	4.36	54
Average	**0.073**	**0.63**	**0.42**	**4**	**2.46**	**21**	**2.68**	**18**	**5.56**	**50**

Table A6.4.6. Fractionation of zinc concentrations and its percentage from the total zinc in sediments of the Muvattupuzha River during July 2005

Station position	Zn_{exch} (ppm)	$\%Zn_{exch}$	Zn_{carb} (ppm)	$\%Zn_{carb}$	Zn_{redu} (ppm)	$\%Zn_{redu}$	Zn_{org} (ppm)	$\%Zn_{org}$	Zn_{resid} (ppm)	$\%Zn_{resid}$
S1	1.11	8	0.76	5	1.50	10	2.86	20	8.32	57
S2	3.25	10	2.22	7	4.39	14	8.39	27	14.71	47
S3	5.33	11	3.65	8	7.21	15	13.77	29	20.94	44
S4	5.69	11	3.90	8	7.69	15	14.69	29	22.01	44
S5	6.32	11	4.33	8	8.55	16	16.34	30	23.91	43
S6	6.89	12	4.72	8	9.31	16	17.79	30	25.59	43
S7	7.31	12	5.01	8	9.89	16	18.89	30	26.86	43
S8	6.86	12	4.70	8	9.28	16	17.73	30	25.52	43
S9	6.72	12	4.60	8	9.09	16	17.37	30	25.10	43
S10	4.13	11	2.83	7	5.58	15	10.67	28	17.35	46
S11	2.77	10	1.90	7	3.74	14	7.15	26	13.28	48
S12	2.43	10	1.66	7	3.28	13	6.27	25	12.26	49
S13	1.95	9	1.34	6	2.64	12	5.04	24	10.84	51
S14	3.84	11	2.63	7	5.19	15	9.91	28	16.48	46
S15	5.56	11	3.81	8	7.52	15	14.37	29	21.63	44
S16	5.84	11	4.00	8	7.90	15	15.09	29	22.46	44
S17	6.96	12	4.77	8	9.41	16	17.97	30	25.80	43
S18	7.19	12	4.93	8	9.72	16	18.58	30	26.50	43
Average	**5.01**	**11**	**3.43**	**7**	**6.77**	**15**	**12.94**	**28**	**19.98**	**46**

Table A6.4.7. Fractionation of zinc concentrations and its percentage from the total zinc in sediments of the Muvattupuzha River during September 2005

Station position	Zn_{exch} (ppm)	$\%Zn_{exch}$	Zn_{carb} (ppm)	$\%Zn_{carb}$	Zn_{redu} (ppm)	$\%Zn_{redu}$	Zn_{org} (ppm)	$\%Zn_{org}$	Zn_{resid} (ppm)	$\%Zn_{resid}$
S1	8.45	12	5.81	8	11.53	16	21.82	30	30.34	42
S2	8.16	12	5.61	8	11.13	16	21.06	30	29.45	43
S3	7.76	12	5.33	8	10.58	16	20.01	30	28.24	43
S4	7.60	12	5.19	8	10.26	16	19.59	30	27.67	43
S5	7.78	12	5.34	8	10.61	16	20.07	30	28.31	43
S6	8.22	12	5.64	8	11.21	16	21.20	30	29.54	42
S7	8.34	12	5.73	8	11.37	16	21.51	30	29.98	42
S8	7.99	12	5.49	8	10.80	16	20.63	30	28.96	43
S9	7.98	12	5.48	8	10.87	16	20.57	30	28.89	43
S10	4.29	11	2.95	8	5.85	15	11.07	28	17.86	46
S11	3.25	10	2.22	7	4.43	14	8.39	27	14.75	47
S12	2.64	10	1.81	7	3.57	13	6.81	26	12.89	49
S13	2.11	9	1.45	6	2.88	13	5.45	24	11.34	51
S14	5.93	11	4.07	8	8.09	16	15.30	29	22.77	44
S15	8.32	12	5.71	8	11.34	16	21.46	30	29.92	42
S16	9.26	12	6.36	8	12.50	16	23.88	31	32.72	42
S17	8.16	12	5.60	8	11.13	16	21.05	30	29.45	43
S18	8.23	12	5.65	8	11.11	16	21.22	30	29.65	42
Average	**6.91**	**11**	**4.75**	**8**	**9.40**	**16**	**17.84**	**29**	**25.71**	**44**

Table A6.4.8. Fractionation of zinc concentrations and its percentage from the total zinc in sediments of the Muvattupuzha River during November 2005

Station position	Zn_{exch} (ppm)	$\%Zn_{exch}$	Zn_{carb} (ppm)	$\%Zn_{carb}$	Zn_{redu} (ppm)	$\%Zn_{redu}$	Zn_{org} (ppm)	$\%Zn_{org}$	Zn_{resid} (ppm)	$\%Zn_{resid}$
S1	4.54	11	3.11	8	6.11	15	11.78	28	18.55	45
S2	4.03	11	2.74	7	5.39	14	10.40	28	16.96	46
S3	2.87	10	1.96	7	3.85	14	7.43	26	13.56	48
S4	2.13	9	1.45	6	2.86	13	5.52	24	11.35	50
S5	3.75	11	2.56	7	5.14	15	9.72	28	16.19	46
S6	4.37	11	3.00	8	5.84	15	11.27	28	17.97	45
S7	4.99	11	3.41	8	6.70	15	12.93	29	19.87	44
S8	4.16	11	2.84	7	5.59	15	10.79	28	17.42	45
S9	3.86	11	2.64	7	5.19	14	10.02	28	16.53	46
S10	3.69	11	2.55	7	5.06	15	9.58	28	16.02	46
S11	1.26	8	0.86	5	1.69	11	3.26	21	8.76	56
S12	1.04	7	0.71	5	1.39	10	2.68	19	8.09	58
S13	0.88	7	0.60	5	1.18	9	2.27	18	7.62	60
S14	2.57	10	1.76	7	3.52	14	6.66	26	12.67	49
S15	4.34	11	2.99	8	5.83	15	11.25	28	17.93	45
S16	4.77	11	3.25	8	6.38	15	12.31	29	19.16	45
S17	4.38	11	3.00	7	5.89	15	11.36	28	18.06	45
S18	4.63	11	3.17	8	6.23	15	12.01	29	18.81	45
Average	**3.46**	**10**	**2.37**	**7**	**4.66**	**14**	**8.96**	**26**	**15.31**	**48**

Table A6.4.9. Fractionation of zinc concentrations and its percentage from the total zinc in sediments of the Muvattupuzha River during January 2006

Station position	Zn_{exch} (ppm)	$\%Zn_{exch}$	Zn_{carb} (ppm)	$\%Zn_{carb}$	Zn_{redu} (ppm)	$\%Zn_{redu}$	Zn_{org} (ppm)	$\%Zn_{org}$	Zn_{resid} (ppm)	$\%Zn_{resid}$
S1	3.81	11	2.62	7	5.16	14	9.95	28	16.44	46
S2	3.73	11	2.54	7	4.99	14	9.63	28	16.08	46
S3	3.59	11	2.45	7	4.82	14	9.31	27	15.70	46
S4	3.50	10	2.41	7	4.73	14	9.13	27	15.50	46
S5	4.19	11	2.88	7	5.66	15	10.92	28	17.57	45
S6	4.60	11	3.16	8	6.22	15	12.00	29	18.79	45
S7	4.90	11	3.37	8	6.63	15	12.78	29	19.70	44
S8	4.03	11	2.77	7	5.46	15	10.53	28	17.10	45
S9	2.78	10	1.90	7	3.74	14	7.22	26	13.31	48
S10	2.74	10	1.89	7	3.71	13	7.15	26	13.23	48
S11	2.69	10	1.85	7	3.64	13	7.03	26	13.06	48
S12	1.57	9	1.07	6	2.10	12	4.06	22	9.66	53
S13	0.51	5	0.35	4	1.06	11	1.34	13	6.55	66
S14	2.73	10	1.88	7	3.69	13	7.13	26	13.17	48
S15	4.34	11	2.98	7	5.87	15	11.32	28	17.97	45
S16	7.14	12	4.91	8	9.65	16	18.63	30	26.33	42
S17	5.05	11	3.48	8	6.83	15	13.18	29	20.16	44
S18	4.97	11	3.42	8	6.72	15	12.97	29	19.86	44
Average	**3.72**	**10**	**2.55**	**7**	**5.04**	**14**	**9.68**	**27**	**16.12**	47

Table A6.5.0. Fractionation of zinc concentrations and its percentage from the total zinc in sediments of the Muvattupuzha River during March 2006

Station position	Zn_{exch} (ppm)	$\%Zn_{exch}$	Zn_{carb} (ppm)	$\%Zn_{carb}$	Zn_{redu} (ppm)	$\%Zn_{redu}$	Zn_{org} (ppm)	$\%Zn_{org}$	Zn_{resid} (ppm)	$\%Zn_{resid}$
S1	8.95	12	6.20	8	12.08	16	23.53	31	31.85	42
S2	6.59	11	4.49	8	8.97	15	17.31	30	24.76	43
S3	4.19	11	2.86	7	5.65	14	11.01	28	17.57	45
S4	3.50	10	2.43	7	4.72	14	9.20	27	15.51	46
S5	2.97	10	2.03	7	4.01	14	7.81	27	13.92	47
S6	1.84	9	1.26	6	2.51	12	4.84	24	10.53	51
S7	0.88	7	0.59	5	1.18	9	2.29	18	7.63	59
S8	2.97	10	2.03	7	4.05	14	7.81	27	13.92	47
S9	3.10	10	2.11	7	4.22	14	8.15	27	14.31	47
S10	3.22	10	2.20	7	4.35	14	8.47	27	14.67	47
S11	5.80	11	3.93	8	7.77	15	15.14	29	22.34	43
S12	2.07	9	1.43	6	2.79	13	5.44	24	11.22	50
S13	1.86	9	1.27	6	2.53	12	4.89	24	10.59	51
S14	3.42	10	2.34	7	4.62	14	9.00	27	15.28	46
S15	4.50	11	3.12	8	6.07	15	11.83	28	18.51	45
S16	6.42	14	4.38	9	8.74	19	16.87	36	24.25	52
S17	1.86	9	1.27	6	2.51	12	4.89	24	10.59	51
S18	2.40	10	1.63	7	3.26	13	6.30	25	12.19	49
Average	**3.70**	**10**	**2.53**	**7**	**5.00**	**14**	**9.71**	**27**	**16.09**	**48**

Table A6.5.1. Fractionation of zinc concentrations and its percentage from the total zinc in sediments of the Muvattupuzha River during May 2006

Station position	Zn_{exch} (ppm)	$\%Zn_{exch}$	Zn_{carb} (ppm)	$\%Zn_{carb}$	Zn_{redu} (ppm)	$\%Zn_{redu}$	Zn_{org} (ppm)	$\%Zn_{org}$	Zn_{resid} (ppm)	$\%Zn_{resid}$
S1	8.28	12	5.69	8	11.20	16	21.82	30	29.81	42
S2	6.26	11	4.30	8	8.36	15	16.46	30	23.79	43
S3	1.22	8	0.83	5	1.65	11	3.21	21	4.66	30
S4	0.55	5	0.38	4	0.73	7	1.44	14	5.65	55
S5	0.88	7	0.60	5	1.17	9	2.31	18	5.64	44
S6	0.89	7	0.61	5	1.19	9	2.35	18	5.69	44
S7	1.13	8	0.77	5	1.51	10	2.94	20	6.36	43
S8	0.44	5	0.30	3	0.59	6	1.17	12	4.34	46
S9	0.45	8	0.33	6	0.58	10	0.85	14	2.13	36
S10	0.92	7	0.63	5	1.23	9	2.41	18	5.76	44
S11	1.03	7	0.70	5	1.38	10	2.68	19	5.06	36
S12	0.91	7	0.63	5	1.22	9	2.40	18	5.75	44
S13	0.54	5	0.37	4	0.73	7	1.43	14	4.64	45
S14	3.54	10	2.42	7	4.78	14	9.32	27	15.61	46
S15	7.29	11	5.00	8	9.73	15	19.16	30	26.79	42
S16	7.48	11	5.15	8	10.02	15	19.72	30	27.51	42
S17	0.77	6	0.53	4	1.05	9	2.04	17	5.33	44
S18	0.91	7	0.63	5	1.23	9	2.40	18	5.75	44
Average	**2.42**	**8**	**1.66**	**5**	**3.24**	**11**	**6.34**	**21**	**10.57**	**43**

Table A6.5.2. Fractionation of cadmium concentrations and its percentage from the total cadmium in sediments of the Muvattupuzha River during July 2005

Station position	Cd_{exch} (ppm)	$\%Cd_{exch}$	Cd_{carb} (ppm)	$\%Cd_{carb}$	Cd_{redu} (ppm)	$\%Cd_{redu}$	Cd_{org} (ppm)	$\%Cd_{org}$	Cd_{resid} (ppm)	$\%Cd_{resid}$
S1	0.069	39	0.0169	9	0.0044	2	0.0146	8	0.0266	15
S2	0.114	41	0.0276	10	0.0084	3	0.0266	10	0.0511	18
S3	0.141	43	0.0329	10	0.0107	3	0.0329	10	0.0621	19
S4	0.162	43	0.0396	11	0.0125	3	0.0387	10	0.0742	20
S5	0.165	44	0.0397	11	0.0123	3	0.0389	10	0.0736	19
S6	0.174	43	0.0434	11	0.0130	3	0.0419	10	0.0793	20
S7	0.179	44	0.0436	11	0.0132	3	0.0427	10	0.0819	20
S8	0.184	44	0.0447	11	0.0138	3	0.0437	10	0.0826	20
S9	0.187	44	0.0463	11	0.0146	3	0.0450	11	0.0857	20
S10	0.192	44	0.0472	11	0.0145	3	0.0468	11	0.0870	20
S11	0.146	42	0.0366	11	0.0110	3	0.0351	10	0.0662	19
S12	0.128	42	0.0302	10	0.0091	3	0.0294	10	0.0557	18
S13	0.125	42	0.0295	10	0.0090	3	0.0289	10	0.0541	18
S14	0.132	42	0.0319	10	0.0095	3	0.0317	10	0.0605	19
S15	0.140	42	0.0356	11	0.0103	3	0.0323	10	0.0621	19
S16	0.142	42	0.0350	10	0.0107	3	0.0335	10	0.0636	19
S17	0.179	43	0.0442	11	0.0136	3	0.0422	10	0.0816	20
S18	0.183	43	0.0456	11	0.0140	3	0.0430	10	0.0842	20
Average	**0.152**	**43**	**0.0372**	**10**	**0.0114**	**3**	**0.0360**	**10**	**0.0685**	**19**

Table A6.5.3. Fractionation of cadmium concentrations and its percentage from the total cadmium in sediments of the Muvattupuzha River during September 2005

Station position	Cd_{exch} (ppm)	$\%Cd_{exch}$	Cd_{carb} (ppm)	$\%Cd_{carb}$	Cd_{redu} (ppm)	$\%Cd_{redu}$	Cd_{org} (ppm)	$\%Cd_{org}$	Cd_{resid} (ppm)	$\%Cd_{resid}$
S1	0.139	43	0.0343	11	0.0103	3	0.0327	10	0.0616	19
S2	0.124	42	0.0297	10	0.0096	3	0.0291	10	0.0548	18
S3	0.120	42	0.0290	10	0.0086	3	0.0273	10	0.0517	18
S4	0.112	41	0.0271	10	0.0085	3	0.0253	9	0.0482	18
S5	0.143	43	0.0342	10	0.0105	3	0.0336	10	0.0626	19
S6	0.174	43	0.0415	10	0.0136	3	0.0421	11	0.0786	20
S7	0.165	43	0.0405	11	0.0121	3	0.0401	10	0.0748	20
S8	0.120	42	0.0282	10	0.0090	3	0.0277	10	0.0524	18
S9	0.108	41	0.0263	10	0.0080	3	0.0254	10	0.0468	18
S10	0.074	39	0.0159	8	0.0049	3	0.0160	8	0.0295	15
S11	0.062	38	0.0166	10	0.0036	2	0.0121	7	0.0233	14
S12	0.048	35	0.0142	10	0.0025	2	0.0098	7	0.0167	12
S13	0.114	41	0.0289	10	0.0083	3	0.0355	13	0.0511	18
S14	0.152	43	0.0378	11	0.0111	3	0.0347	10	0.0681	19
S15	0.166	44	0.0411	11	0.0124	3	0.0395	10	0.0753	20
S16	0.181	44	0.0445	11	0.0135	3	0.0438	11	0.0823	20
S17	0.134	42	0.0322	10	0.0099	3	0.0320	10	0.0599	19
S18	0.138	43	0.0327	10	0.0101	3	0.0301	9	0.0601	19
Average	**0.126**	**42**	**0.0308**	**10**	**0.0093**	**3**	**0.0298**	**10**	**0.0554**	**18**

Table A6.5.4. Fractionation of cadmium concentrations and its percentage from the total cadmium in sediments of the Muvattupuzha River during November 2005

Station position	Cd_{exch} (ppm)	$\%Cd_{exch}$	Cd_{carb} (ppm)	$\%Cd_{carb}$	Cd_{redu} (ppm)	$\%Cd_{redu}$	Cd_{org} (ppm)	$\%Cd_{org}$	Cd_{resid} (ppm)	$\%Cd_{resid}$
S1	0.194	44	0.0476	11	0.0151	3	0.0463	11	0.0880	20
S2	0.172	43	0.0410	10	0.0125	3	0.0416	11	0.0781	20
S3	0.152	43	0.0382	11	0.0114	3	0.0371	10	0.0687	19
S4	0.150	43	0.0364	10	0.0112	3	0.0355	10	0.0668	19
S5	0.145	43	0.0357	11	0.0105	3	0.0339	10	0.0652	19
S6	0.170	43	0.0428	11	0.0131	3	0.0409	10	0.0772	20
S7	0.191	44	0.0462	11	0.0145	3	0.0465	11	0.0877	20
S8	0.189	44	0.0468	11	0.0104	2	0.0454	10	0.0869	20
S9	0.180	44	0.0432	10	0.0132	3	0.0438	11	0.0810	20
S10	0.161	44	0.0388	10	0.0115	3	0.0378	10	0.0716	19
S11	0.145	43	0.0359	11	0.0113	3	0.0345	10	0.0655	19
S12	0.130	42	0.0311	10	0.0100	3	0.0301	10	0.0574	19
S13	0.118	42	0.0267	9	0.0090	3	0.0271	10	0.0513	18
S14	0.149	43	0.0359	10	0.0111	3	0.0349	10	0.0661	19
S15	0.164	43	0.0390	10	0.0125	3	0.0349	9	0.0731	19
S16	0.179	44	0.0440	11	0.0136	3	0.0431	10	0.0810	20
S17	0.194	44	0.0479	11	0.0147	3	0.0465	11	0.0884	20
S18	0.190	44	0.0470	11	0.0145	3	0.0461	11	0.0868	20
Average	**0.165**	**43**	**0.0402**	**11**	**0.0122**	**3**	**0.0392**	**10**	**0.0745**	**19**

Table A6.5.5. Fractionation of cadmium concentrations and its percentage from the total cadmium in sediments of the Muvattupuzha River during January 2006

Station position	Cd_{exch} (ppm)	$\%Cd_{exch}$	Cd_{carb} (ppm)	$\%Cd_{carb}$	Cd_{redu} (ppm)	$\%Cd_{redu}$	Cd_{org} (ppm)	$\%Cd_{org}$	Cd_{resid} (ppm)	$\%Cd_{resid}$
S1	0.223	44	0.0567	11	0.0174	3	0.0544	11	0.1030	20
S2	0.221	44	0.0551	11	0.0170	3	0.0435	9	0.1019	20
S3	0.209	44	0.0509	11	0.0155	3	0.0409	9	0.0955	20
S4	0.203	44	0.0503	11	0.0155	3	0.0497	11	0.0930	20
S5	0.218	44	0.0534	11	0.0164	3	0.0134	3	0.1006	20
S6	0.221	44	0.0548	11	0.0170	3	0.0541	11	0.1018	20
S7	0.208	44	0.0516	11	0.0154	3	0.0511	11	0.0503	11
S8	0.182	44	0.0438	11	0.0138	3	0.0431	10	0.0825	20
S9	0.161	43	0.0392	11	0.0125	3	0.0384	10	0.0731	20
S10	0.156	43	0.0369	10	0.0117	3	0.0368	10	0.0701	19
S11	0.150	43	0.0362	10	0.0111	3	0.0351	10	0.0675	19
S12	0.161	44	0.0396	11	0.0119	3	0.0375	10	0.0716	19
S13	0.127	42	0.0301	10	0.0089	3	0.0301	10	0.0562	19
S14	0.094	40	0.0226	10	0.0066	3	0.0216	9	0.0398	17
S15	0.154	43	0.0374	10	0.0119	3	0.0371	10	0.0691	19
S16	0.215	44	0.0522	11	0.0166	3	0.0528	11	0.0983	20
S17	0.185	44	0.0457	11	0.0141	3	0.0451	11	0.0841	20
S18	0.189	44	0.0466	11	0.0143	3	0.0457	11	0.0856	20
Average	**0.182**	**44**	**0.0446**	**11**	**0.0137**	**3**	**0.0406**	**10**	**0.0802**	**19**

Table A6.5.6. Fractionation of cadmium concentrations and its percentage from the total cadmium in sediments of the Muvattupuzha River during March 2006

Station position	Cd_{exch} (ppm)	$\%Cd_{exch}$	Cd_{carb} (ppm)	$\%Cd_{carb}$	Cd_{redu} (ppm)	$\%Cd_{redu}$	Cd_{org} (ppm)	$\%Cd_{org}$	Cd_{resid} (ppm)	$\%Cd_{resid}$
S1	0.380	46	0.0972	12	0.0298	4	0.0649	8	0.1797	22
S2	0.255	45	0.0643	11	0.0198	3	0.0622	11	0.1183	21
S3	0.197	44	0.0485	11	0.0145	3	0.0466	10	0.0896	20
S4	0.175	44	0.0430	11	0.0133	3	0.0415	10	0.0790	20
S5	0.155	43	0.0377	10	0.0113	3	0.0371	10	0.0696	19
S6	0.126	42	0.0300	10	0.0093	3	0.0290	10	0.0555	18
S7	0.099	41	0.0225	9	0.0065	3	0.0216	9	0.0410	17
S8	0.106	41	0.0248	10	0.0079	3	0.0228	9	0.0459	18
S9	0.115	42	0.0270	10	0.0083	3	0.0260	9	0.0495	18
S10	0.209	44	0.0519	11	0.0163	3	0.0511	11	0.0956	20
S11	0.078	40	0.0167	9	0.0051	3	0.0157	8	0.0308	16
S12	0.069	38	0.0149	8	0.0049	3	0.0135	7	0.0276	15
S13	0.124	42	0.0293	10	0.0090	3	0.0281	10	0.0541	18
S14	0.142	43	0.0342	10	0.0104	3	0.0336	10	0.0636	19
S15	0.151	43	0.0367	10	0.0113	3	0.0352	10	0.0681	19
S16	0.178	44	0.0438	11	0.0132	3	0.0419	10	0.0806	20
S17	0.100	41	0.0230	9	0.0071	3	0.0223	9	0.0426	17
S18	0.096	40	0.0221	9	0.0068	3	0.0213	9	0.0409	17
Average	**0.153**	**42**	**0.0371**	**10**	**0.0114**	**3**	**0.0341**	**9**	**0.0684**	**19**

Table A6.5.7. Fractionation of cadmium concentrations and its percentage from the total cadmium in sediments of the Muvattupuzha River during May 2006

Station position	Cd_{exch} (ppm)	$\%Cd_{exch}$	Cd_{carb} (ppm)	$\%Cd_{carb}$	Cd_{redu} (ppm)	$\%Cd_{redu}$	Cd_{org} (ppm)	$\%Cd_{org}$	Cd_{resid} (ppm)	$\%Cd_{resid}$
S1	0.248	45	0.0627	11	0.0192	3	0.0606	11	0.1150	21
S2	0.231	44	0.0571	11	0.0173	3	0.0558	11	0.1071	21
S3	0.223	44	0.0550	11	0.0171	3	0.0535	11	0.1018	20
S4	0.215	44	0.0544	11	0.0163	3	0.0521	11	0.0997	20
S5	0.128	42	0.0311	10	0.0094	3	0.0293	10	0.0561	18
S6	0.067	37	0.0174	10	0.0047	3	0.0182	10	0.0375	21
S7	0.023	35	0.0075	12	0.0020	3	0.0060	9	0.0120	18
S8	0.028	38	0.0083	11	0.0024	3	0.0076	10	0.0135	18
S9	0.035	40	0.0078	9	0.0026	3	0.0081	9	0.0182	21
S10	0.039	39	0.0083	8	0.0023	2	0.0081	8	0.0180	18
S11	0.076	39	0.0170	9	0.0052	3	0.0161	8	0.0406	21
S12	0.093	41	0.0207	9	0.0064	3	0.0201	9	0.0483	21
S13	0.116	42	0.0276	10	0.0085	3	0.0252	9	0.0500	18
S14	0.119	41	0.0281	10	0.0087	3	0.0269	9	0.0521	18
S15	0.180	44	0.0445	11	0.0135	3	0.0425	10	0.0814	20
S16	0.234	45	0.0580	11	0.0180	3	0.0566	11	0.1076	21
S17	0.024	36	0.0068	10	0.0022	3	0.0060	9	0.0120	18
S18	0.025	37	0.0076	11	0.0020	3	0.0065	9	0.0128	19
Average	**0.117**	**41**	**0.0289**	**10**	**0.0088**	**3**	**0.0277**	**10**	**0.0546**	**20**

Table A6.5.8. Fractionation of lead concentrations and its percentage from the total lead in sediments of the Muvattupuzha River during July 2005

Station position	Pb_{exch} (ppm)	$\%Pb_{exch}$	Pb_{carb} (ppm)	$\%Pb_{carb}$	Pb_{redu} (ppm)	$\%Pb_{redu}$	Pb_{org} (ppm)	$\%Pb_{org}$	Pb_{resid} (ppm)	$\%Pb_{resid}$
S1	2.45	73	0.019	0.58	0.17	5	0.25	8	0.52	16
S2	3.36	73	0.036	0.77	0.23	5	0.46	10	0.64	14
S3	6.09	72	0.084	0.99	0.39	5	1.09	13	0.90	11
S4	8.37	72	0.124	1.06	0.53	5	1.61	14	1.17	10
S5	7.75	72	0.113	1.05	0.49	5	1.47	14	1.27	12
S6	7.19	72	0.103	1.03	0.46	5	1.34	13	1.19	12
S7	6.81	72	0.097	1.02	0.44	5	1.25	13	1.19	13
S8	7.81	72	0.114	1.05	0.50	5	1.48	14	1.17	11
S9	8.06	72	0.119	1.06	0.51	5	1.54	14	1.17	10
S10	9.29	72	0.141	1.08	0.58	5	1.82	14	1.37	11
S11	9.20	72	0.139	1.08	0.58	5	1.80	14	1.47	11
S12	9.07	72	0.137	1.08	0.57	5	1.77	14	1.42	11
S13	6.12	72	0.084	0.99	0.39	5	1.09	13	1.08	13
S14	5.72	72	0.077	0.97	0.37	5	1.00	13	1.22	15
S15	7.63	72	0.111	1.05	0.72	7	1.44	14	1.55	15
S16	11.99	71	0.188	1.12	0.82	5	2.44	15	1.82	11
S17	7.15	72	0.103	1.03	0.54	5	1.33	13	1.35	14
S18	6.83	72	0.097	1.02	0.55	6	1.26	13	1.35	14
Average	**7.27**	**72**	**0.105**	**1.00**	**0.49**	**5**	**1.36**	**13**	**1.21**	**12**

Table A6.5.9. Fractionation of lead concentrations and its percentage from the total lead in sediments of the Muvattupuzha River during September 2005

Station position	Pb_{exch} (ppm)	$\%Pb_{exch}$	Pb_{carb} (ppm)	$\%Pb_{carb}$	Pb_{redu} (ppm)	$\%Pb_{redu}$	Pb_{org} (ppm)	$\%Pb_{org}$	Pb_{resid} (ppm)	$\%Pb_{resid}$
S1	10.93	72	0.169	1.11	0.68	4	2.20	14	1.55	10
S2	12.01	72	0.188	1.12	0.75	4	2.45	15	1.65	10
S3	12.60	72	0.199	1.13	0.78	4	2.57	15	1.70	10
S4	13.55	72	0.215	1.14	0.84	4	2.80	15	1.78	9
S5	12.36	72	0.195	1.13	0.77	4	2.53	15	1.68	10
S6	11.62	72	0.181	1.12	0.73	4	2.35	14	1.61	10
S7	11.63	72	0.182	1.12	0.73	4	2.36	15	1.61	10
S8	3.43	73	0.037	0.78	0.23	5	0.48	10	0.90	19
S9	5.98	72	0.082	0.99	0.39	5	1.06	13	1.12	14
S10	9.11	72	0.137	1.08	0.57	5	1.77	14	1.39	11
S11	7.06	72	0.101	1.03	0.45	5	1.31	13	1.22	12
S12	5.00	72	0.065	0.93	0.33	5	0.84	12	1.04	15
S13	5.19	72	0.068	0.95	0.34	5	0.89	12	1.05	15
S14	5.85	72	0.079	0.98	0.38	5	1.03	13	1.11	14
S15	8.76	72	0.131	1.07	0.64	5	1.69	14	1.36	11
S16	13.57	72	0.216	1.14	0.84	4	2.81	15	1.78	9
S17	5.12	72	0.067	0.94	0.24	3	0.87	12	1.05	15
S18	3.77	73	0.043	0.82	0.23	5	0.56	11	0.83	16
Average	**8.75**	**72**	**0.131**	**1.03**	**0.55**	**5**	**1.70**	**13**	**1.36**	**12**

Table A6.6.0. Fractionation of lead concentrations and its percentage from the total lead in sediments of the Muvattupuzha River during November 2005

Station position	Pb_{exch} (ppm)	$\%Pb_{exch}$	Pb_{carb} (ppm)	$\%Pb_{carb}$	Pb_{redu} (ppm)	$\%Pb_{redu}$	Pb_{org} (ppm)	$\%Pb_{org}$	Pb_{resid} (ppm)	$\%Pb_{resid}$
S1	6.44	72	0.090	1.00	0.41	5	1.17	13	1.16	13
S2	5.70	72	0.076	0.97	0.37	5	0.99	13	1.09	14
S3	5.05	72	0.065	0.93	0.33	5	0.85	12	1.04	15
S4	4.84	72	0.062	0.92	0.32	5	0.80	12	1.02	15
S5	6.32	72	0.088	1.00	0.41	5	1.14	13	1.15	13
S6	8.26	71	0.122	1.06	0.52	5	1.58	14	1.32	11
S7	11.03	71	0.171	1.10	0.69	4	2.22	14	1.56	10
S8	8.94	72	0.133	1.07	0.56	5	1.73	14	1.37	11
S9	7.74	72	0.112	1.04	0.49	5	1.45	14	1.27	12
S10	6.75	72	0.095	1.01	0.43	5	1.24	13	1.19	13
S11	6.40	72	0.089	1.00	0.41	5	1.16	13	1.16	13
S12	5.04	72	0.065	0.93	0.33	5	0.85	12	1.04	15
S13	5.46	72	0.073	0.95	0.36	5	0.94	12	1.08	14
S14	7.13	72	0.102	1.03	0.46	5	1.33	13	1.23	12
S15	10.82	71	0.167	1.10	0.83	5	2.17	14	1.55	10
S16	13.99	71	0.223	1.14	1.03	5	2.90	15	1.83	9
S17	8.57	71	0.128	1.06	0.11	1	1.65	14	1.35	11
S18	8.58	71	0.128	1.06	0.11	1	1.66	14	1.35	11
Average	**7.61**	**72**	**0.110**	**1.02**	**0.45**	**4**	**1.43**	**13**	**1.26**	**12**

Table A6.6.1. Fractionation of lead concentrations and its percentage from the total lead in sediments of the Muvattupuzha River during January 2006

Station position	Pb_{exch} (ppm)	$\%Pb_{exch}$	Pb_{carb} (ppm)	$\%Pb_{carb}$	Pb_{redu} (ppm)	$\%Pb_{redu}$	Pb_{org} (ppm)	$\%Pb_{org}$	Pb_{resid} (ppm)	$\%Pb_{resid}$
S1	8.22	75	0.116	1.05	0.50	5	1.49	14	1.28	12
S2	7.86	75	0.110	1.04	0.48	5	1.42	13	1.25	12
S3	7.97	75	0.111	1.04	0.48	5	1.43	13	1.26	12
S4	8.00	75	0.112	1.04	0.49	5	1.44	13	1.27	12
S5	9.55	75	0.138	1.08	0.57	4	1.78	14	1.39	11
S6	9.40	71	0.143	1.08	0.59	4	1.85	14	1.41	11
S7	10.01	75	0.146	1.09	0.60	4	1.88	14	1.43	11
S8	8.52	75	0.121	1.06	0.52	5	1.56	14	1.31	11
S9	7.70	75	0.107	1.04	0.47	5	1.38	13	1.24	12
S10	7.35	75	0.101	1.03	0.45	5	1.31	13	1.21	12
S11	7.45	75	0.103	1.03	0.45	5	1.32	13	1.22	12
S12	6.05	75	0.079	0.98	0.37	5	1.02	13	1.10	14
S13	5.33	75	0.067	0.94	0.33	5	0.86	12	1.05	15
S14	7.47	75	0.103	1.03	0.46	5	1.33	13	1.22	12
S15	12.21	75	0.183	1.12	0.04	0	2.36	14	1.61	10
S16	13.92	74	0.212	1.13	0.82	4	2.73	15	1.75	9
S17	9.03	75	0.129	1.07	0.54	4	1.67	14	1.35	11
S18	9.18	75	0.132	1.07	0.55	4	1.70	14	1.36	11
Average	**8.62**	**74**	**0.123**	**1.05**	**0.48**	**4**	**1.58**	**14**	**1.32**	**12**

Table A6.6.2. Fractionation of lead concentrations and its percentage from the total lead in sediments of the Muvattupuzha River during March 2006

Station position	Pb_{exch} (ppm)	$\%Pb_{exch}$	Pb_{carb} (ppm)	$\%Pb_{carb}$	Pb_{redu} (ppm)	$\%Pb_{redu}$	Pb_{org} (ppm)	$\%Pb_{org}$	Pb_{resid} (ppm)	$\%Pb_{resid}$
S1	8.27	71	0.121	1.04	0.52	4	1.58	14	1.32	11
S2	8.23	75	0.114	1.03	0.50	4	1.48	13	1.28	12
S3	8.21	71	0.120	1.04	0.52	4	1.58	14	1.31	11
S4	8.41	71	0.124	1.04	0.53	4	1.61	14	1.33	11
S5	7.14	75	0.096	1.00	0.44	5	1.25	13	1.19	12
S6	4.47	72	0.055	0.88	0.30	5	0.71	11	0.99	16
S7	3.60	72	0.039	0.79	0.24	5	0.51	10	0.91	18
S8	4.08	72	0.048	0.84	0.27	5	0.63	11	0.95	17
S9	4.94	72	0.063	0.91	0.32	5	0.82	12	1.03	15
S10	6.70	75	0.088	0.98	0.41	5	1.15	13	1.15	13
S11	8.52	71	0.126	1.05	0.54	4	1.64	14	1.34	11
S12	6.41	71	0.089	0.98	0.41	5	1.16	13	1.15	13
S13	3.51	72	0.038	0.78	0.24	5	0.49	10	0.90	19
S14	6.53	71	0.091	0.99	0.42	5	1.19	13	1.17	13
S15	10.75	75	0.155	1.08	0.64	4	2.04	14	1.48	10
S16	13.51	71	0.213	1.11	0.84	4	2.78	15	1.77	9
S17	3.53	72	0.038	0.78	0.24	5	0.50	10	0.91	19
S18	3.45	72	0.037	0.77	0.23	5	0.48	10	0.90	19
Average	**6.68**	**72**	**0.092**	**0.95**	**0.42**	**5**	**1.20**	**12**	**1.17**	**14**

Table A6.6.3. Fractionation of lead concentrations and its percentage from the total lead in sediments of the Muvattupuzha River during May 2006

Station position	Pb_{exch} (ppm)	$\%Pb_{exch}$	Pb_{carb} (ppm)	$\%Pb_{carb}$	Pb_{redu} (ppm)	$\%Pb_{redu}$	Pb_{org} (ppm)	$\%Pb_{org}$	Pb_{resid} (ppm)	$\%Pb_{resid}$
S1	6.36	71	0.090	1.01	0.41	5	1.14	13	1.15	13
S2	5.63	71	0.077	0.97	0.36	5	0.98	12	1.09	14
S3	5.55	71	0.076	0.97	0.36	5	0.97	12	1.08	14
S4	5.26	71	0.071	0.95	0.34	5	0.89	12	1.06	14
S5	4.13	72	0.050	0.87	0.27	5	0.63	11	0.96	17
S6	1.71	74	0.025	1.08	0.13	6	0.28	12	0.45	19
S7	1.42	75	0.021	1.12	0.11	6	0.22	11	0.32	17
S8	1.44	75	0.022	1.13	0.11	6	0.22	12	0.33	17
S9	1.64	74	0.025	1.14	0.13	6	0.27	12	0.39	18
S10	3.58	72	0.045	0.91	0.24	5	0.51	10	0.91	18
S11	5.00	71	0.066	0.94	0.33	5	0.83	12	1.03	15
S12	4.53	71	0.057	0.90	0.30	5	0.73	11	0.99	16
S13	5.44	71	0.074	0.96	0.35	5	0.93	12	1.07	14
S14	8.08	71	0.121	1.06	0.51	4	1.54	13	1.30	11
S15	13.32	70	0.216	1.14	0.82	4	2.76	15	1.75	9
S16	16.58	70	0.275	1.16	1.02	4	3.48	15	2.13	9
S17	1.35	75	0.021	1.18	0.11	6	0.23	13	0.18	10
S18	1.37	75	0.023	1.28	0.11	6	0.23	13	0.19	10
Average	**5.13**	**72**	**0.075**	**1.04**	**0.33**	**5**	**0.94**	**12**	**0.91**	**14**