

**GEOCHEMICAL FRACTIONATION OF METALS IN
THE SURFICIAL SEDIMENTS OF ACHANKOVIL
RIVER BASIN, KERALA**

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MASTER OF PHILOSOPHY

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CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled "Geochemical Fractionation of Metals in the Surficial Sediments of Achankovil River Basin, Kerala" has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, for the partial fulfilment of the award of the degree of Master of Philosophy. This work is original and has not been submitted in part or full for any other Degree or Diploma in any other University.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

CHAPTER – 1

1.1 INTRODUCTION

The sedimentary reservoir of the aquatic system plays an important role in elucidating many natural processes occurring within the system. The role of sediments playing in the maintenance of water quality by removing the contaminants from the water column induces the researchers to undertake the study on the chemistry of sediments. Different elemental phases release metals and contaminants under different environmental conditions. Hence the knowledge on the sediment chemistry including its mineral and chemical phases present and to the extent they bind contaminants, is vital for understanding the geochemistry of sediments and the fate of the contaminants within an aquatic system. In the present study on the Achankovil river an attempt has been made to understand the distribution and fractionation of metals and to evaluate its environmental pollution status.

The Achankovil river flows through a forested, urbanized and industrialized region of the Kerala and forms an integral part of this region. It is a valuable recreational and ecological asset, but owing to the rapidly expanding urban areas, it is subject to the effects and influence of these developments.

The Achankovil river supports large human population, provides water for irrigation and drinking purposes. Various developments occurring around the river catchments impose a threat to the quality of Achankovil river water. In this connection, the measurements of trace metals in the surficial sediments and the

geochemical fractionation can be a good indication to understand the natural weathering process and the man induced pollution in the river system.

1.2 LITERATURE REVIEW

Metal concentration in the sediments depends not only on the input from the natural resources such as weathering of minerals, emissions from active volcanoes, forest fire, sea-salt sprays etc (Chester and Aston, 1976; Cook 1977), but also anthropogenic sources such as metal mining and industrial processing, sewage sludge and dumped waste material, pesticides, use of motor vehicles, leaching of garbage from solid waste and animal and human excretions and other sources (Dean et al., 1972; Klein et. al., 1974; Lewin et.al., 1977). Nriagu (1979) has concluded that natural emission of metal has been much lower than the anthropogenic contribution.

According to Forstner and Wittmann (1983), two important factors involved in the transport of metals in river system -water discharge and primary production by biological materials, which show large seasonal variations. Sediment is a major sink for heavy metals and sediment analysis in particular is a unique to trace such point source of metals (Duddridge and Wainwright, 1981). Since there is always an interaction between the hydrosphere and atmosphere, a great majority of trace elements are injected into the sediments from land-run off and atmospheric fall out. There for, assessment of sediment chemistry reflects to some extent the pollution in a given area like river system.

There are two types of metals in sediments of river system .First, the residual trace elements which are the part of the silicate matrix of the sediments and which are located mainly in the lattice structure of the mineral components. Second group of metals are called nonresidual metals because they are not the part of the silicate matrix but have been incorporated into the sediments from aqueous solution by processes such as adsorption, organic complexation etc.The metals concentration in sediments also depends on the factors(Chester and Hughes,1967),such as pH, conductivity, salinity, grain size, organic matter, mineral composition,rate of deposition, sulphide content, upward migration, reduction, sorption / adsorption, complexation and reprecipitation of previously sedimented material (Gibbs, 1973; Ramamoorthy and Rust, 1976; Jackson, 1978).Life depends upon the availability of chemical elements in the right proportion and combinations. Elements such as heavy elements are essential for life in normal concentrations, but are toxic when present in higher concentrations in any component of environment because of their potential toxicity to micro-organisms, plants and animals. Considerably high metal levels in water and sediments of the Yamuna river have already been reported (Ajamal et. al. 1985; Subramanian et. al. 1987).These earlier studies were restricted either to a few sampling stations or bulk sediment analysis without considering grain size. In the present study, Achankovil River surface sediments from Kerala, were analyzed to establish the concentration and distribution of six heavy metals (Cu, Zn, Cd, Mn, Pb and Fe) in order to understand the effects of natural processes and human impact on the quality of river sediments.

Heavy metals present in streams were the result of chemical leaching of bed rock, water drainage and runoff from banks and discharge of urban and industrial waste water (Birch and Taylor,1999;Soares et al.,1999).Association with suspended matter largely mediates the transfer of metals from terrestrial to the riverine and coastal environment. The transfer and distribution of heavy metals in sediments is largely dependent on sources and input, hydrodynamics factors controlling the flow, nature and amount of suspended solids and biological processes occurring in the system (Horowitz,1991).

The behaviour of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition and the water chemistry. Sediment composed of fine sand ,silt and clay minerals generally have higher levels of absorbed metals than major rock forming minerals such as quartz, feldspar and detrital carbonate. Metals also have a high affinity for humic acids, organo-clays and oxides coated with organic matter (Connel et al.,1984).

Sediments are widely used as environmental indicators due to their ability to be trace contamination sources and monitor contaminants (Soares et al.,1999).They play an important role in the assessment of metals contamination in natural waters (Jha et al.,1990).They have a high capacity to accumulate and integrate over time low concentrations of trace metal in water and hence allow the determination of metals even when the level in water may be extremely low(Sores et al.,1999).

1.3 DEPOSITIONAL ENVIRONMENT

In those areas where sediments were deposited temporarily. The transportational dynamic zone has shown to contain moderate amount of heavy metals between those levels in sediment accumulation zone and sediment erosion zone (Hakanson and Ahl, 1975).

Depositional environment is influence by both physical as well chemical factors. They actually responsible for the occurrence of aerobic (oxidizing) or anaerobic (reducing) condition. The igneous or sedimentary or metamorphic rocks are having profound impact on depositional environment.

1.4 COMPOSITION OF SEDIMENTS:-

The concentration of metals in river sediments depends upon many interacting factors, such as, sources of sedimentary materials, the processes which lead to the presence in the water column of suspended metal –containing particles and the hydraulic and chemical factors.

Point sources of contamination which produce concentrates these effluent streams may increase the concentration of these metals in near by sediments by over hundred times .Enrichment of this order have been observed in river sediments and in estuarie sediments due to the input from the battery factory(Bower et al.,1978).

River sediment is a mixture of three main components –detrital sediments, authogenic sediments, biogenic sediments ferro-manganese oxides (Calvert, 1976), precipitated carbonates (Leland, 1975), precipitated sulphides (Berner, 1971), interstitial waters of sediments and oxic and anoxic sediments, all play an

important role in the mobilization and immobilization of metals in river sediments. Determination of sediment composition in river system also depends on the seasonal fluctuation. Organic matter is a highly potent factor in the evolution of the biosphere. The study of the factors governing distribution, transformation and cycling of organic matter and its accumulation in sediments is of considerable practical and theoretical value, particularly for the evolution of lithology and for understanding the formation pattern of deposits of numerous useful minerals. There could be two sources of organic matter in the river systems-autochthonous organic matter derived from insitu weathering and by photosynthesizing plants and allochthonous organic matter due to runoff etc.

1.5 PATHWAY AND MECHANISM OF INCORPORATION INTO THE SEDIMENTS:-

Trace metals reach the sediment, in or on particles which settle to the bottom, particles which are transported along the bottom and by the sorption of dissolved metals from waters in contact with the sediment. Here biogenic, detrital and anthigenic sedimentation play critical role

The another pathway by which particles may reach a sediment is by horizontal transport along the bottom which is distinct from vertical fall out through the water column. Bottom transport is known to occur in rivers, where ripples or dunes of sediment migrate downstream until they are trapped in reservoirs or the sea (Houschild, 1973).

A third pathway involves direct uptake by sediment particles of dissolved metal species. Uptake can occur from the water above the sediment surface or from below the sediment surface (Croman, 1976).

1.6 GRAIN SIZE CONTROL OF ELEMENTAL CONCENTRATION:-

In general a strong correlation exists between sediment grain size and metal concentration. More specially, the percentage of fines in the sediment and the concentration of metals in the sediment $[Me]_{sed}$ are strongly correlated. $[Me]_{sed}$ tends to be higher in the finer fractions. This is especially true for Cu, Cd, Fe and Zn. This is so because –

- (1) As grain size decreases, the surface to volume ratio increases, so for surface processes like ion exchange, absorption, and coating formation and the smaller particles predominates.
- (2) The fines includes organics (humic acids, etc), clays and oxyhydroxides of Fe and Al.

As grain size decreases, the silica fraction decreases, surface area increases, ion exchange capacity increases and clay mineral content increases (Lecture No.6. Grain size control USGS). Heavy metals in aquatic ecosystem tend to accumulate in bottom sediments and can be released by various processes of remobilisation. The concentration in sediments do not fluctuate to the same degree as in surface water. Thus sediments of aquatic systems are usually studied when studying the quality of water system. The most mobile fraction of the sediment is that of the <63 microgram grain size. This fraction also contains proportionately more sorbed metal of the sediment due to its larger surface area. Both bioavailable

and concentration of metals are studied in detail (Kominar, 1994). Swift et al., (1972) has recognized the particle size analysis as one of the potentially most powerful tools available for the interpretation of any population of sedimentary particle.

1.7 SPATIAL AND TEMPORAL VARIATION:-

The pronounced temporal and spatial variation in the heavy metals distribution was observed by Subramanian et al. (1984) and it is estimated that particulates are strongly enriched relative to bed sediments of Ganges and Brahmaputra rivers. Furthermore the average chemical composition of river borne sediments from the Indian subcontinent has been calculated by Subramanian et al. (1984) and it is concluded that the average bed sediment chemistry for the Indian subcontinent appears to agree with the global average and chemical composition of individual river basins for Ganges, Brahmaputra, Godavari, Krishna, Narmada, Tapti and Cauvery; differ among themselves only in those elements such as Ca, Fe, Mg, etc which are active in the river sediment system.

The surface and depth distribution of Mg, Al, Ca, Cr, Mn, Fe, Ni, Cu, Sr, Ba, Th and U have been determined in several sediments cores from the Bay Of Bengal, equatorial Indian ocean and some of the major rivers draining into them. Mg, Fe and Al, are strongly correlated with each other and their distribution in these sediments seems to be controlled primarily by weathering products from Himalayan region, transported through the Ganges-Brahmaputra river system (Sarin et al., 1979). Distribution of trace elements in Periyar river has been studied in details (Paul and Pillai, 1983).

Study of grain size fraction in sediments between Vengurla and Mangalore (Hashimiet.al.,1978) and distribution pattern of Al,Mn,Cu,and Ti (Murty et al.,1978) in sediments have been reported from Northern half of the Western Continental shelf of India.

Subramanian et al.(1998) measured the metal/Al ratio to describe the mobility of different metals in different river sediments of Kerala.Variation in ratio shows the influences of tributaries ,water –sediment exchange of elements and increase in authogenic deposition rates. The work of Ramanathan et al.(1994) on Cauvery river sediments gives an idea about enrichment of metals in different grain size.

The mineralogical contribution of rivers also has been taken care of in due course (Gibbs, 1997; Subramanian, 1980; 1988; 1994).They have observed that clay mineralogy is controlled by size segregation and hence most of the studies centered around two micron size fraction.

Sediment conserve important environmental information (VonGunten et.al.,1997) and are increasingly recognized as both a carrier and a possible source of contaminants in aquatic systems(Forstner and Salomons,1991;Tessier etal.,1994).Much work has been performed on heavy metal pollution in river-lake sediments(Unlu and Gumgumetal.,1996;Minissiet al.,1998;Avila-Perez et al.,1999;Liu et al.,1999;Mather et al.,1999;Ramos et al.,1999).Singh(1999) used the total digestion method to determine heavy metal concentration in the Yamuna river system. Karen Binning and Dan Baird (2001) studied the distribution and levels of sediment contamination by heavy metals in the Swartkotos River and

estuary by Teflon Bomb Digestion Method They performed the analysis of heavy metals in different sediment particles size classes.

In order to study the speciation of particulate trace elements in river sediments , an analytical technique involving sequential chemical extraction (soluble with water, really exchangeable ,bound to carbonates ,manganese oxides, amorphous iron oxides, crystalline iron oxides ,and to organic matter) has been evolved for the speciation studying of Si, Ca, Fe, K,Mn, Al, Co, Rb, Sr, Y, Sb, Cs, Pb, U(Leleyter and Probst,1999).They observed that this method is better than that of the determination of total trace elements in suspended load or surface sediments or bottom sediments, because it is the chemical form of the element that determine its mobility ,bioavailability and so its toxicity. They improved the efficiency and selectivity of commonly used sequential extraction procedures. In spite of long analysis times, many studies have been carried out using this method (Baruah et al.,1996; Pempkowak et al.,1999;Ginepro et al.,1996; Sanchez et al.,1996).The second technique is the three stages, BCR sequential procedure proposed by the Commission of the European Committees Bureau of reference (BCR,now SMT) needs less time than the first one but it is less efficient than the previous one.

The role of organic matter and sediment grain size in relation to the accumulation of heavy metals to the sediment has often been emphasized(Davies et al.,1991).Increase in heavy metals concentration tend to be associated with fine grained sediments .The heavy metal concentration in average shale is taken as the worldwide standard and is used as reference for identifying uncontaminated sediments(Turekian and wedephol 1961).The geoaccumulation index proposed by

Muller(1979)has often been used successfully in the quantification of metal accumulation in river sediments.

1.8 OBJECTIVES:-

The above review highlights the importance of fraction of metals in surface sediment. Hence in present study following aspects of Achankovil rivers systems has been proposed to be carried out-

- (1) Physical separation of surface sediments (Textural analysis) into different grain size classes.
- (2) Sampling of surface sediments from various sites from upstream to downstream along Achankovil (AC) River system.
- (3) Chemical sequential extraction of surface sediment samples of Achankovil river to study the speciation of heavy metals.
- (4) Analysis of metal concentration in different grain size classes (Cd, Cu, Mn, Fe, Pb and Zn).
- (5) Analysis of percentage of organic matter in different grain size classes.

CHAPTER 2
STUDY AREA AND CLIMATE

CHAPTER -2

STUDY AREA

2.1 AREA AND LOCATION:-

The Kerala state comprises a narrow strip of land with an area of 38,863 square kilometer extending between north latitudes 8o17' 30" and 12o 27' 40" and east longitude 74o 51' 57" and 77o 24' 47" and drained by 44small rivers. The Western Ghats with the magnificent array of sky scrapping peaks on the east and the Arabian Sea washing its shore on the west are the natural boundaries of the state, providing it distinctive physical features.

On the basis of physical features, the state ids divided into three natural divisions, namely, the low land consisting of sea board, the mid land consisting of the undulating country east of the low land and the forest clad high land on the extreme east. The hilly or the eastern portion is broken by a long spurs, extensive ravines dense forest and tangled jungles full of flora and fauna, rising terrain after terrain, to an elevation more than 275 meter above the sea-level.

The present study mainly concentrated on the Achankovil covering mainly four districts of Kerala i.e. Allepy, Pathanamthitta, Kottam and Alappuzha. The length of Achankovil, length of is 128,176 and 90 km respectively.

2.2 CLIMATE

2.2.1 Temperature

From last 30 years average data of temperature variation from Indian Meterological Department, Pune , the day temperatures are more or less uniform

over the plains throughout the year except during January, December and months of July when these temperature lower over the plateau and at high level stations than over the plain. Day temperatures of coastal places are less than those of interior places. March-April is hottest month with a mean maximum temperature range from 32°C to 37°C on different stations.

2.2.2 Humidity

Kerala posses a very high humidity over all the year because its very close to Arabian Sea. In months of December to March it posses relatively low humidity about 74% to 77% while in months of June-July humidity rises to its peak 90% to 92%.The humidity also varying from 35% in the interior to 71% in the coastal area.

The diurnal variation in relative humidity during January-March is maximum and ranges from 4% to 16% depending upon the proximity of sea. The diurnal variations in monsoon period is minimum and ranges from 2% to 12% maritime influence playing most important role in governing this variations.

2.2.3 Cloudiness

Minimum cloudiness prevails over state in the period January to March when sky remains cloudless for 12 to 13 days per month towards the extremely southern parts of the state during this period, about 3 oktas of sky remains cloudy in the months in general and cloudiness varies from 3.9 oktas of sky towards the northern coast to 2.3 oktas of sky towards interior and southern most part of state. Mornings are more cloudy than evening except at southernmost and interior of the

state where afternoon was more cloudy than morning. During monsoon season skies are heavily clouded specially during June and July when about 7 oktas of sky remains covered with cloud in a month. On an average in each of these two months the sky remains overcast for more than 16 days per month and is not generally found clear even for a single day. In this season morning and evening are equally cloudy. Cloudiness starts decreasing from August decreases till September. A secondary maxima of cloudiness is observed in the state in October when the post monsoon storms of Bay of Bengal and Arabian Sea affect the state again it decreases from November till January when the cloudiness in state is minimum(Annual report of Indian Meteorological Department).

2.2.4 Rainfall

The total annual rainfall in the state varies from 380 cm over the extreme northern parts to about 180 cm in the southern parts. The SW monsoon (June –mid October) is the principal rainy season when the state receives about 73% of its annual rainfall, monsoon rainfall as percentages of annual decreases from north to south and varies from 85% in northernmost district of Cannanore to 54% southern most district of Trivandrum. Rainfall in the NE monsoon season (mid October to February) and hot weather season (March to May) constitute 7 to 25 and 10 to 20 %. Ne monsoon rainfall as percentage of rainfall increases from North to South and varies from 7% in Northern most district of Cnnanore to 25% in Southern most district of Trivendrum. As from monthly average rainfall data, maximum rainfall observed in month of June –July i.e. from SW monsoon and minimum observed in

month of December and January (annual report of Indian Meteorological Department).

2.3 SOIL

The soil type of the study area is most predominantly lateritic, especially in the midlands. These are weathering products of rocks under the tropical humid conditions existing in the study area. It shows a developed ABC profile, which are deep to very deep. The B-horizon is well developed in most area and has abundant in ferruginous quartz gravels. The other dominant soil type is Hapludolls-Tropudafs-Tropeptic-Eutrothox (Loam) type of soil, which is developed on the weathered crystalline rocks in the eastern part of study area. They are rich in organic matter. Tropofluvents-Eutropepts-Dystropepts (alluvium) Type of soil is well developed along the river valleys and cut across the laterite cover. They are very fertile with high water holding capacity. Tropaqualps-Tropaquepts (Brown hydromorphic) type of soil is present in patches in the area of wetlands and are rich in organic matter and potash. Troporthents (grey onattukara) type of soil is found only in Allepy and Quilon districts. It is grey in color, coarse grained and acidic in nature (Anon, 1968).

2.4 ACHANKOVIL RIVER BASIN:-

Achankovil river is in south of Kerala with an area of 1484 km² and annual average discharge of water about 1.5 km² yr bounded by hills on three sides on the south. The land lies at a height of 20-120 meters above mean sea level. Side slope of the valley is moderate (50-180 meter). The area receives an annual rainfall of 289

mm. Geology is same like Pamba basin (pyroxene, granulites, charnokitic gneiss, khondalites and associated calc-granulite bands). The basin displays dendritic to sub-dendritic and rarely rectangular and trellis drainage patterns. The river discharges into the Vembanad Lake extends from Cochin to Allepey for a distance of 83km and is the largest estuary in Kerala. Its width varies from a few hundred meters to 15 km. It is elongated and oriented in NW-SE direction. Five major rivers, viz. Muvattupuzha, Meenachil, Manimala, Achankovil and Pamba discharge into this lake.

2.5 PHYSIOGRAPHY:-

Physiographically, the state is divided into three divisions, viz., (1) The highland region in the east consisting of the forests of the Western Ghats and its slopes (2) The midland region, (3) the lowland region in the west coast. These three regions run parallel to each other from one end of the State to the other. The topography of the highland region is mountainous with altitudes ranging from 400-2000m above the sea level. The midland region has a rolling or hilly topography roughening into slopes and gradually joining the mountains, the altitude varying from a few meters in the west to about 400 meters in the east. The narrow coastal belt of lowlands in the extreme west has a nearly level and flat topography. A series of natural backwaters connected together by man-made canals is characteristics of this region. The entire face of land is intercepted by a number of rivers, which originate in the mountains in the east and flow the backwaters for the in the west.

2.6 GEOLOGY:-

The main geological formations of the State belong to the Archean period except for the coastal tracts where the more recent sedimentary formations known as the Varkalai series and extend almost continuously from Varkalai in the south to Kasargod in the north. The sands alluvium, organic deposits and lacustrine beds of recent formations. According to the time scale, the geological formation of Kerala is given as follows:

1. Recent: Sands alluvium, organic deposits and lacustrine beds.
2. Tertiary: Sedimentary laterites of the Varkalai series and residual laterites of the Upper tertiary.
3. Archaean: Crystalline rocks.

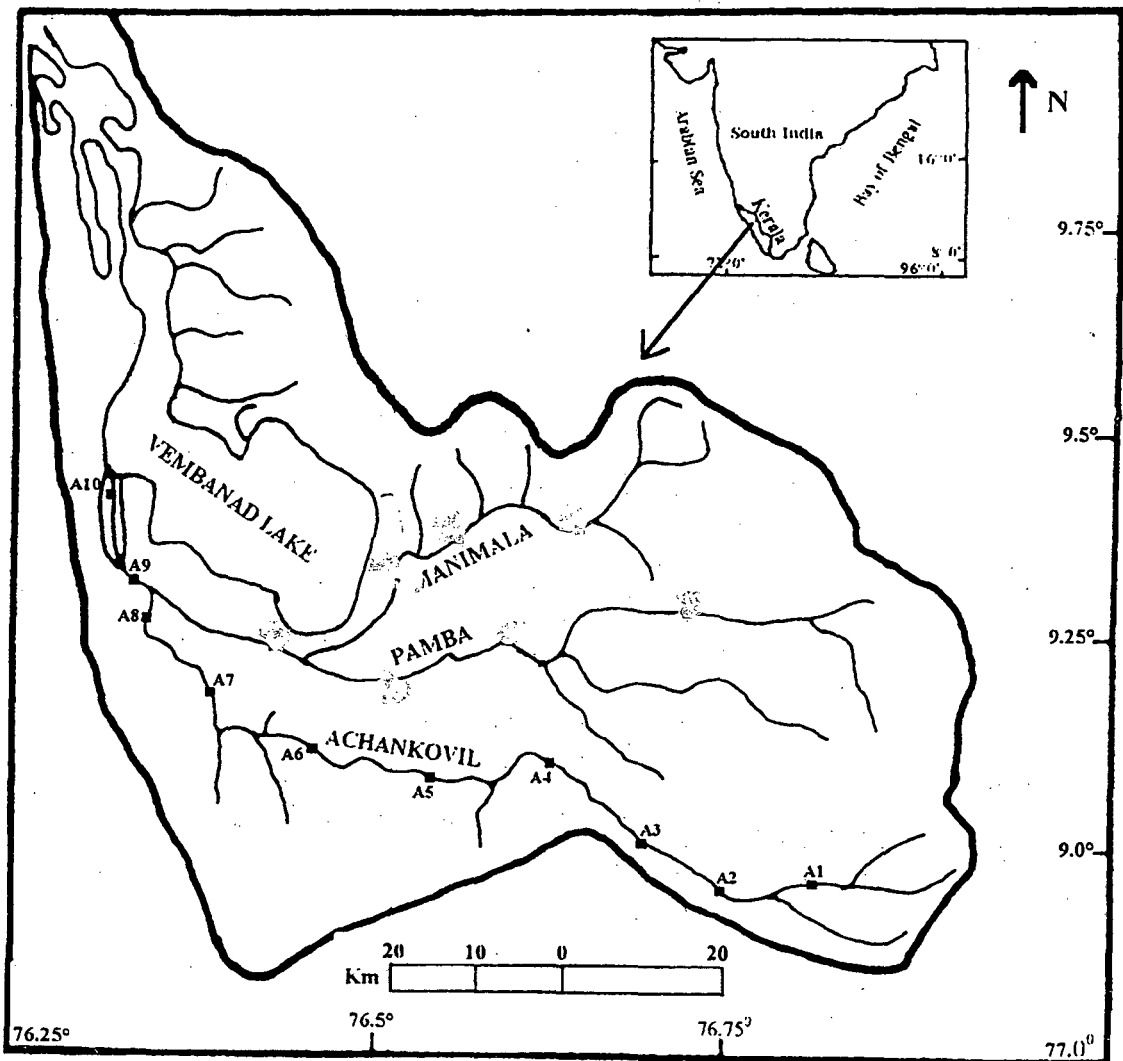
2.7 VEGETATION:

In spite of the small area of the State the vegetation is extremely varied and exhibits a wide range of plant formations characteristics of the following climatic zones:

1. The humid Temperate Zone of the high ranges (above 1350m).
2. The sub-tropical zone (750-1350m)
3. The monsoon forest (450-750m).
4. The midland and coastal region (0-450m).

Natural vegetation is now found only in the first three zones which together constitute about 25 percent of the total area of the State. Along the lower altitudes of the humid temperate zone trees of the cypress and Eucalyptus species are seen. Shrubby forms are rare, but many perennial herbs and grasses are found. The tea

shrub, *Camellia sinensis*, is cultivated extensively in this region. The climate of the sub-tropical zone is suitable for the growth of huge trees such as the teak (*Tectona grandis*), and the rosewood (*Dalbergia latifolia*). Saprophytic plants like orchids and fungi grow in the decaying organic matter on the forest floor. Extensive plantation of Para rubber (*Hevea brasiliensis*), and of cardamom (*Elettaria cardamom*) as well as that of tea are found in this region. The chief characteristic of the monsoon forests is that the trees are mainly of the deciduous type so that leaf fall occurs at the beginning of the dry seasons. The whole of the midland and coastal regions is under human habitation and vegetation consists of secondary species.



STUDY AREA

CHAPTER 3
MATERIALS AND METHODS

CHAPTER – 3

MATERIAL AND METHODS

3.1 FIELD METHOD:-

Surface sediment samples were collected from the sampling location by scooping the top 5-10 cm layer using a small steel scoop along the river bed at sediment water interface. The surface sediment samples were then transferred to a polythene bag, which was sealed to air by fastening the mouth immediately. These samples were brought to the laboratory for studying geochemical properties.

3.2 LABORATORY METHODS:-

In laboratory bed sediments spread on glass plate to become air-dried and then homogenized by hard plastic rod.

3.2.1 Organic Content Analysis

Oven dried and crushed samples of known weight (0.5g) were treated with hydrogen peroxide (H_2O_2) (30%) repeatedly to oxidize the organic matter present. Difference in weight of dried sample before and after H_2O_2 treatment was taken as total organic matter.

3.2.2 The Mechanical Sediment Textural Analysis

The mechanical analysis normally begins with sieve procedures, the separation of sediment samples into different size classes i.e. $>250\mu m$, $125-250\mu m$, $63-125\mu m$, $<63\mu m$ from homogeneous sediment samples. Further separation of $<63\mu m$ samples into 50, 30, 20, 10, 5, $<2\mu m$ were carried by Atterberg

sedimentation cylinders with dry and organic content free samples in order to minimize the possibilities of flocculation of clay minerals.

Atterberg Sedimentation Cylinders:

It is a 35 cm long cylinder having 5 cm diameter and is provided with a siphon at 3 to 4 cm above the base. Cylinders were graduated in centimeter with the zero mark coinciding with the siphoning layer of the liquid. The siphon tube was connected to a rubber (latex) tube which was provided with a birch cork. Cylinder at mouth was provided with a glass. A homogenized suspension in water was prepared from samples. Homogenisation was carried out with the aid of mechanical stirring. The strength of the suspension was maintained. The suspension was transferred to Atterberg sedimentation Cylinders and again was shaken before keeping for size separation. The different fractions were evaporated at 60°C in a porcelain dish on hot plate.

Principle of size separation by Atterberg sedimentation Cylinder:

Stokes law governs the size separation of sediments which states the law of settling velocity:

$$V = \frac{2}{9} \frac{(d_1 - d_2) g}{n}$$

Where V = velocity of settling, cm/sec

d_1 = density of particles, gm/cm³ = 2.65

d_2 = density of fluid medium, gm/cm³

g = acceleration due to gravity, cm/sec² = 980

n = viscosity of fluid in centipoises

r =radius of sphere, cm

Fall time for a given diameter of particles is,

$$t=h/v$$

Where, h =fall height of suspended column in cm.

V =settling velocity for a given diameter in cm/sec.

3.2.3 Analysis Of Major And Minor Elements

The samples from each grain size class were taken in the beaker and boiled with 30% (v/v) H₂O₂ (Jackson, 1973) for removal of organic matter. The treatment is repeated until the emission stopped.

Analyses of major and minor elements were carried out by the two solution method (Shapiro, 1975). Solution "A" was used for Silica, Alumina and Solution "B" was used for metal analysis.

3.2.3.1 Solution "A"

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

TH-10304



(1) SILICA ANALYSIS:

0.8ml of solution "A" standard solution (Canadian standards i.e. SO₁, SO₂, SO₃ and SO₄) and sample solutions were taken in test-tube. 0.2ml Ammonium molybdate solution was added and kept for 10 minutes. 4 ml of 10%(v/v) of tartaric acid was added by swirling the beaker. 0.1 ml of reducing agent was added and samples properly stirred and kept for 30 minutes. Absorbency was measured by spectrophotometer at 650 nm.

Ammonium molybdate solution was prepared by dissolving 1.875 gm Ammonium molybdate in 19 distilled water and adding 6 ml 20% (v/v) H₂SO₄. The reducing reagent was prepared by dissolving 0.07 gm Sodium Sulphite in 1.0 ml distilled water then 0.015 gm 1-amino-2-naphthol-4-Sulphonic acid was added and stirred well until dissolved 9 ml of 10% (w/v) Sodium bisulphate solution was added to it and mixed well.

(2) ALUMINUM ANALYSIS:

15 ml of solution "A" (standard, sample and blank) were taken in 100 ml volumetric flask of CaCl₂ solution (prepared by dissolving 7 gm CaCl₂ in 1000 ml distilled water) was added. 1 ml of Hydroxylamine – Hydrochloride (prepared by dissolving 5 gm of Hydroxylamine – Hydrochloride in 50 ml) was added by swirling the flask. 1 ml of potassium ferricyanide (0.75 %) was added to each flask and mixed 2ml of thioglycolic acid solution (4%) was added and left for five minutes. 10 ml of buffer solution (prepared by dissolving 100 gm of sodium acetate in water and adding 30 ml of glacial acetic acid and diluted to 500 ml) was added to each flask and the volume was diluted to 100 ml sample were properly stirred

and left for 50 minutes. The absorbency was measured at 470 nm using spectrophotometer.

3.2.3.2 Solution "B":

0.1g of sample was taken in Teflon bomb and 0.5ml HNO₃+1.5ml HCl and 2ml HF were added. The Teflon was kept in sealed bomb which was heated in an electric oven for about 1 hour at 105°C. In the case of a seal bomb, some pressure develops inside which facilitates the decomposition of relatively resistant minerals. Further bombs were allowed for cooling to room temperature and 5g of Boric Acid was added followed by transfer to polypropylene bottle to maintain 100 ml volume by adding double distilled water. Then metals were analyzed in the final solution by ASS.

3.2.4 Chemical Extraction Technique

The mobility, the transport and the toxicity of trace elements in aquatic systems depend on the chemical form of the elements which is controlled by the physico-chemical and biological characteristics of that environment such as salinity, pH, redox potential and concentration of chelators. In order to study the bioavailable fraction of river sediments, an analytical procedure involving sequential chemical extraction [soluble with water (eua), really exchangeable (ech), bound to carbonates (carb), manganese oxides (MnO), amorphous iron oxides (AFeO), crystalline iron oxides (CFeO) and organic matter (org)]. This procedure has been developed by Leleyter and Probst, from an improvement of

Tessier et al.(1979) and Schuman(1985) procedures to determine the speciation of various trace elements .

The leaching procedure takes place in a watertight container to prevent evaporation, with continuous agitation to increase the interaction surface between the reagent and the sediment. The 1g sediment (dry weight at 100°C) of the original sample used for the initial extraction. After each reaction, the residue is filtered with 0.45 micrometer pore size Millipore filters made of polyvinylidene of fluoride (CHR-CFF-) and washed with 20 ml of distilled water. Then the leachate is stored in a polypropylene bottle at 4°C until chemical analysis, whereas the residue (dried at 40°C in order to prevent any dilution of the following reagent) undergoes the following extraction step. The percentage of each element in the various fractions was calculated on the basis of the total element concentration which was determined by digesting the sample by either a tri-acid attack or an alkaline-melting attack.

TABLE 1: Protocal summary of the 7-step sequential extraction procedure (Leleyter and Probst, 1999):

Fraction	Reagent	Reaction time	Temperature	Leachet density
1.Dissolved with water	10 ml water	30 min.	20°C	1.000
2.Really exchangeable	10 ml of 1M nitrate magnesium	2 hours	20°C	1.085
3.Bound to carbonates	10 ml 1 M sodium acetate,pH=4.50(HOAc)	5 hours	20°C	1.027
4.a.Bound to manganese oxides	10 ml 0.1M hydrixylammonium chloride	30 min.	20°C	1.002
4.b.Bound to amorphous iron oxides	10 ml {0.2M ammonium oxalate -0.2 M oxalate acid	4 hours in the dark	20°C	1.018
4.c.Bound to crystalline iron oxides	10 ml(0.2M ammonium oxalate,0.2M oxalate acid,0.1M ascorbic acid	30 min.	80°C	1.024
5.Bound to organic matter	1)3 ml 0.02M HNO ₃ and 8 ml of 35% H ₂ O ₂ 2)5 ml 3.2 ml ammonium acetate(20%(v/v)HNO ₃)	1)5 hours 2)30 min.	85°C 85°C	1.057 1.057

CHAPTER 4
RESULTS AND DISCUSSION

CHAPTER – 4

RESULTS AND DISCUSSION

4.1 SILICON DISTRIBUTION:-

The distribution of Silicon (Si) in different grain size of surface sediments (from $> 250\mu\text{m}$ to $< 2\mu\text{m}$) is given in Table-1 and shown in Fig. 1. The results shows that as grain size decreases, the concentration of Silicon (Si) decreases because of low sand proportion down the decreasing particle size. In the upstream (AC 1 to AC4), midstream (AC 5 to AC 8) and down stream (AC 9 to AC 12) the trend of Silicon (Si) is almost similar except few fluctuations with coarse size fractions

4.2 SILICON AND % ORGANIC MATTER:-

There commonly is a strong correlation between sediment grain size, Silicon (Si) concentration and % organic matter. The results are given in Table 2 and relationship is shown in Fig.2 for each site (AC 1 to AC 12). In figure, it is very clear that as grain size decreases, the fraction of Silicon (Si) decreases and % organic matter increases. This so because, small grain size supports accumulation of high organic matter i.e., clay is predominant.

4.3 DISTRIBUTION OF TRACE ELEMENTS (Fe, Cu, ZN, Mn, Pb & Cd):-

Analysis of metals by bomb digestion method in different grain size of surface sediments of Achankovil river, including Fe, Cu, Mn, Zn, Pb, Cd show

very typical pattern. These pattern are results of chemical leaching of bed rock, water drainage and runoff from banks and discharge of urban and industrial waste water.

Iron

Iron content in different grain size ($> 250\mu\text{m}$, $125\text{-}250\mu\text{m}$, $63\text{-}125\mu\text{m}$, $50\mu\text{m}$, $30\mu\text{m}$, $20\mu\text{m}$, $10\mu\text{m}$, $5\mu\text{m}$ and $< 2\mu\text{m}$) of bed sediment of Achankovil river is given in table 3 and distribution pattern in shown in figure 3. Iron at AC1 ranges from 8200 to 20000 $\mu\text{g/g}$, at AC 2 ranges from 1340 to 18000 $\mu\text{g/g}$, at AC 3 ranges from 1440 to 18000 $\mu\text{g/g}$, at AC4 ranges from 9424 to 19856 $\mu\text{g/g}$, at AC5 ranges from 7700 to 14600 $\mu\text{g/g}$, at AC 6 ranges from 10700 to 17550 $\mu\text{g/g}$, at AC 7 ranges from 4000 to 19900 $\mu\text{g/g}$, at AC8 ranges from 4020 $\mu\text{g/g}$ to 17580 $\mu\text{g/g}$, at AC 9 ranges from 4140 $\mu\text{g/g}$ to 17861 $\mu\text{g/g}$, AC 11 at ranges from 4580 to 16640 $\mu\text{g/g}$ and at AC 12 ranges from 4400 to 19108 $\mu\text{g/g}$. Fe enriched more in 63 micron to 5 micron but trend is to same for all sample. In general all the grains seems to control the distribution of Fe in the river system

Copper

The copper content in different grain size of Achankovil river surface sediment is given in Table 4 (the results clearly show that mobility of copper in very high in less than $63\mu\text{m}$ grain sizes i.e., $50\mu\text{m}$, $30\mu\text{m}$, $20\mu\text{m}$, $10\mu\text{m}$, $5\mu\text{m}$ and $< 2\mu\text{m}$. The average value of copper with standard deviation are comparable with other river systems of Indian subcontinent. At AC 1 (upstream) and AC 10 (Downstream) high concentration of copper in found in $53\text{-}125\mu\text{m}$ grain size. At AC 2 and AC 3 (upstream), and AC 6, AC 7 and AC 8 (midstream) maximum

concentration of copper is present in 30 μ m grain size. At AC 4 (upstream) and at AC 9 (Downstream) the maximum concentration of copper is present in the 50 μ m grain size. At AC 11 (Downstream), it is 20 μ m grain size contain maximum amount of copper while at AC 12 (downstream), > 250 μ m grain size contain minimum concentration of copper. Overall result shows that high concentration of copper is controlled by less than 63 μ m grain size surface sediment particles.

Zinc

The zinc distribution in different grain size of Achankovil river bed sediment is given Table 5 and shown in Fig. 5. The pattern of Zn is similar to Cu with slight variation. At AC 1 (upstream), AC 5 (midstream), and AC 9 and AC 10 (downstream), the maximum concentration is present in 63-125 μ m grain size. At AC 2 (upstream), and AC 11 and AC 12 (downstream) 5 μ m grain size contain maximum amount of Zn.

At AC 4 (upstream) and AC 6 (Midstream), 125-250 μ m grain size has strong control over Zn distribution. At AC 3 (upstream) – 20 μ m amount of Zn while at AC 7 and AC 8 (midstream) – 30 μ m grain size regulate the distribution of Zn.

Manganese

Result for Mn is given in table 6 and distribution pattern is shown in fig. 6. In case of Mn, except AC 1 and AC 8, at other sites, it is less than 63 μ m grain size sediment particles have control over distribution of Mn. This trend is similar to Fe.

Lead and Cadmium

Lead concentration in different grain size of Achankovil river surface sediment is given Table 8 and shown in figure 7. The picture depicts the role of less than 63 μm grain size surface sediment particle in controlling the mobility of lead (Pb) in bed sediment. The similar pattern was observed for Cd which is shown in figure 8.

Overall results give idea about the enrichment of metals in the smaller size sediments i.e. the <63 μm (50 μm , 30 μm , 20 μm , 10 μm , 5 μm < 2 μm) in comparison to higher grain size i.e. > 250 μm , 125 μm and 63 μm . This fraction also contain proportionately more sorbed metals of sediment due to its larger surface area.

4.4 COMPARATIVE MOBILITY OF ALUMINIUM, IRON AND ZINC:-

Figure 9 to 20 shows that mobility of Al, Fe and Zn in different grain size of Achankovil river surface sediment. Aluminum and Iron shows very low mobility in comparison to Zinc. This is so because weathering of Aluminum containing minerals is slow in comparison to Zinc containing minerals. This may also due to different sources of these elements in Achankovil river sediments. Al is used to normalize elements of sediments in aquatic system because it is a non conservative element (Window et al 1989). It is also an major element and chemically unreactive constituent of clay minerals.

Iron in next abundant element in the river sediment. It occurs as mineral – oxide, hydroxide and sulphides as well as associated with silicates. The figure 9 shows that Iron is immobile next to Aluminum in this river system also. Zinc

indicate that, this element is quite mobile in the aquatic system and transported fast in the river system. The other metals also will behave similar to Zn.

4.5 CHEMICAL SPECIATION OF TRACE METALS :

The determination of total trace element content in aquatic system either in suspended load or bottom sediments is not sufficient, because it is the chemical form of the element that determine the mobility, bioavailability and so its toxicity. Metals absorbed on the solid particle of sediments are potentially available because they may be dissolved due to changes in physico-chemical properties of the aquatic environment such as salinity, redox potential and concentration of chelators.

From table – 9 it is found that, the iron-manganese oxide fraction has higher metal concentration for all of the investigated metals, followed by organic fraction especially for Zn, Mn, Pb, and Fe. In general iron-manganese oxide is followed by exchangeable fraction especially for Cd and Cu. Cd is higher in the carbonate fraction. Dissolved with water fraction was highest for Cu followed by Pb, Cd, Zn, and least for Fe. Distribution of Cd, Zn, Pb, Fe, Mn and Cu is given in figure A, B, C, D, E and F respectively.

There are following advantages of this procedure:-

1. Magnetic agitation is applied to increase the surface interaction between the reagent and the sediment.
2. Filtration process is preferred to centrifugation to avoid precipitation problem on the bottom of centrifugation tubes.

3. In fraction 2 (ech), magnesium nitrate replaces magnesium chloride to avoid complexation problem and pH is lowered to prevent readsorption problem.
4. In fraction 3 (Carb), the pH is lower in order to improve the efficiency of this step.

In fraction 4 (MnO, AFeO, CFeO) the procedure is completely modified to optimise the dissolution of oxides.

Figure 1

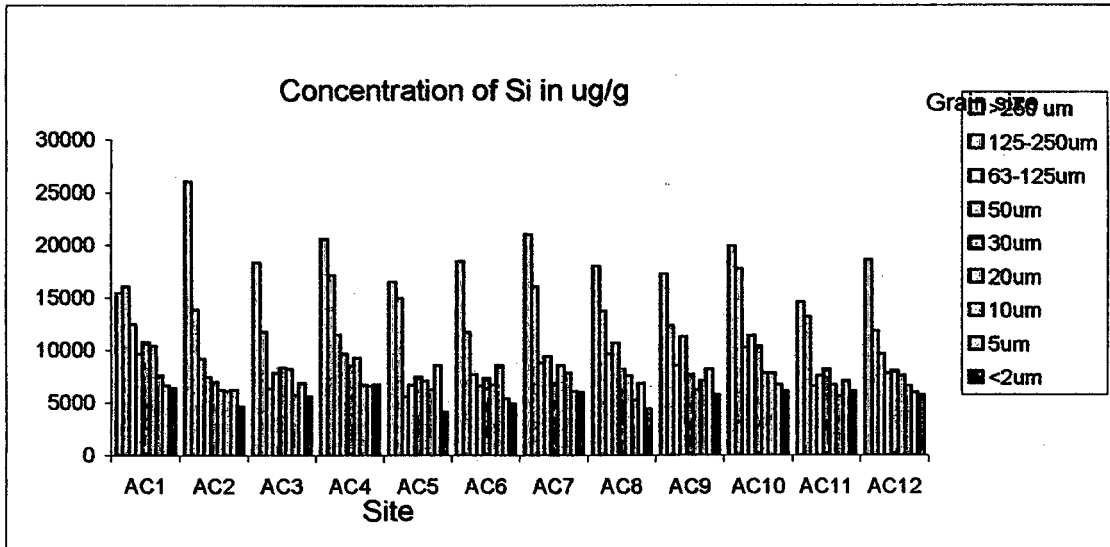


Table 1

Concentration of Si in different grain size

SiO ₂ SITE	>250 um	125-250um	63-125um	50um	30um	20um	10um	5um	<2um	Total
AC1	15405	16016	12471	9675	10760	10393	7582	6604	6360	95266
AC2	26040	13816	9171	7471	6970	6237	6115	6237	4648	86705
AC3	18339	11738	6359	7838	8315	8193	5748	6848	5626	79005
AC4	20593	17116	11493	9675	8560	9293	6726	6604	6727	96787
AC5	16505	14916	5626	6736	7459	7093	6237	8560	4159	77291
AC6	18461	11738	7704	6614	7337	6726	8560	5381	4893	77414
AC7	21028	16016	8804	9430	6848	8560	7826	6115	5993	90620
AC8	17972	13694	9660	10654	8193	7582	5259	6848	4438	84300
AC9	17239	12349	8560	11267	7704	6237	7093	8193	5749	84391
AC10	19928	17728	10271	11389	10393	7826	7826	6726	6115	98202
AC11	14549	13205	6604	7593	8193	6726	5626	7093	6115	75704
AC12	18583	11860	9660	7838	8071	7582	6604	5993	5749	81940

Table 2a

AC1 Grain Size	Si	% OM
>250	15405	2.4
125-250	16016	2
63-125	12471	2
< 63	8562	3.6
Ac2 Grain Size	Si	% OM
>250	26040	2
125-250	13816	3.2
63-125	9171	4.6
< 63	6282	5.2
AC3 Grain Size	Si	% OM
>250	18339	3
125-250	11738	3
63-125	6359	3.2
< 63	7094	3.8
AC4 Grain Size	Si	% OM
>250	20593	2.2
125-250	17116	2.6
63-125	11493	3.2
< 63	7931	3.4
AC5 Grain Size	Si	% OM
>250	16505	2.4
125-250	14916	2.4
63-125	5626	3
< 63	5707	3.2
AC6 Grain Size	Si	% OM
>250	18451	2.2
125-250	11738	2.4
63-125	7704	2.6
< 63	6585	4.6

Table 2b

AC7 Grain Size	Si	% OM
>250	21028	1.4
125-250	16016	2.2
63-125	8804	2.6
< 63	7462	2.8
AC8 Grain Size	Si	% OM
>250	17972	1
125-250	13694	1.4
63-125	9660	2.8
< 63	6426	3.4
C9 Grain Size	Si	% OM
>250	17239	2
125-250	12349	2
63-125	8560	2.4
< 63	7707	2.8
AC10 Grain Size	Si	% MO
>250	19928	2.8
125-250	17728	2.4
63-125	10271	3
< 63	7360	4
Ac11 Grain Size	Si	% OM
>250	14549	3
125-250	13205	3.8
63-125	6604	3
< 63	6491	4.2
AC12 Grain Size	Si	% OM
>250	18583	3
125-250	11860	3.2
63-125	9660	3.6
< 63	6973	4

Organic matter (%) in different grain size

Figure 2a

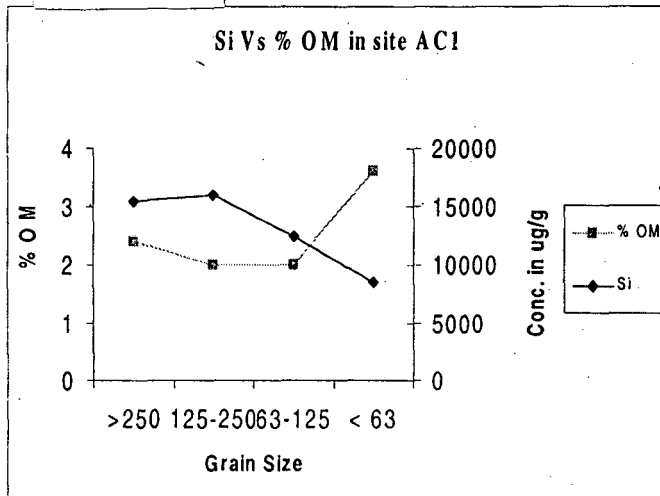


Figure 2b

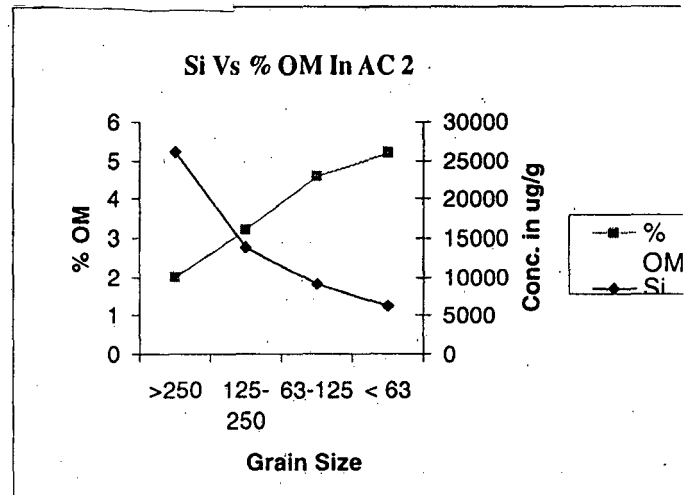


Figure 2c

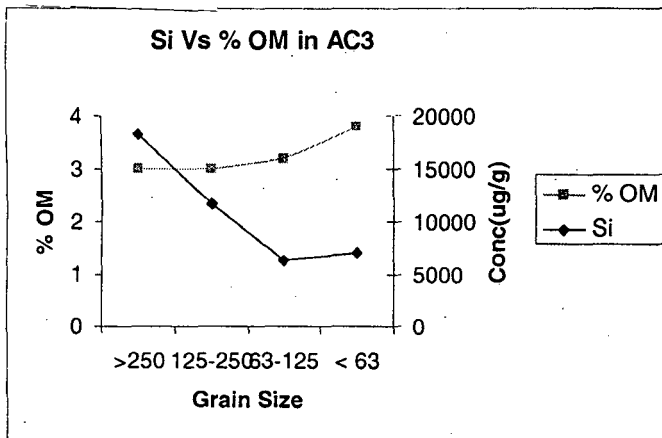


Figure 2d

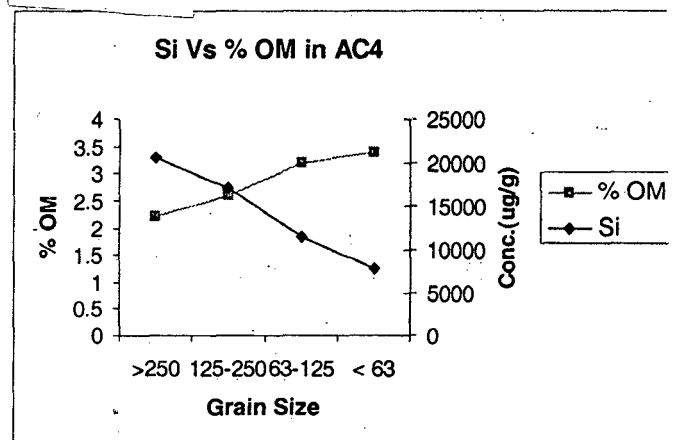


Figure 2e

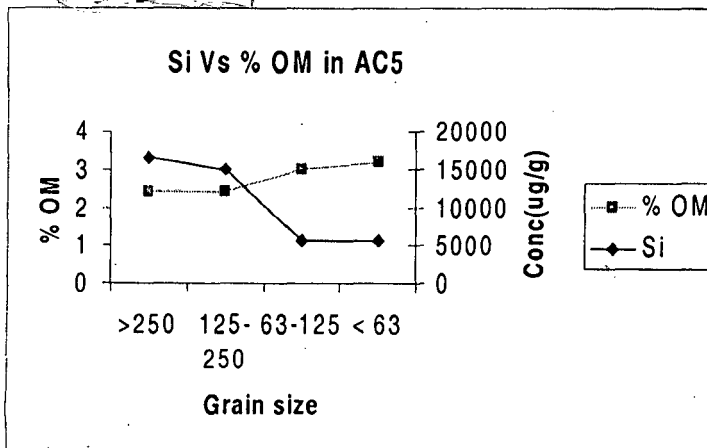


Figure 2f

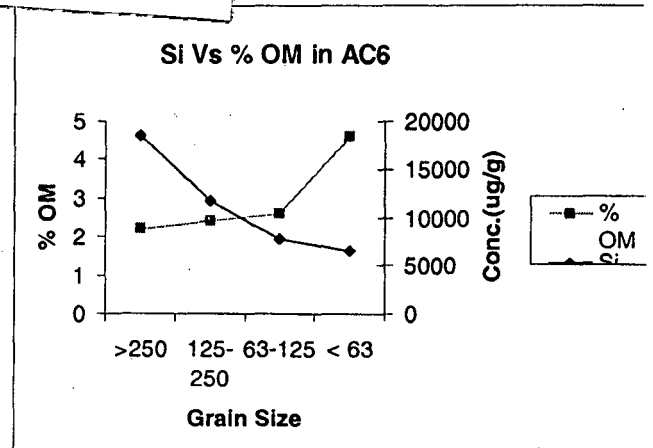


Figure 2g

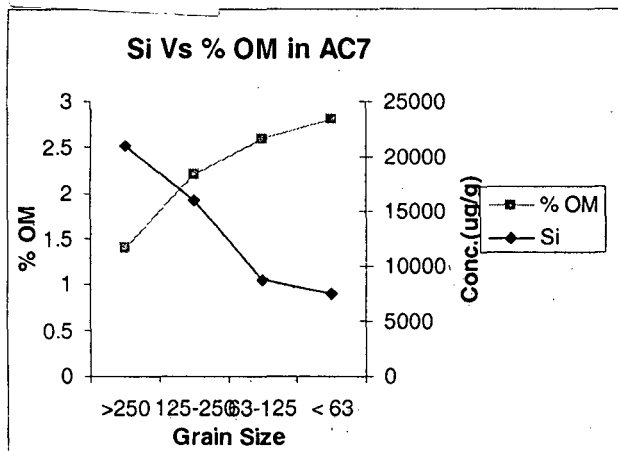


Figure 2h

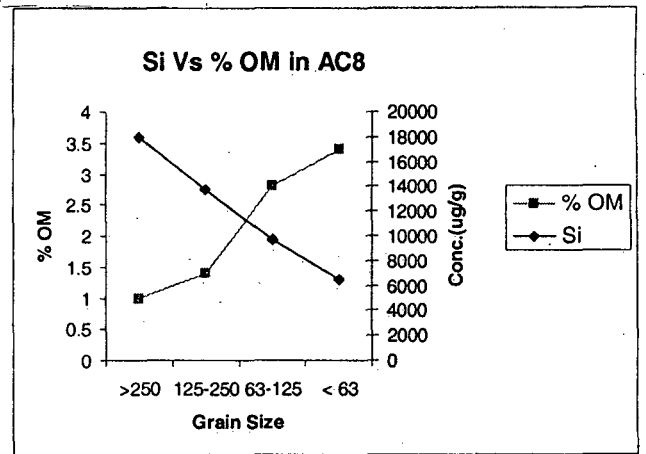


Figure 2j

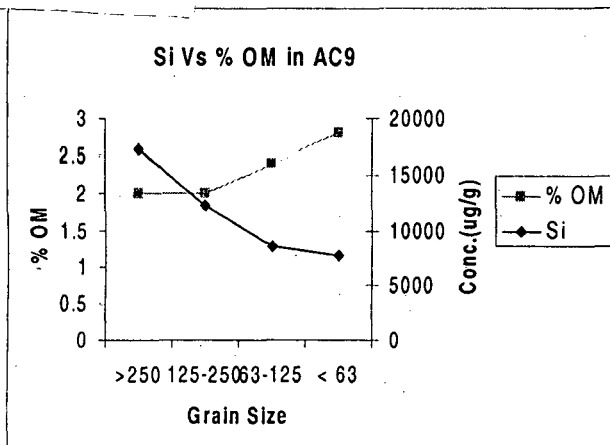


Figure 2j

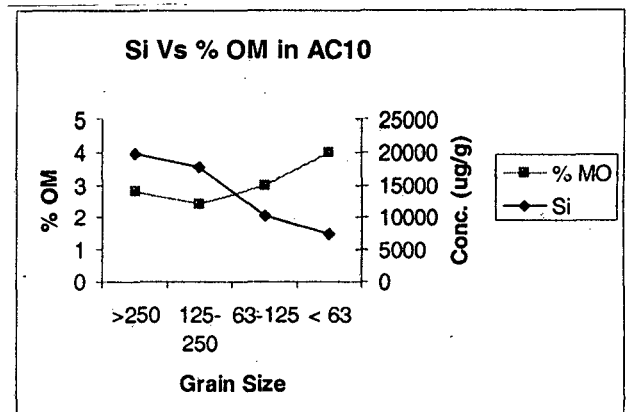


Figure 2k

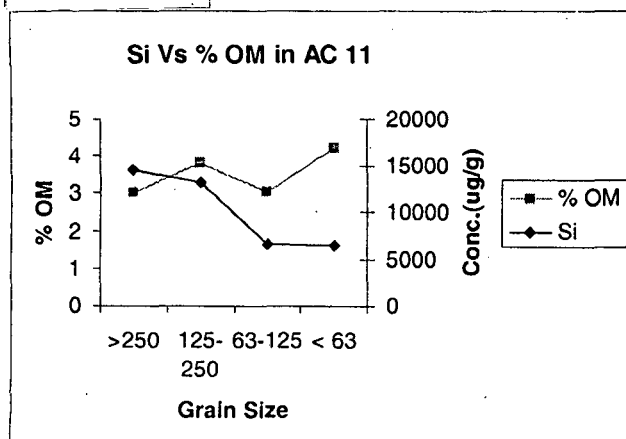
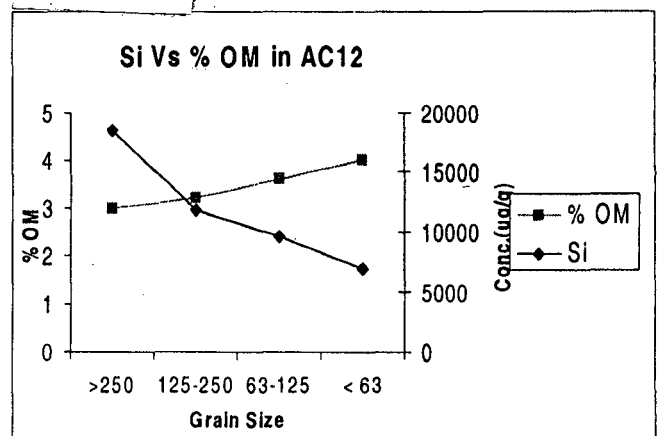


Figure 2l



Zn												
Grain Size	>250µm	125-250µm	63-125µm	50 µm	30 µm	20 µm	10 µm	5 µm	<2 µm	TOTAL	Avg	SD
SITE												
AC1	139	594	734	48	79	104	539	436	664	3337	370	277
AC2	14	769	944	99	59	73	59	972	734	3683	409	425
AC3	454	524	769	54	81	1000	664	967	489	5002	556	338
AC4	783	874	594	44	67	59	699	820	594	4534	504	348
AC5	349	594	874	9	39	79	31	351	734	3060	340	320
AC6	349	664	364	92	12	94	106	629	189	2499	278	240
AC7	314	524	119	16	974	559	302	559	664	4031	448	293
AC8	278	524	699	32	909	9	86	699	734	3970	441	344
AC9	349	699	909	88	54	32	57	804	509	3501	389	332
AC10	349	629	993	27	18	23	524	454	734	3751	416	346
AC11	597	983	47	37	45	91	238	998	934	3770	419	435
AC12	499	754	98	62	21	79	33	954	316	2816	313	347

Table 5 Concentration of Zn in different grain size

Cu												
Grain Size	>250µm	125-250µm	63-125µm	50 µm	30 µm	20 µm	10 µm	5 µm	<2 µm	TOTAL	Avg	SD
SITE												
AC1	20	100	900	400	200	200	100	200	50	2170	241	271
AC2	50	150	251	110	437	277	314	90	165	1844	204	150
AC3	20	100	200	50	540	326	60	30	221	1547	172	172
AC4	50	301	200	442	381	308	102	70	55	1909	212	150
AC5	19	50	200	55	276	393	131	145	386	1655	184	141
AC6	50	158	251	99	497	110	86	66	177	1494	166	138
AC7	25	150	200	143	646	276	301	110	50	1911	212	187
AC8	37	200	150	338	823	497	114	110	55	2324	258	259
AC9	50	100	150	491	386	331	76	165	150	1996	222	154
AC10	50	200	854	338	233	331	204	221	63	2494	277	238
AC11	30	50	420	220	183	450	97	44	217	1711	190	157
AC12	263	102	221	105	215	143	42	114	49	1254	139	78

Table 4 Concentration of Cu in different grain size

Fe												
Grain Size	>250µm	125-250µm	63-125µm	50 µm	30 µm	20 µm	10 µm	5 µm	<2 µm	TOTAL	Avg	SD
SITE												
AC1	13766	12435	13400	20000	13000	9700	8200	10000	10000	110505	12278	3487
AC2	12089	11060	18000	1420	1340	17000	15000	7000	12000	94909	10445	6149
AC3	16425	13000	18000	1440	11600	11700	11400	11000	11000	105563	11729	4610
AC4	19856	14100	13000	14800	11200	17000	13000	11400	9424	123780	13753	3191
AC5	10222	13000	14500	14600	9150	7700	9150	9800	9000	97122	10791	2564
AC6	13474	13878	16382	15009	13110	17550	15290	10700	15260	130653	14517	1994
AC7	17920	18874	15749	16800	19900	16960	9145	8130	4000	127478	14164	5605
AC8	13459	13017	16827	12700	17580	8630	4720	5000	9310	101243	11249	4658
AC9	17716	9725	6189	4140	17540	9100	7810	6000	9625	87845	9760	4829
AC10	14823	17861	15897	12990	9732	8740	9490	8770	6254	104557	11617	3916
AC11	10222	10347	12999	16640	9100	8209	13400	8700	4580	94197	10466	3498
AC12	17644	19108	4400	16790	15710	9520	6124	5530	9117	103943	11549	5764

Table 3 Concentration of Fe in different grain size

Pb

Grain Size(μm)	>250	125-250	63-125	50	30	20	10	5<2	Total	Avg	SD	
SITE												
AC1	26.4	94.4	52.9	272	245.5	19	75.5	22.7	34	842.2	94	97
AC2	162	105	30	249	227	7.2	117	64.2	19	980.5	109	89
AC3	147	30.2	19	204	166	23	106	64.2	15	774.4	86	72
AC4	87	79	76	178	193	53	94	60.4	57	877.4	97	52
AC5	79	42	23	178	166	19	117	19	42	685	76	63
AC6	110	91	60	200	253	57	91	30	49	941	104	74
AC7	109.5	87	38	49	19	23	42	98	57	522.5	58	32
AC8	30	23	30	11	38	57	14	68	60.4	331.4	37	21
AC9	45	49	30	94	53	34	23	34	30.2	392.2	43	21
AC10	147	87	30	246	4	83	4	19	75.5	695.5	77	79
AC11	95	94	30	33	29	59	80	63	19	422	47	31
AC12	43	49	20	67	20	95	65	21	30	410	46	26

Table 8

Concentration of Pb in different grain size

Cd

Grain Size(μm)	>250	125-250	63-125	50	30	20	10	5<2	Total	Avg	SD	
SITE												
AC1	1	8	1.5	1.5	2.9	3.4	0.2	9.7	9.7	37.9	4.2	3
AC2	1.7	3.4	1.7	6.1	4.6	7.2	3.4	9.7	9.7	47.5	5.2	3
AC3	1	7.2	4.3	8.3	1.7	3.8	1.7	6.1	16.3	50.4	5.6	4.7
AC4	1	3.8	9.5	14.6	14.6	14.6	7	11.8	11.8	88.7	9.8	5
AC5	1.5	2.8	16.1	0.8	2.7	2.8	4.3	10.2	20.5	61.7	6.8	7
AC6	2	4.3	8.3	7.9	1.2	4.3	9.5	0.3	8.9	54.7	6	3
AC7	0.9	9.7	10	7.9	2	9.7	1.6	9.7	4.9	56.4	6.2	4
AC8	4	3.6	1.6	9.8	6.8	1	8.3	9.8	11.3	56.2	6.1	4
AC9	6.8	6	1.2	9	7.6	9.7	41.6	7.9	15.2	105	11.6	12
AC10	7.6	4.9	7.2	0.6	0.4	3.6	3.8	7.9	10.3	46.3	5.2	3.4
AC11	2.7	1.8	10	4	1.6	1.6	0.5	8.7	1.6	32.6	3.6	3.5
AC12	0.8	2.6	1.4	8.7	4.2	2.8	3.8	0.8	15	40	4.4	4.6

Table 7

Concentration of Cd in different grain size

Mn

Grain Size	>250μm	125-250μm	63-125μm	50 μm	30 μm	20 μm	10 μm	5 μm	<2 μm	Total	Avg	SD
SITE												
AC1	1087	865	674	1341	1103	3	1049	244	371	6737	748	454
AC2	1120	53	1196	2003	1406	23	1034	934	221	7990	888	668
AC3	1339	530	1404	597	1458	21	1005	112	436	6902	767	553
AC4	1372	777	915	6	46	18	1244	748	1024	6150	683	553
AC5	796	525	1497	1352	1292	8	1034	310	244	7058	784	540
AC6	365	612	612	888	1157	8	15	500	530	4687	521	370
AC7	408	893	1219	393	30	53	30	220	2143	5389	599	709
AC8	50	689	1594	1482	1	48	1018	607	998	6487	721	606
AC9	439	847	1053	413	34	52	1011	311	820	4980	553	391
AC10	557	847	1471	1484	13	26	1014	434	838	6684	743	541
AC11	1003	707	1353	1436	244	18	1044	112	404	6321	702	534
AC12	1294	743	892	530	446	11	1342	606	403	6267	696	425

Table 6

Concentration of Mn in different grain size

Figure 4 Cu concentration at different sites (Upstream, Midstream & Downstream)

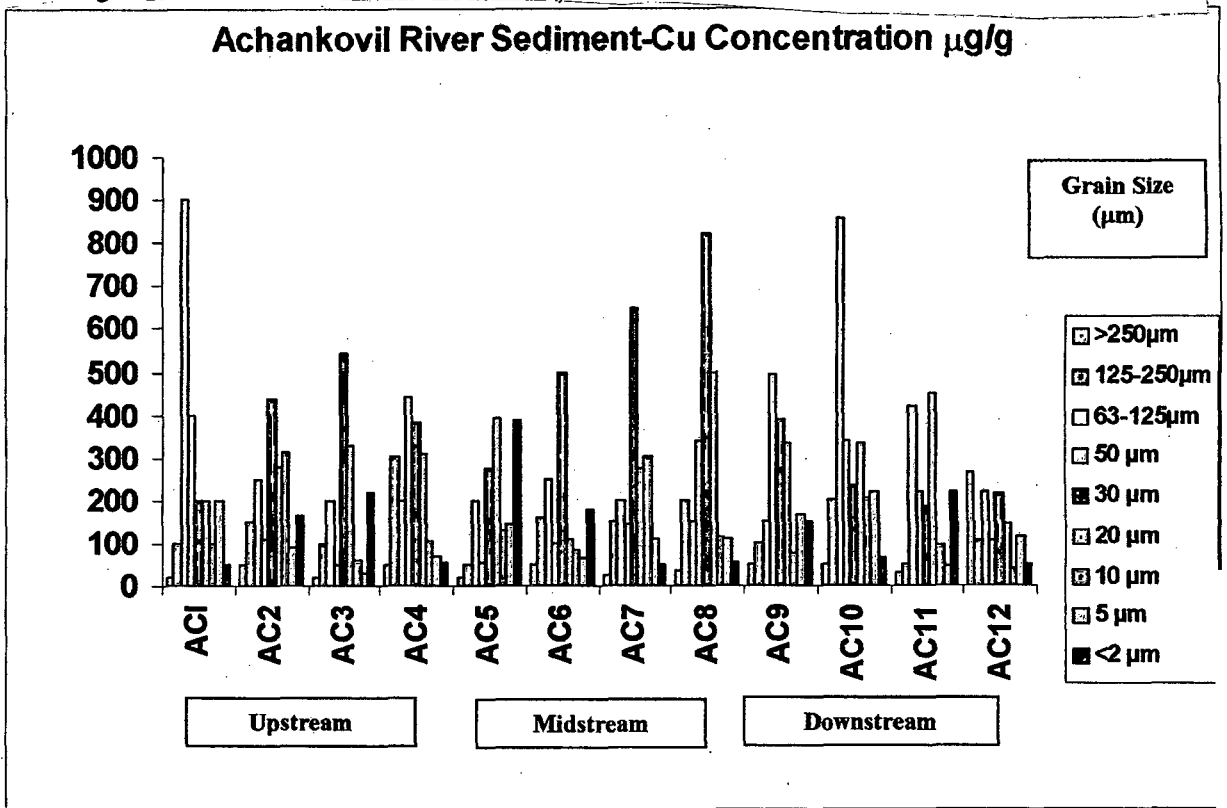


Figure 3 Fe concentration at different sites (Upstream, Midstream & Downstream)

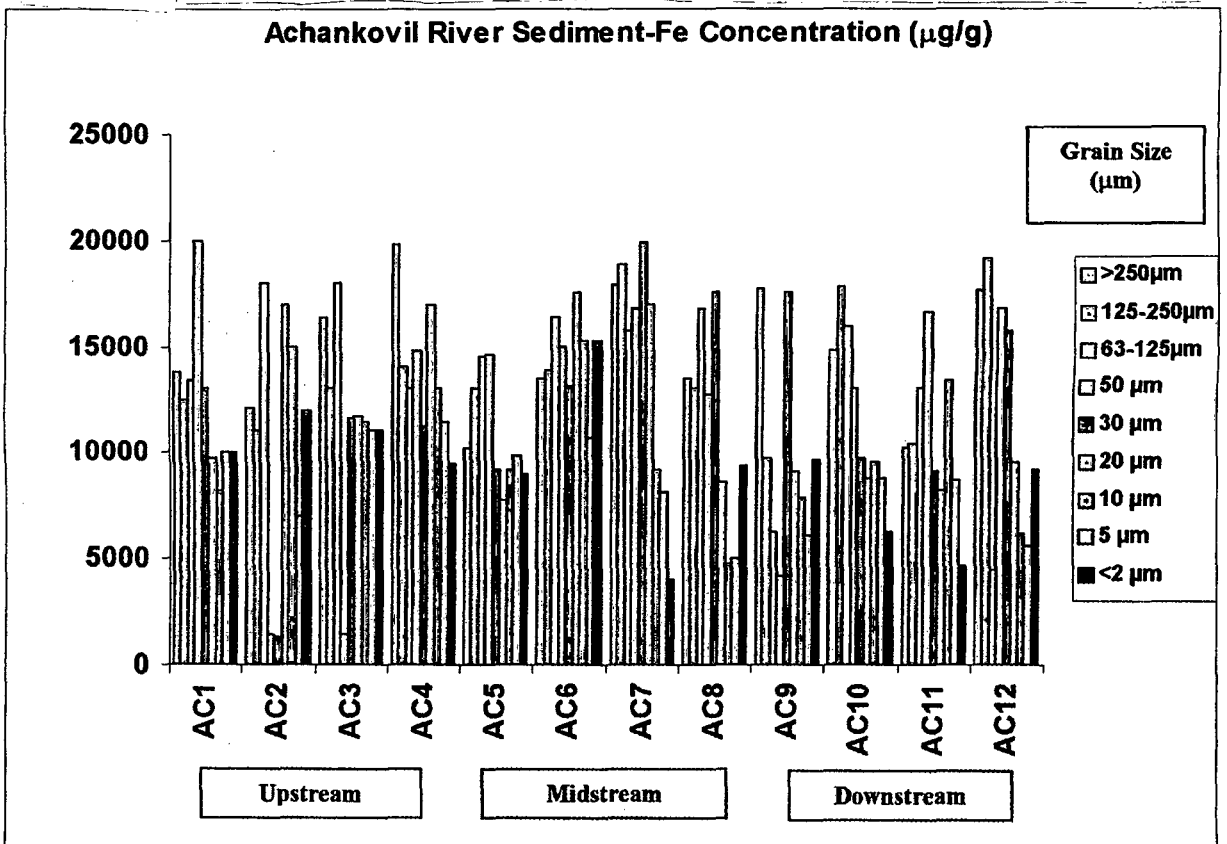


Figure 6 Mn concentration at different sites (Upstream, Midstream & Downstream)

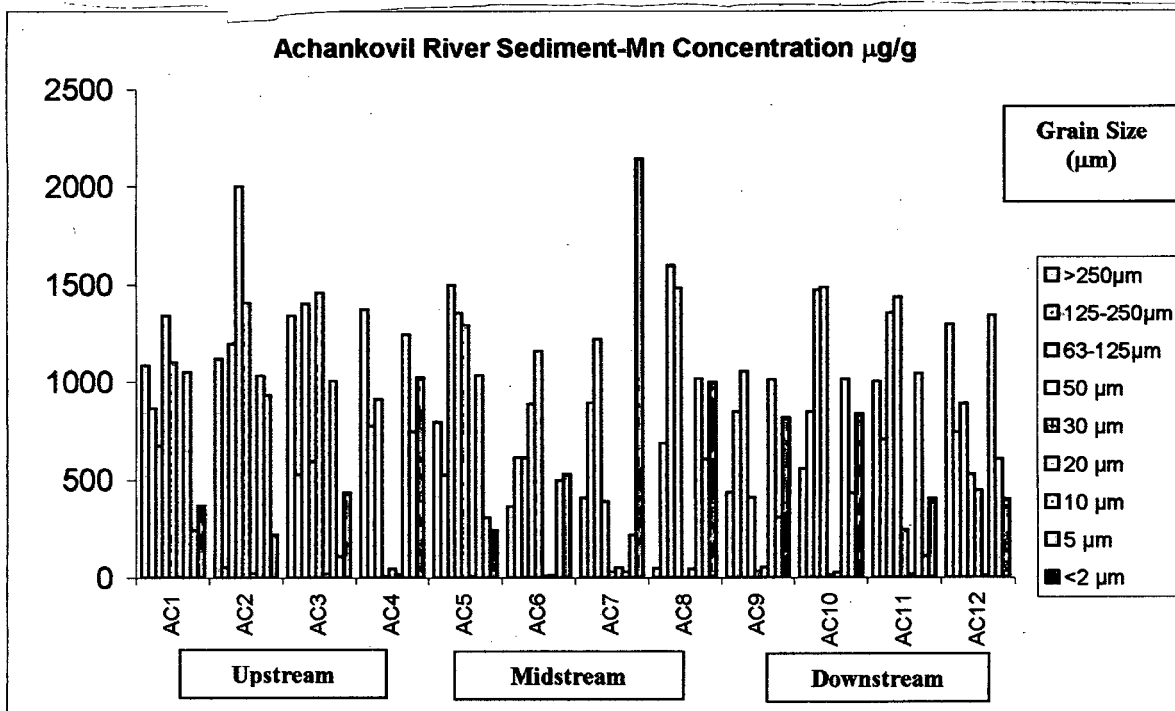


Figure 5 Zn concentration at different sites (Upstream, Midstream & Downstream)

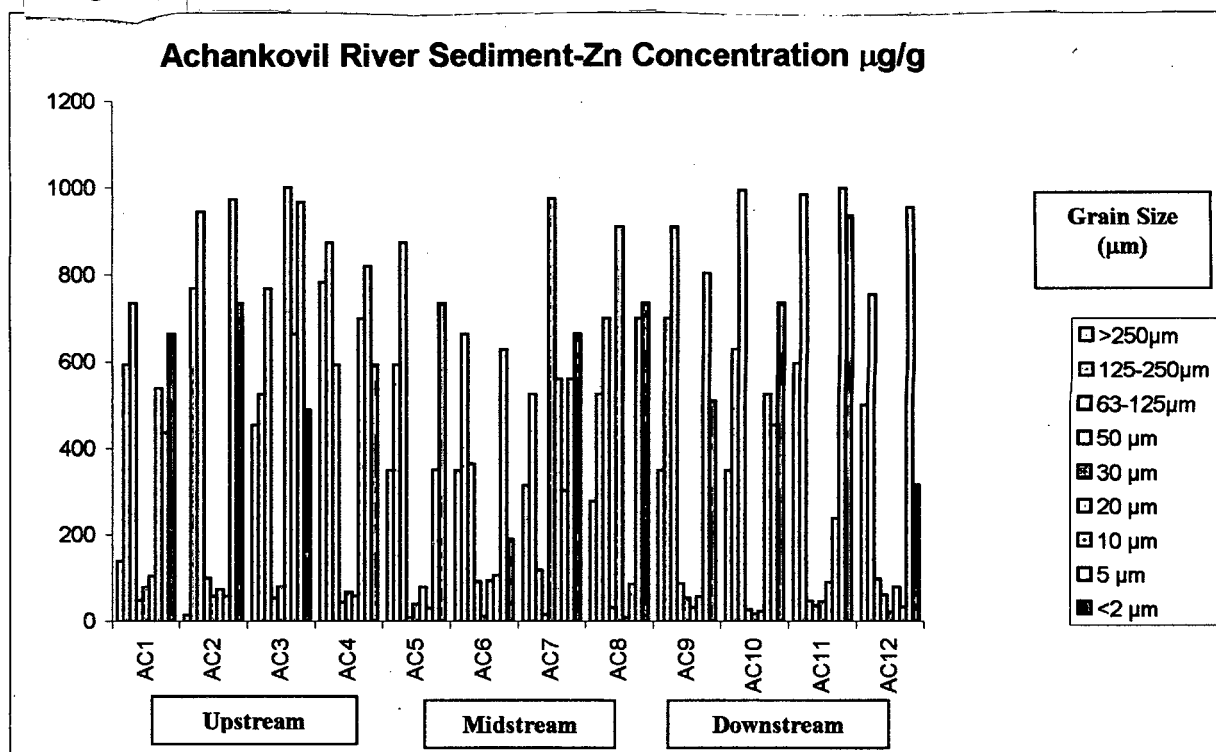


Table - 9 Percentage value of metals in different chemical fraction

Cd(%)									
SITE	eua	ech	Carb	MnO	AFeO	CFeO	Org		
AC1	5.98	24.06		18.08	18.08	24.06	0.13		9.5
AC2	5.4	22.03		19.1	16.56	27.51	0.5		8.78
AC5	11.39	28.6		13.24	11.39	28.6	0.13		9.27
AC6	1.72	26.75		25.16	11.39	22.91	0.13		11.92
AC9	1.77	29.46		17.73	11.73	25.78	4.22		9.27
AC10	2.17	22.15		16.64	21.76	20.99	5.5		10.75

Zn(%)									
SITE	eua	ech	Carb	MnO	AFeO	CFeO	Org		
AC1	5.45	3.64		3.64	10.45	38.18	18.19		20.38
AC2	4.32	2.91		2.91	8.36	29.11	29.11		23.28
AC5	2.6	1.6		2.6	7.48	33.84	24.72		27.07
AC6	3.55	2		2.46	11.06	29.56	29.56		21.67
AC9	4.67	1.62		1.62	16.17	16.58	30.76		28.49
AC10	4.37	2.91		2.91	14.55	33.52	20.39		20.97

Cu(%)									
SITE	eua	ech	Carb	MnO	AFeO	CFeO	Org		
AC1	17.49	24.45		3.48	6.96	31.42	10.45		5.57
AC2	9.92	13.87		1.97	3.95	7.9	5.93		6.32
AC5	19.07	26.67		3.79	7.59	19.07	19.07		12.15
AC6	23.42	42.95		3.89	3.89	15.56	11.67		6.22
AC9	22.03	36.6		3.66	3.66	14.64	7.32		11.71
AC10	30.31	27.97		4.31	4.31	12.95	12.95		6.9

Mn(%)									
SITE	eua	ech	Carb	MnO	AFeO	CFeO	Org		
AC1	0.42	3.96		1.49	26	0.18	28.82		39.7
AC2	0.28	4.07		2.55	6.53	1.89	14.7		69.22
AC5	0.84	3.09		3.31	21.83	2.59	16.08		52.21
AC6	0.54	1.45		1.28	0.83	1	38.84		56.5
AC9	0.16	0.81		1.34	0.46	24.23	29.13		43.8
AC10	1.38	3.32		5.22	0.75	32.65	38.51		18.08

Pb(%)									
SITE	eua	ech	Carb	MnO	AFeO	CFeO	Org		
AC1	12.4	2.77		2.77	15.14	22.04	20.69		24.23
AC2	8.97	1.77		2.01	14.94	20.9	13.43		38.18
AC5	19.4	7.97		2.29	13.68	6.86	2.29		47.47
AC6	9.01	23.98		5.99	23.98	15.09	5.16		16.75
AC9	3.51	7.92		3.51	16.73	16.73	11.44		43.63
AC10	7.16	7.16		13.45	1.8	18.81	7.16		44.42

Fe(%)									
SITE	eua	ech	Carb	MnO	AFeO	CFeO	Org		
AC1	0.03	0.07		0.32	0.05	44.11	40.96		14.44
AC2	0.15	0.13		0.35	0.02	46.85	44.85		7.62
AC5	0.4	0.1		0.26	0.21	37.87	36.23		24.89
AC6	0.43	0.1		0.2	0.1	39.76	40.38		18.84
AC9	0.1	0.2		0.2	0.1	37.54	36.44		25.13
AC10	0.1	0.3		0.2	0.3	42.5	42.3		14.04

Figure A

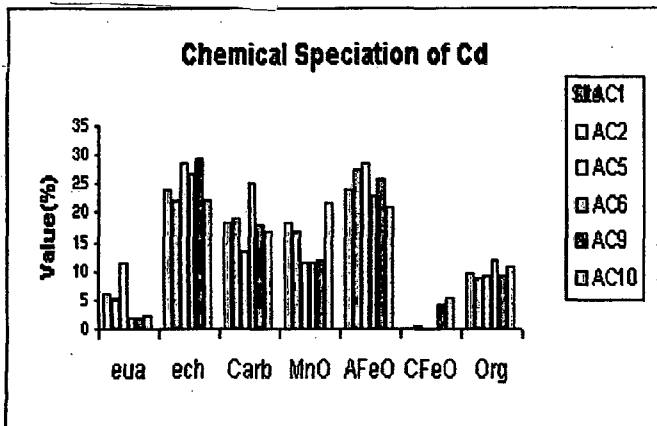


Figure B

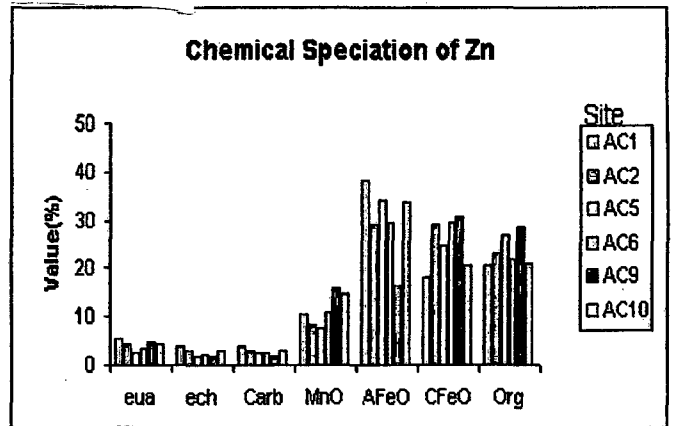


Figure C

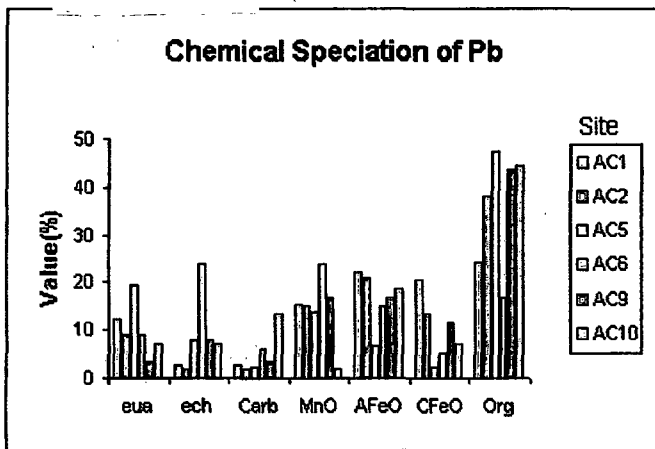


Figure D

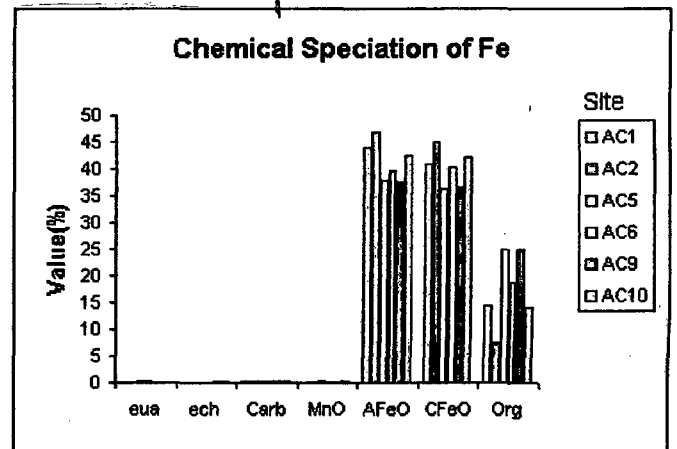


Figure E

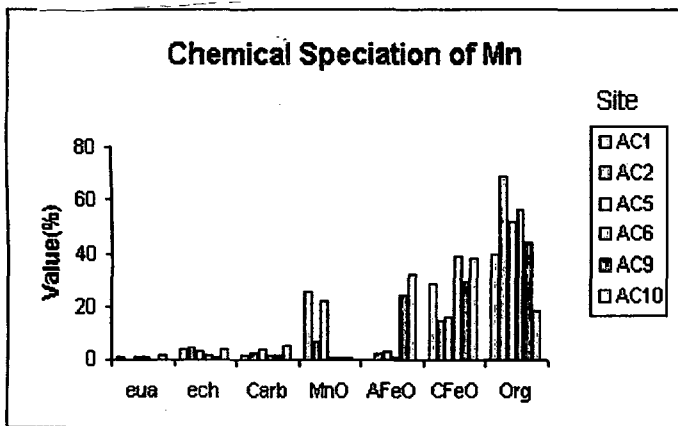
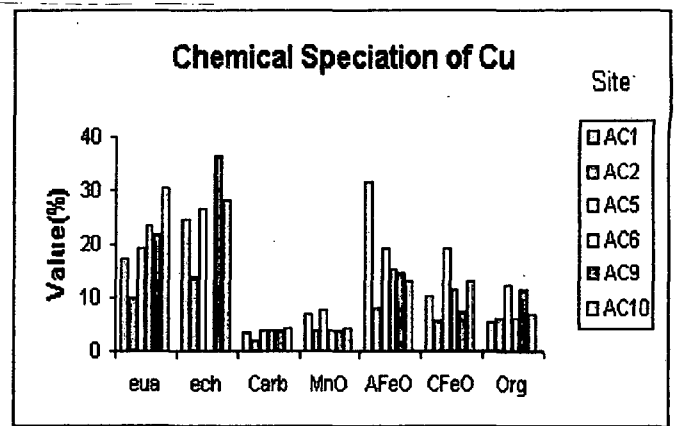


Figure F



Comparative mobility of metals (Al, Zn, Fe) at different sites

Figure 9

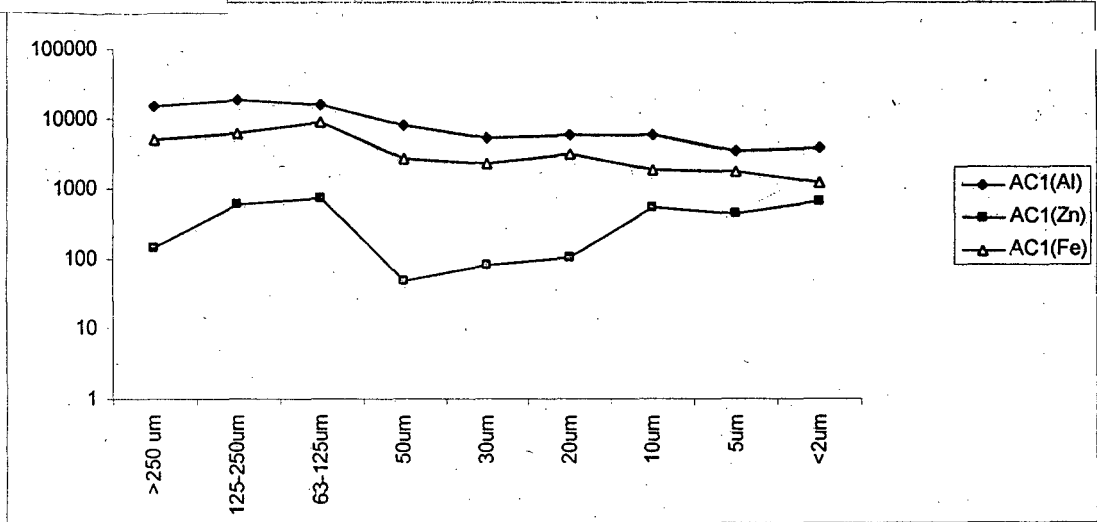


Figure 10

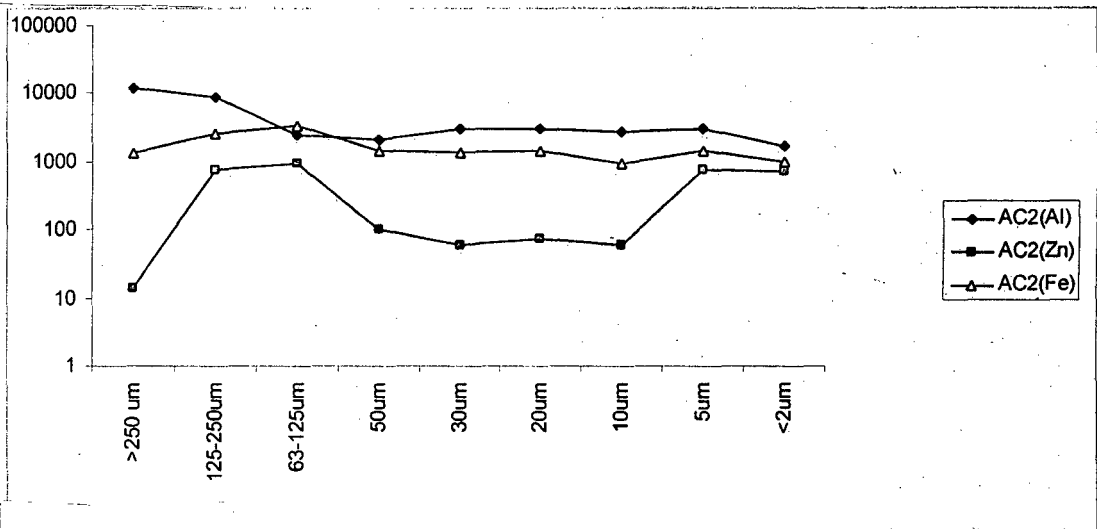


Figure 11

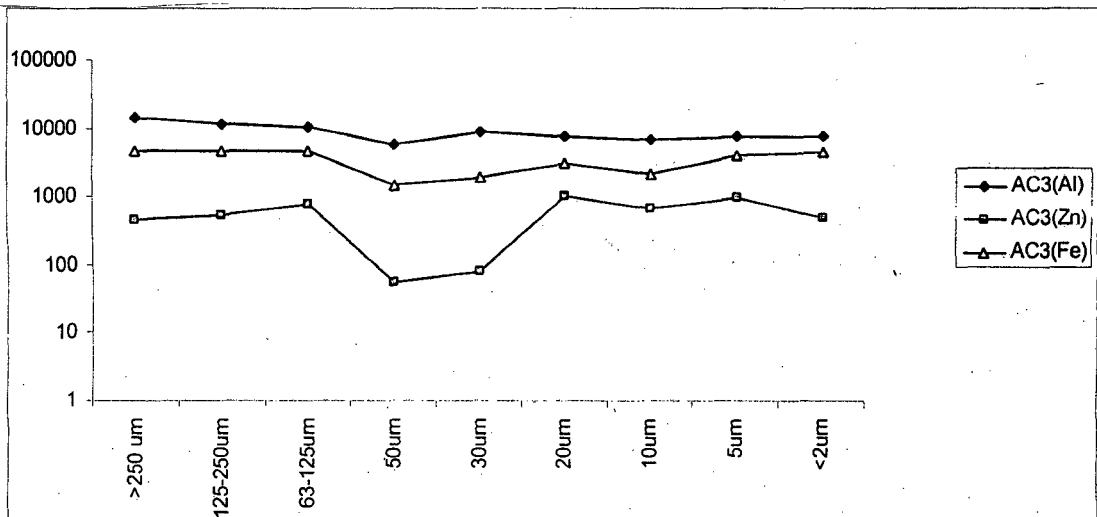


Figure 12

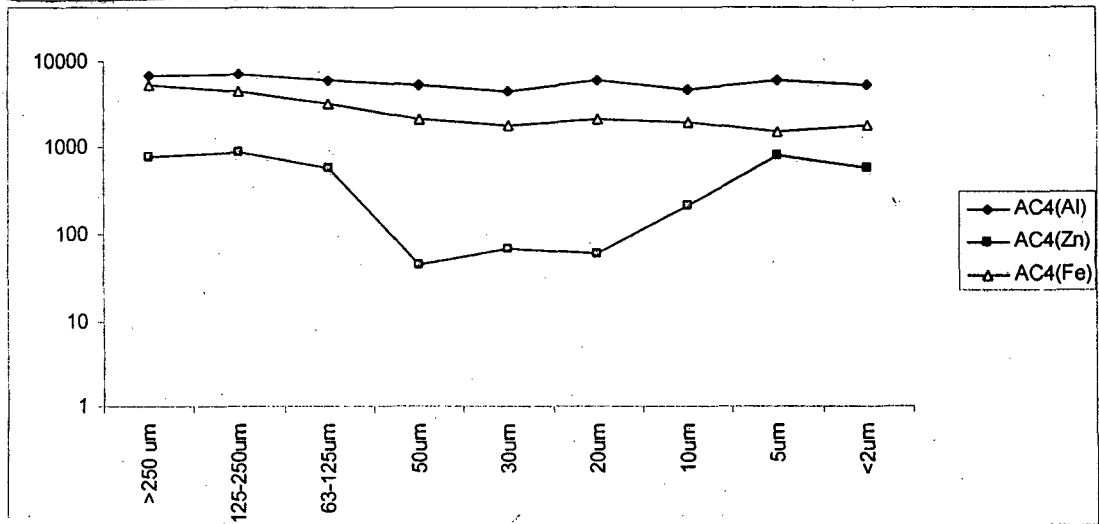


Figure 13

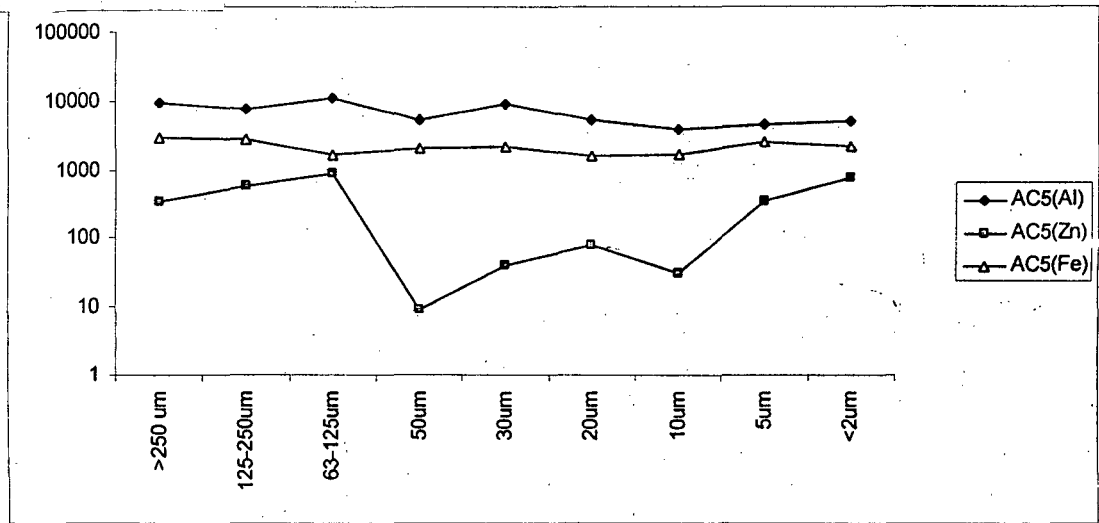


Figure 14

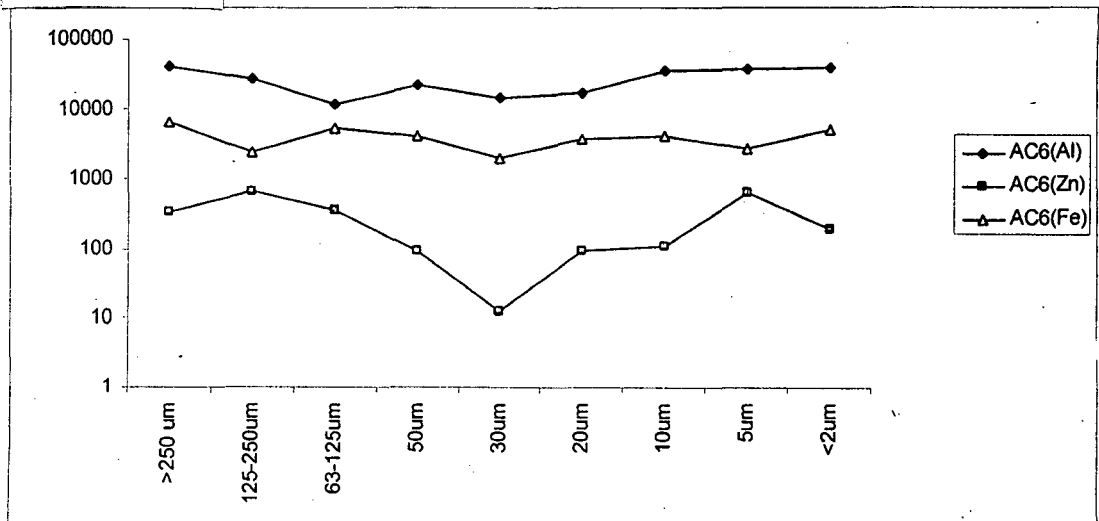


Figure 15

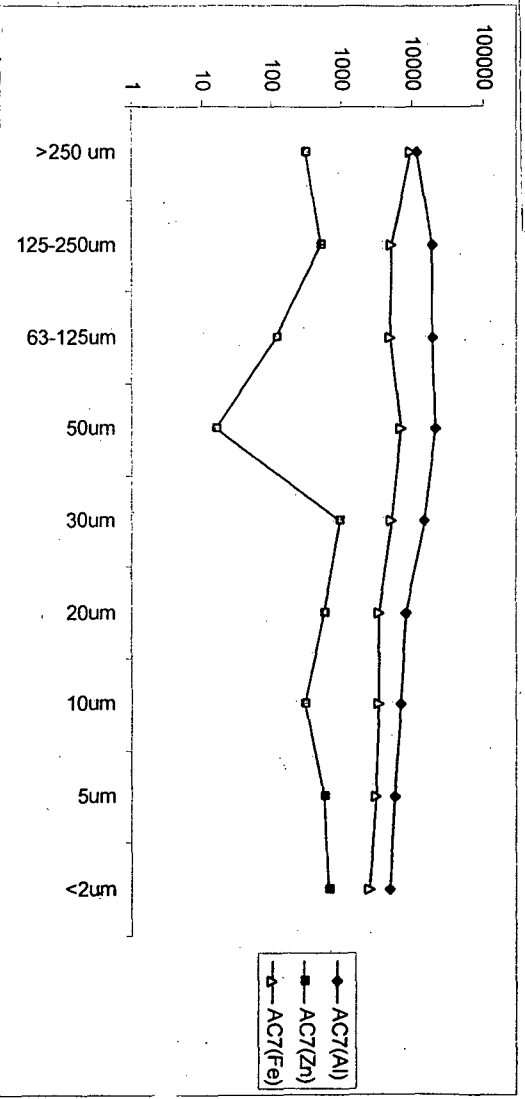


Figure 16

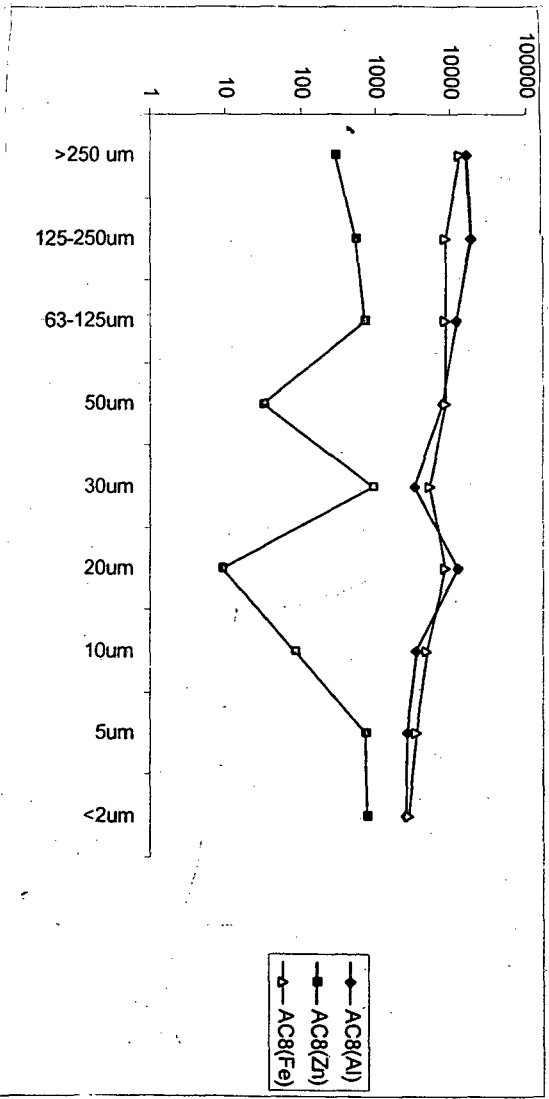


Figure 17

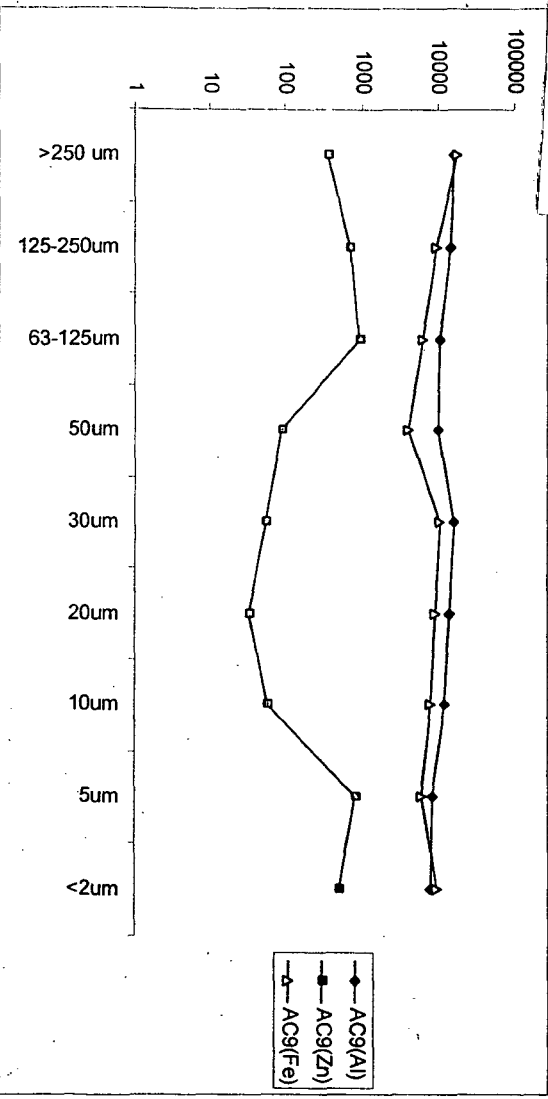


Figure 18

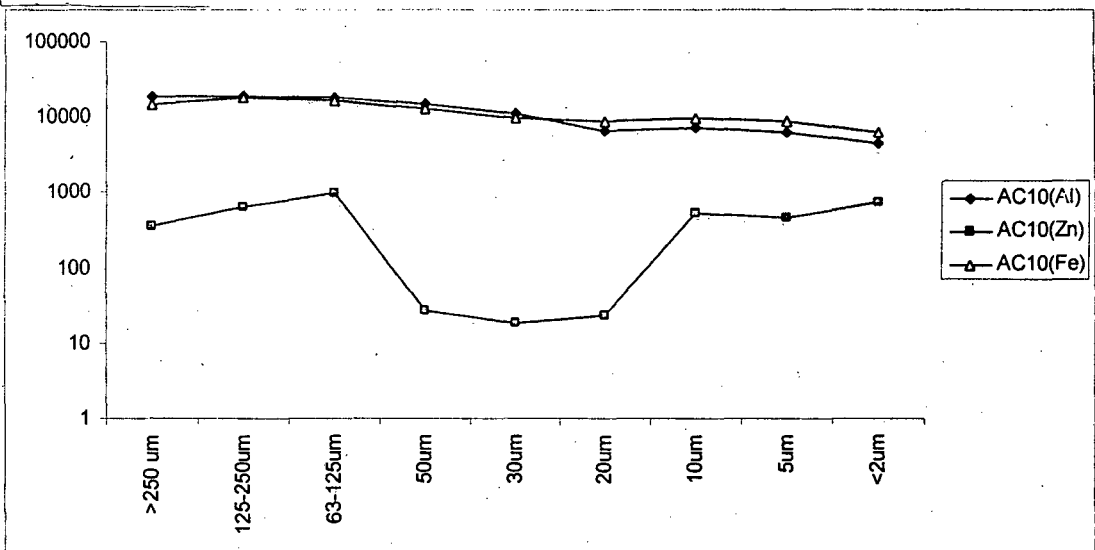


Figure 19

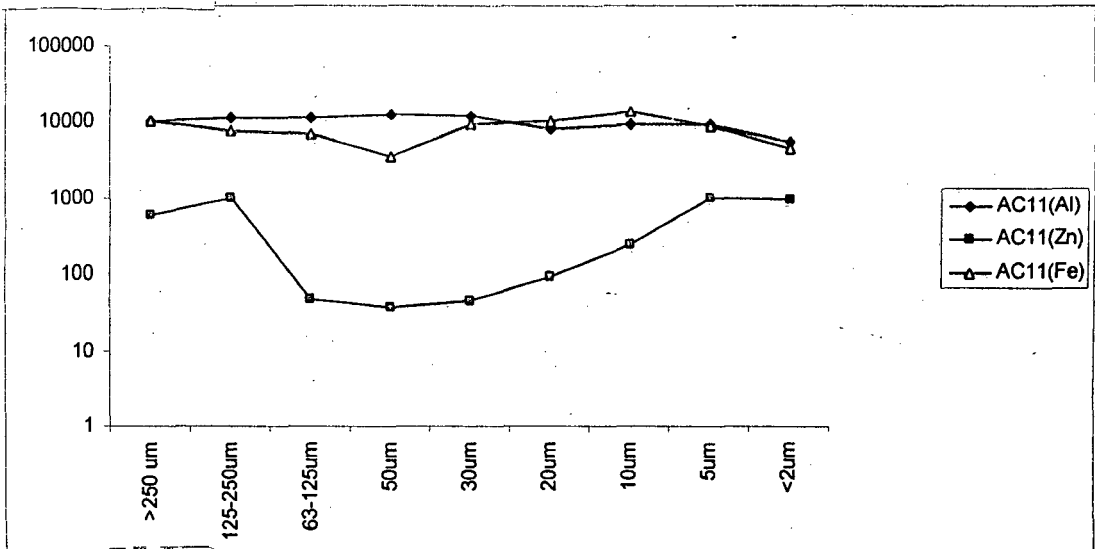
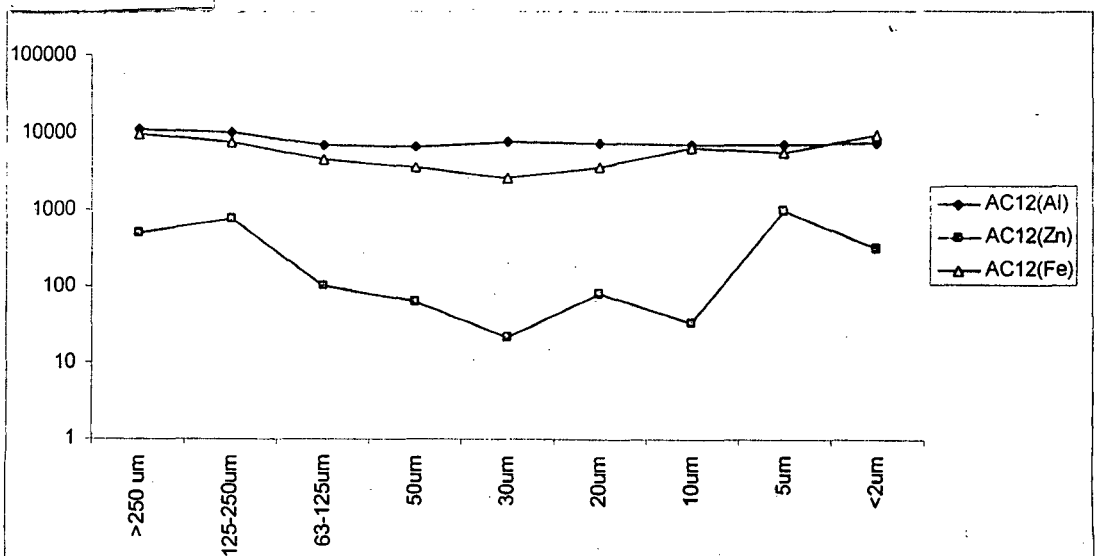


Figure 20



CHAPTER 5

SUMMARY AND CONCLUSION

CHAPTER -5

SUMMARY AND CONCLUSION

In order to evaluate the possible toxicity or risk of environmental pollution of heavy metals presents in sediments, the types of association between metals and the sediments must be assessed. In this connection this study on Achankovil river surface sediments purely deals with the role of grain size in mobility of selected trace metals (Fe, Cu, Zn, Pb, Cd and Mn). Another part of this study completely involves the chemical speciation of the above trace elements.

First part i.e. grain size control of trace elements (Fe, Cu, Zn, Pb, Cd and Mn) mobility shows that not only smaller grain size but also larger grain size particles play a very important role in the distribution, transport mobility of metals in the river system. All Achankovil river sites i.e. AC 1, AC 2, AC 3, AC 4, AC 5, AC 6, AC 7, AC 8, AC 9, AC 10, AC 11 and AC 12 were classified into three groups –

- (b) Upstream (AC 1, AC 2, AC 3, AC 4),
- (c) Midstream (AC 5, AC 6, AC 7 and AC8)
- (d) Down Stream (AC 9, AC 10, AC 11 and AC 12)

In most of the samples, it is $< 63\mu\text{m}$ grain size particle responsible for high mobility of trace elements. This indicates that as grain size decreases when

- (a) Concentration of silica decreases
- (b) Organic matter increases
- (c) Surface to volume ratio increases.
- (d) Mobility of trace elements e.g., Fe, Cu, Zn, Pb, Cd and Mn is very dynamic in nature. It means exchange and adsorption of these metals is

very high. They are readily available for physical, chemical, and biological weathering.

In addition to analysis of trace elements, measurement of silicon (Si) and Al is performed in order to understand the mobility of metals to get insight into nature of residual element, conservative element, non-conservative element and weathering pattern of the elements. Al & Fe are immobile compare to other metals analysed here.

Second part of the present work shows analytical results, obtained using seven step sequential extraction procedure of Lydia Leleyter and Jean – Luc Probst (1999). According to this methods, percentage (%) values of six trace elements (Fe, Cu, Pb, Zn, Cd and Mn) were measured. This method is widely applied because of its selectivity of reagents and experimental conditions.

The aim of this sequential extraction procedure is to leachate the total residual fraction of Achankovil river sediment (which includes soluble with water, readily exchangeable fraction, carbonate fraction, MnO fraction, AFeO fraction, CFeO fraction and Organic matter fraction).

The chemical fractionation study shows the Fe & Mn are mainly in the crystalline form. Whereas Cu unavailable to the system but Cd, Cu, Pb are easily available to the system, which can be utilized for geochemical and biogeochemical processes in the river system. The physical and chemical fractionation studies highlight the size control on the metal distribution and its weathering pattern mobility, transportation and their availability in the biogeochemical processes in the river system.

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