ACCUMULATION OF HEAVY METALS IN TYPIC SULFAQUENTS OF KUTTANAD ECOSYSTEM

By

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THESIS

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DECLARATION

I hereby declare that the thesis entitled **"Accumulation of heavy metals in Typic Sulfaquents of Kuttanad ecosystem."** is a bonafide record of research work done by me during the course of research and the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title, of any other university or society.

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Certified that the thesis entitled **"Accumulation of heavy metals in Typic Sulfaquents of Kuttanad ecosystem."** is a record of research work done independently by **Ms. Aneesa Beegum M. M.** under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to her.

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Aneesa Beegum M.M.

Dedicated to Major
Advisor (Dr. Beena V. I.)
and my family

ABBREVIATIONS

BOD	-	Biochemical Oxygen Demand
DO	-	Dissolved Oxygen
COD	-	Chemical Oxygen Demand
BDL	-	Below Detectable Level
RDe	-	Relative Density
RF	-	Relative Frequency
SDR	-	Summed Dominance Ratio
IVI	-	Importance Value Index
AAS	-	Atomic Absorption Spectrophotometer
ICP-OES	-	Inductively Coupled Plasma Optical Emission Spectrometry
APHA	-	American Public Health Association
AOAC	-	Association of Official Analytical Chemists
WHO	-	World Health Organization
ESRI	-	Environmental System Research Institute
GIS	-	Geographical Information System
EC	-	Electrical Conductivity
OC	-	Organic Carbon
N	-	Nitrogen
P	-	Phosphorus
K	-	Potassium
Ca	-	Calcium

Mg	-	Magnesium
S	-	Sulphur
Fe	-	Iron
Mn	-	Manganese
Zn	-	Zinc
Cu	-	Copper
Pb	-	Lead
Cr	-	Chromium
Hg	-	Mercury
Al	-	Aluminium
Cd	-	Cadmium
kg	-	Kilogram
µg	-	Microgram
dS m^{-1}	-	Deci Siemens per meter

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Introduction

1. INTRODUCTION

Environmental pollution is one of the greatest problems, that the world is facing today, which create irreparable damage to the natural world and human society. Soil, water and air pollution contribute 40 per cent of deaths worldwide. Soil pollution is contamination of soil with toxic materials that are present at a concentration higher than the normal; it may adversely affect living organisms in the ecosystem. Soil pollution is linked with water and air pollution. Toxic chemicals from soil leach into ground water or run off from contaminated land ultimately reach lakes, streams and oceans causing water pollution. Toxic volatile compounds released from soil into the atmosphere cause air pollution.With the development of urbanization heavy metal accumulation in the environment is gradually increasing.

Among all the contaminants, heavy metals are the most toxic soil pollutants, because they are not destroyed or degraded and their toxic effects are long term. Stable metals or metalloids whose density is greater than 5 Mg m^{-3} are known as heavy metals. Mainly heavy metals include mercury, cadmium, cobalt, lead, molybdenum, nickel, copper and zinc (Nies, 1999). Heavy metals can be classified into two categories 1) Essential elements and 2) Non essential elements. Essential elements include Fe, Mn, Zn, Cu, Mo and Ni. Trace amount of essential elements are required by living organisms to perform their life cycle. Insufficient quantity of these elements cause many problems and excess amount cause toxicity and As, Ag, Cd, Hg and Pb are known as non essential plant elements. In the soil environment, heavy metal availability is highly dependent on some soil factors such as soil pH, organic matter, organic clays and oxides coated with heavy metals, amount of heavy metals, cation exchange capacity etc. Soil pH has the major role in the solubility and retention of heavy metal ions in the soil. Chemical and biological properties of soils are altered by heavy metal contamination.

Kuttanad is a region lying 0.6-2.2m below mean sea level, covering the districts of Alappuzha, Pathanamthitta and Kottayam. The rivers such as Pamba, Meenachil, Achencovil and Manimala are flowing into this region. Kuttanad is popular for its extensive paddy cultivation and is known as "rice bowl" of Kerala. An estimated area of 50,000 ha of land is under rice cultivation. Among this, acid sulphate soils (Typic Sulfaquents) cover an area of 14,227 ha. Ambalapuzha, Kallara, Thakazhi, Purakkad, Thotapally and Thuravur were identified as acid sulphate soil series of Kuttanad. Acid sulphate soils are problem soils having pH below 4. Potential acid sulphate soils are rich in pyrite (FeS_2), which upon drainage and subsequent exposure to air, oxidizes to sulphuric acid (H_2SO_4) and creates actual acid sulphate soils. Low pH, high aluminium, iron and sulphate concentrations are the characteristics of acid sulphate soils. Extreme acidity of acid sulphate soils may enhance the availability of some toxic elements including heavy metals which cause damage to plant growth.

Since several water bodies are interconnected with acid sulphate soils of Kuttanad, heavy metal accumulation in soil will lead to contamination of aquatic ecosystem. Heavy metals present in the ecosystem are mainly from natural and anthropogenic sources. Farmers in Kuttanad usually apply fertilizers at a rate higher than the recommended level which leads to heavy metal contamination in soil. Apart from this, other sources of heavy metals are mining, smelting process, disposal of urban and industrial wastes and irrigation using waste water. All these practices will lead to accumulation of heavy metals in soil, water and sediments. Furthermore during monsoon season, river systems of Kuttanad carry upland waste to wetlands. This will also cause accumulation of contaminants especially heavy metals.

Kuttanad wetlands are considered as a necessary source of food and water for people. Heavy metal contamination adversely affects soil ecology, agricultural production and quality of water. The heavy metals in soil through biomagnification can enter into higher trophic levels and can harm human beings. Recently there is an increasing concern towards the pollution due to heavy metals. Accumulation of heavy metals in aquatic system adversely affects the aquatic organisms. So great attention is required in the field of heavy metal removal.

Several remediation techniques are available. Among all the techniques, phytoremediation is one of the best techniques for remediating the contaminated site. It is cost effective and environment friendly. Some aquatic macrophytes are used for phytoremediation. The aquatic macrophytes can take up heavy metals through roots from the sediments. Mangrove ecosystems have the metal remedial capacity and they act as a sink or buffer of the metal reaching nearby aquatic system. Hence study of phytoremedial capacity of mangroves along with terrestrial and aquatic plants is helpful to explore the potential of phytoremediation.

With this background details the present study is undertaken with the following objectives:

- To elucidate the heavy metals present in the soil, sediments, water bodies and native flora of the acid sulphate wetland ecosystem of Kuttanad.
- To examine the effect of soil properties on the bioaccumulation of heavy metals and to prepare georeferenced maps with the generated data.

Review of Literature

2. REVIEW OF LITERATURE

Heavy metals are one of the most dangerous contaminants in the ecosystem which get accumulated both by natural and anthropogenic sources. At low concentration some of the heavy metals are beneficial to plants. When their concentrations exceed the normal range, these are harmful to both plants and animals. Heavy metal contamination in plant, soil and water is one of the most serious issues faced throughout the world and requires immediate attention. In wetlands, mainly in paddy field, excess use of agricultural fertilizers, pesticides, irrigation using waste water, urban and industrial waste disposal, smelting process and mining will lead to accumulation of heavy metals at an increasing rate (Alloway, 1990 and Adriano, 2001).

Kuttanad has been recognized as the "rice bowl" of Kerala. Excess application of fungicides, herbicides and synthetic fertilizers are common in paddy fields of Kuttanad, which can result in accumulation of heavy metals in water and sediments. At this context, a study was undertaken to estimate levels of heavy metals in soil, sediment and aquatic macrophytes of Kuttanad ecosystem. A brief review has been done on the characteristics of acid sulphate soils of Kuttanad, impact of heavy metals on agricultural soils, influence of soil properties on mobility of heavy metals, influence of fertilizers and pesticides on heavy metal accumulation, water quality, heavy metal status of aquatic ecosystem, sediment quality, status of heavy metals in sediments and phytoremediation potential of aquatic macrophytes.

2.1 Characteristics of acid sulphate soils

Acid sulphate soils are naturally developing soil materials formed under anaerobic conditions which either comprise sulphuric acid or have the potential to form it in an amount that can have significant impact on other soil characteristics (Dent and Pons, 1955). The acid sulphate soils have a pH below 4 that is directly or indirectly caused by sulfuric acid formed by oxidation of pyrite. In the field, pH of the soil will be neutral to slightly acid. Upon drainage, the soil becomes strongly acidic which results in iron and aluminium toxicity (Breemen and Pons, 1978). It directly affects the growth of plants and indirectly decreases the availability of phosphorus and other micronutrients. Langenhoff (1986) reported that out of 12 million hectares of potential acid sulphate soils in the world, six million hectare is found in South East Asia. In Kuttanad it is estimated that 14,227 ha of land is under acid sulphate (Typic Sulfaquents) soils (Beena, 2005).

2.1.1 Physical characteristics

In the natural wetlands of Kerala, clay was dominating particle size fraction but in *karappadam* soils, silty and clayey texture was predominant (Sreedevi *et al.*, 1975). The texture of Kuttanad soils were clay to clay loam (Raju, 1988). Throughout the profile of *kari* soils, texture was clay loam but in case of *karappadam* soils, surface soils showed clay loam texture and down the depth silty loam was the dominant texture (Soil Survey Staff, 1994). Water holding capacity of surface soils from six series of acid sulphate soils ranged from 40 to 65.3 per cent. Among them, Thuravur series showed the highest water holding capacity and pore space (65.3 and 63.1 % respectively). Thakazhi series showed the highest hydraulic conductivity (10.46 cm h^{-1}) (Beena, 2005).

2.1.2 Electro-chemical characteristics

2.1.2.1 pH

Main anarchy of the acid sulphate soils is soil acidity (Ponnamperuma *et al.*, 1973). Beena and Thampatti (2013) studied the acidity characteristics of acid sulphate soils of Kuttanad by analysing surface and subsurface acid sulphate soil samples from 20 locations of six soil series (Ambalapuzha, Thakazhi, Thottapally, Thuravur, Kallara and Purakkad). They found that the soils were extremely acidic; pH ranged from 2.5 to 5.2. The lowest pH was noticed in Thakazhi series and the highest pH was recorded in

Thottapally. *Kari* soils were highly acidic compared to *kayal* and *karappadam* soils. *Kari* soils from Kallara reported the lowest pH of 2.6 (Marykutty and Aiyer, 1987).

Release of soluble aluminium in the acid soils of Kerala was studied by Abraham (1984). She reported that the main constituent of soil acidity is presence of exchangeable aluminium. The chief sources of toxicity in Kuttanad were extreme acidity, solubility of iron chlorides and sulphates (Money, 1961). In flooded condition, peat soils and some of the acid sulphate soils showed a pH value of 5 (Ponnamperuma, 1972; Ponnamperuma, 1978).

2.1.2.2 Electrical conductivity

Soils of Kuttanad are saline in nature. Kurup and Aiyer (1973) reported that maximum EC values were observed during summer (March to April) and minimum during October to November. *Kayal* soils were more saline compared to *kari* and *karappadam* soils. Different workers reported that EC values ranged from 0.1 to 43.6 dS m^{-1} in Kuttanad soils (Ghosh *et al.*, 1976; Aiyer and Nair, 1979; Kabeerthumma and Patnaik, 1980; Marykutty and Aiyer, 1987).

2.1.3 Chemical properties

2.1.3.1 Organic carbon

In wetland paddy soils of Kuttanad, average organic carbon content was 4.63 per cent, which was higher than normal low land rice soils. Content of organic carbon varied from 5.35 to 17.55 per cent (Usha and Varghese, 2001). Large carbon input through organic fertilizers and plant residues were the main characteristics of paddy soil residues (Gong and Xu, 1990 and Tanji *et al.*, 2003). Neue *et al.* (1997) and Lal (2002) found that organic carbon accumulation was also due to the water logging associated with rice cropping. They also suggested that slower rate of decomposition of organic matter under anaerobic condition than under aerobic condition could be a reason for organic carbon accumulation. Among the six acid sulphate soil series, organic carbon content was fairly high in Purakkad, Kallara and Thuravur series. High organic carbon was due to the presence of organic matter debris in these areas (Beena, 2005).

2.1.3.2 Major nutrients

Pillai (1964) reported that available nitrogen content of *kari* soils of Kuttanad ranged from 140 to 590 mg kg^{-1}. Thampatti (1997) also reported that available nitrogen content was very high in Kuttanad soils. Available nitrogen content of surface soils ranged from 81 to 319 mg kg^{-1}. Acid sulphate wetlands of Kerala showed high content of total nitrogen and this can be attributed to the presence of high amount of organic matter.

One of the major nutritional problems of Kuttanad soils was P deficiency and more than 50 per cent of the area was P deficient (Kuruvilla and Patnaik, 1973; KAU, 1994). Thampatti (1997) reported that about 67 per cent of the area was deficient in total P. The presence of large quantities of Fe and Al oxides and hydroxides together with 1:1 type clay were responsible for high P fixation.

Thampatti and Jose (1999) studied vertical distribution of potassium in acid sulphate soils of South India. They reported that mean values of available potassium ranged from 83 to 251 mg kg^{-1}. The potassium content increased with depth due to accumulation of salts in the lower layers.

The Ca and Mg contents of Kuttanad soils were fairly high compared to other acid soils of Kerala. The frequent additions of liming materials, intrusion of sea water and the marine origin of soils have increased the Ca and Mg contents. The available Ca content varied fro 377 to 1404 mg kg^{-1} in surface soils. The available Mg contents ranged from 172 to 788 mg kg^{-1} in the surface layers (Thampatti, 1997).

The Kuttanad soils were rich in S content. These soils contained large amounts of S compounds, principally mineral sulphates of iron and aluminium which on hydrolysis produce free sulphuric acid (Chattopadhyay and Sidharthan, 1985). Among the karappadam, kayal and kari soils, kari soils contained more total S than the other two types (Gosh *et al.,* 1976).

2.1.3.3 Micronutrients

Red scum in paddy fields was indicated by the presence of high soluble iron content in the submerged soils of Kuttanad (Subramoney and Kurup, 1961). Tanaka *et al.* (1968) reported that rice plant showed iron toxicity because excess iron easily entered the shoot of rice plant and induced iron toxicity. Available iron content in *kari* soils was high and could cause iron toxicity to rice (Aiyer *et al.*, 1975). Iron content was more than 6 per cent in upper Kuttanad soils compared to lower Kuttanad soils (Kannan *et al.*, 2014).

Aluminium toxicity was dominant when the acid sulphate soils have pH below 4 and plants grown on these soils suffered from aluminium toxicity. Rorison (1972) found that high level of aluminium disturbed cell division, certain enzyme systems and hampered uptake of phosphorus, calcium and potassium. Rice growth was limited by the toxicity of both iron and aluminium (Kuruvilla and Patnaik, 1973).

When available Zn concentration was below 0.2 mg kg^{-1}, Zn deficiency was observed in rice fields (Aiyer, 1946). They also reported that three soil types (*kari, kayal* and *karappadam*) were highly deficient in available copper (90%). Among the three soils, copper deficiency was much pronounced in *kari* soils. *Kari, kayal* and *karappadam* soils contained 0.16 to 0.22, 0.04 to 0.62 and 0.2 to 0.56 mg kg^{-1} of copper, respectively. Available zinc was deficient in 50 per cent of the *kayal* soils (Aiyer *et al.,* 1975). Cu and Zn content of six acid sulphate soil series showed wide variation (Beena, 2005).

2.1.4 Heavy metals

Heavy metals occur naturally on earth and the concentration of these metals varied among different ecosystems. Burning of fossil fuels, mining and smelting of metalliferous ores, municipal wastes, sewage, pesticides and fertilizers are the primary sources of metal pollution (Pendias and Pendias, 1989).

Heavy metals of varying quantity are required by living organisms. Iron, cobalt, copper, manganese, molybdenum and zinc are required by humans. At a higher concentration, all these heavy metals are toxic and cause damage to the organisms. Heavy metals such as mercury, plutonium and lead are toxic and they have no known beneficial effect on organism (Chronopoulos *et al.,* 1997).

2.1.4.1 Impact of heavy metals in soils

Concentration and form of heavy metals in the environment determine its impact and deleterious effect on organism (Barbara and Lorris, 1994). Heavy metal contamination of soils has been a rising environmental problem affecting agricultural production, food quality and threatening of human health. Some metals such as Fe, Zn, Mn and Cu are essential at low level; other metals like Cd, Cr, Pb and Ni are toxic and may pose great danger to humans, plants and animals through the food chain (Clemens, 2006). High concentration of heavy metals in the agriculture soil can reduce the crop output and quality and it also deteriorates the growth, morphology and metabolism of the soil microorganisms (Rodriguez *et al.,* 2008 and Giller *et al.,* 1998).

Kannan *et al.* (2014) studied the geochemistry and heavy metal concentration in Kuttanad. They found that Zn comes under highly polluted class. Except Cu, all metals were under threshold level. Copper was between threshold effect level and threshold effect concentration. The metals like Zn, Cd and Pb are highly available forms and could cause serious problems. Soils of upper Kuttanad showed maximum value for Zn and minimum value was obtained from North Kuttanad. Soils of Vaikom *kari* and North Kuttanad showed the presence of Cd. In case of lead, maximum concentration was detected from soils of lower Kuttanad and least value was observed in Vaikom *kari*. The value of Cu was observed maximum at upper Kuttanad followed by Vaikom *kari*, North Kuttanad and Purakkad *kari*. The copper was absent in the soils of lower Kuttanad.

2.1.4.2 Influence of soil properties on mobility of heavy metals

2.1.4.2.1 pH

Many factors influence the plant availability of Zn in soil (Shuman, 1986). Among all factors the most important factor is soil pH (Anderson and Christensen, 1988). Reddy and Patrick (1997) reported that the soil properties like oxidation-reduction status (Eh) and pH affect the solubility of heavy metals in flooded soils and improve their availability to plants. Heavy metals show low mobility when pH was neutral to slightly alkaline. Mobility increases with decreasing pH. Lead became soluble when the pH was lowered from 6 to 3. More amounts of metals are present in solution and mobilized at a low pH condition. Mobility of metal increased when pH was below 5 due to increased proton concentration. With increasing pH, sorption also increased (Sherene, 2010). Total, mobile and bioavailable mercury fractions were present in the soils of Kuttanad agricultural wetland ecosystem. The availability of mercury may lead to methylation in this system. Anaerobic conditions and acidic nature of the soils in these paddy fields enhanced the mobilization of inorganic mercury from the soil (Navya *et al.*, 2015).

Distribution and the origin of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) in soils from non polluted areas were studied by Dragovic *et al.* (2008). They found that a positive correlation was observed between organic matter and clay content but not with pH. All the metals were positively correlated with pH and OC except Zn which showed negative correlation with OC in Kuttanad soil (Kannan *et al.*, 2014). Prasanth *et al.* (2013) studied heavy metals and its fractions in soils of Koratty region, Kerala. They estimated different fractions such as exchangeable, reducible, oxidizable and residual fractions and they found that among the heavy metals, iron was the easily mobilized element, while cadmium and copper were least mobile. The order of mobility in the exchangeable fractions was Fe>Mn>Pb>Ni>Zn>Cu=Cd.

Frageria *et al.* (2002) reported that plant availability of Fe and Mn was influenced by soil properties and plant types. Among different soil properties, two important soil properties are soil pH and organic carbon content. Behera and Shukla (2013) studied the total and extractable manganese and iron in some cultivated acid soils of India. They reported that properties such as soil pH, soil organic carbon content and exchangeable cations like potassium, calcium and magnesium had greater influence on total and DTPA-extractable Mn and Fe contents in acid soils.

2.1.4.2.2 Organic matter

Lindsay (1979) found that solubility of iron in soil decreased 1000 fold for each unit increase of soil pH in the range of 4 to 9 and 100 fold decrease was observed for Mn, Cu, and Zn. Plant availability of Mn was enhanced by soil organic matter. Addition of organic matter in drained and waterlogged soil improved the Fe availability (Tisdale *et al.*, 1985). In the case of lead, once it is introduced into the soil matrix, it is very difficult to remove. This is mainly because of the soil properties like pH, cation exchange capacity, organic carbon content, soil/water redox potential and phosphate levels. With the increase in all these soil properties, ability of soil to absorb lead also increased. Organic matter is important property for retension of heavy metals by soil solids and thereby it reduced its mobility and availability. Addition of organic matter would enhance the release of metals from solid to soil solution because these metals form complexes with soluble organic matter. At a higher pH, dissolution of humic acid enhanced the dissolution of Cu and Pb from soil (Sherene, 2010).

2.1.4.2.3 Ionic strength

At a lower ionic strength, adsorbtion of metal ion was increased. Metal sorption decreased with increasing ionic strength due to competition of other cations for adsorption site (Sherene, 2010).

2.1.4.2.4 Soil texture

Another important property which determines the mobility of heavy metals is soil texture. Soil texture is particle size distribution of sand, silt and clay. More amounts of heavy metals are retained by clay soil than sandy soil. When comparing the retention capacity of fine and coarse textured soils, fine textured soil could retain 3889 mg kg^{-1} Pb and coarse textured soil retained only 530 mg kg^{-1} Pb (Sherene, 2010).

2.1.4.3 Influence of fertilizers and pesticides on heavy metal accumulation

Heavy metal accumulation in agriculture ecosystem is mainly due to excess application of fertilizers and pesticides. Among the fertilizers, phosphatic fertilizers are the main source of heavy metals. The two non essential heavy metals like lead and cadmium are derived from single super phosphate. Garcia *et al.* (1996) studied heavy metal concentration in inorganic fertilizers and pesticides. They reported that concentration of Cd, Co, Cu and Zn was highest in phosphatic fertilizers. Nickel was detected from copper sulphate and iron sulphate. Herbicides showed highest concentration of Fe, Mn, Zn, Pb and Ni.

Parameswari *et al.* (2014) studied soil degradation due to heavy metal accumulation under long term fertilization of paddy. They performed six fertilizer treatments and reported that higher heavy metal accumulation was found in field applied with phosphatic fertilizers. Total content of cadmium and lead in soil was high but their availability was below detectable limit. So they concluded that these two heavy metals were present in unavailable form in the soil.

2.2 Properties that affect water quality

2.2.1 Physical properties of water

Season and location have a great influence on the physical properties of water. A significant variation was observed among the properties like colour, turbidity and amount of suspended solids. Maximum values of physical properties were reported during monsoon season (Kamal, 2011). Radhika *et al.* (2004) studied the physico-chemical characteristics of Vellayani lake water during two seasons, pre-monsoon and post-monsoon. They observed that temperature, turbidity, pH, conductivity, dissolved oxygen, biochemical oxygen demand, total solids, total suspended solids, total dissolved solids, alkalinity, chloride, hardness, nitrate, phosphate and silicate were higher during pre-monsoon season.

2.2.1.1 Temperature

Temperature is an important factor which can affect the metabolic rates and biological activity of aquatic ecosystem. Temporal variation in the hydrobiology of Vembanad lake at Panangad mangrove patches of Kumbalam was studied by Mogalekar *et al.* (2015). They reported that the average annual temperature was comparatively normal *ie,* 28.94°C. Temperature was invariably low during June- July (25^0C) which gradually increased from August onwards and reached highest value in March (32^0C) (Harikrishanan and Kurup, 2003). The Karamana river, Thiruvananthapuram showed a temperature, ranging from 28.5°C to 31°C. Highest temperature was obtained during premonsoon period (Sujitha *et al.*, 2012). Sanjeev (1994) reported that during different seasons, not much variation was observed in temperature of Vellayani Lake.

2.2.1.2 Turbidity

Turbidity of water is a measure of how cloudy or murky it is. Presence of suspended and dissolved particles in water caused turbidity. Clay, silt, fine organic and inorganic matter, algae and other microscopic organisms caused turbidity. Radhika *et al.* (2004) reported that Vellayani lake showed very high turbidity during pre-monsoon season. The runoff pollutants contained suspended solids which greatly influenced the turbidity of the receiving water which in turn affected the light penetration resulting in reduced photosynthesis (Patel *et al.*, 1983).

2.2.2 Electro- chemical properties

2.2.2.1 pH

Water quality is determined by the pH of a water body (Fakayode, 2005). The pH of water determines the solubility (amount that can be dissolved in the water) and biological availability (amount that can be utilized by aquatic life) of chemical constituents such as nutrients (carbon, nitrogen and phosphorus) and heavy metals (lead, copper, cadmium etc.) (Sujitha *et al.*, 2012). Metals tend to be more toxic at lower pH because they are more soluble. The average pH of Vembanad Lake from June 2012 to May 2013 was 7.38. The highest pH (8.50) was observed during June 2012, whereas the lowest pH (6.00) was observed during July 2012 (Mogalekar *et al.*, 2015). Fresh water lakes of Kerala showed a pH ranging from 6.3 to 7.5. The spatial and temporal variation of water chemistry was mainly due to the land use changes in the catchment area as well as impact of dams on river (Nikhil and Azeez, 2009).

2.2.3 Chemical properties

One of the principal nutrients in aquatic environment is phosphorus. According to Parry (1998) increased loading of phosphorus in aquatic system from cultivated lands, domestic and industrial sewage could lead to eutrophication. Sobha *et al.* (2009)

reported that phosphorus content in aquatic systems of Thiruvananthapuram district ranged from 0.012 to 0.096 µg g^{-1} during post monsoon and 0.012 to 0.097 µg g^{-1} during pre monsoon season. Sujatha *et al.* (2009) studied the nutrient dynamics in two lakes of Kerala and they reported that NO_2- N concentration was high in Vembanad compared to Ashtamudi. NO_2-N was released during oxidation of NH_3. This was produced as a result of the digenetic decomposition of organic matter rich in estuarine sediments and brought to the sediment water interface during sediment compaction. The surface water of Karamana river, Thiruvananthapuram showed 0.12 to 1.78 mg L^{-1} of nitrate during premonsoon and 0.24 to 2.61 mg L^{-1} during monsoon. The concentration of sulphate was 0.49 to 2.48 mg L^{-1} and 0.20 to 0.79 mg L^{-1} during pre-monsoon and monsoon season respectively (Sujitha *et al.*, 2012).

2.2.4 Biochemical oxygen demand (BOD)

Jayaraman *et al.* (2003) studied the water quality of Karamana river, Thiruvananthapuram district, Kerala. They observed that BOD was higher during pre-monsoon season which indicated organic matter contamination and discharge of sewage effluents to the river. Dissolved oxygen of Karamana river varied from 4.8 to 5 mg L^{-1} in premonsoon and 5 to 5.5 mg L^{-1} in monsoon season (Sujitha *et al.*, 2012). Microorganisms consumed dissolved oxygen during the oxidation of reduced substances. BOD is a measure of dissolved oxygen required by microorganisms. Radhika *et al.* (2004) reported that during pre-monsoon, monsoon and post monsoon seasons, BOD values of Vellayani lake varied from 10.2 to 21.9, 2.9 to 20.1 and 4.1 to 18.3 mg L^{-1}, respectively.

2.2.5 Heavy metal status of aquatic ecosystem

Aquatic system is more vulnerable to the harmful effect of heavy metal pollution because organisms in aquatic environment are in close and extended contact with the soluble metals. Heavy metal concentration in aquatic environment is of critical concern due to toxicity of metals and their accumulation in aquatic habitats. A large part of heavy metal inputs ultimately accumulates in aquatic system. Sources of heavy metal in surface water system are both natural and anthropogenic. Among these sources, anthropogenic sources are more. Sobha *et al.* (2009) studied the geochemistry of different aquatic systems in Thiruvananthapuram district. They also reported that reason behind the increased nutrient level in these systems was anthropogenic sources of pollution.

Kaushik *et al.* (2003) had done the analysis of heavy metal pollution in various canals originating from river Yamuna in Haryana and found that metals like Fe, Ni, Pb, Cd, Co were exceeding the permissible limits. They also noticed that in Sunderbans branch, the concentration was relatively high. Kotteeswaran *et al.* (2015) studied the occurrence of heavy metal in Pulluyankunnu lake at Ranipet, Tamil Nadu. They found that occurrence of heavy metals were in the order of Fe >Mn >Al >Cu >Cr >Zn >Pb >Cd. Pollution due to heavy metals in Coimbatore wetland was studied by Pavithrapriya *et al.* (2015). They collected water samples from twelve wetlands and results showed that Cd-0.2 to 0.7 mg L,$^{-1}$ Cr- 3 to 518 mg L^{-1}, Cu- 1.0 to 98 mg L^{-1}, Ni- 7 to 33 mg L^{-1} and Pb-0.9 to 3 mg L^{-1} respectively. They concluded that relative proportion of heavy metals were in the increasing order of Cr >Cu >Ni >Pb >Cd.

The order of heavy metals in Vembanad lake water were in order of Fe > Al > Mn > Zn > Cr > Pb > Ni > Cu >Cd (Sasidharan *et al.*, 2013). Barua *et al.* (2011) studied the seasonal variation of heavy metal accumulation in water and oyster inhabiting central and western sector of Indian sunderbans. He found that distribution of heavy metals in water were in the order of Fe >Mn >Zn >Cu >Pb >Cd. The heavy metal concentration varied significantly among different seasons. Monsoon period showed particularly high metal concentration compared to pre- monsoon and post- monsoon seasons.

2.3 Characteristics of sediments in wetland ecosystems

Sediments are defined as the organic and inorganic materials or solid fragments derived from the weathering process of sand, pebbles, silt, mud and fine grained soil (Cohen, 2003). Sediments can also be defined as the materials at the bottom of aquatic systems originating from soil erosion and precipitation by chemical and biological processes. Sediments act as a store house of nutrients in the aquatic environment. Sediment not only acts as sink but also as a source of contaminants in aquatic system (Adams *et al.*, 1992 and Burton and Scott, 1992). Balakrishnan *et al.* (1984) reported that the nutrient economy of an aquatic system is mostly governed by the sediments and knowledge on the role of nutrients in sediment was especially useful in determining the sediment water interaction, which eventually affects the productivity.

2.3.1 Physical properties of sediments

In an aquatic ecosystem, sediment is the ultimate recipient of nearly all heavy metal pollutants. According to Hakanson and Janson (1983), one of the important physical parameters of an aquatic environment is sediment texture, which influences the physical, chemical and biological characteristics of the system. Through the process of adsorption or by complexation, heavy metals may associate with sediment particles. Some of the studies suggest that compared to marine zone; heavy metal concentration is more in the riverine zone. This is mainly because of the textural properties of sediments. Marine zone had finer and coarse sand as substratum but in river, finer particles like silt and clay dominate. It is a proven fact that compared to coarse particles; finer particles can retain more metal (Fernandez and Jones, 1987).

Sediment texture varied from sandy to sandy clay loam (Kamal, 2011). Sediment characteristics of the *Thekkumbhagom kayal* of the Ashtamudi estuary, Kerala were studied by Sumesh *et al.* (2014). They reported that sand was a dominant component (75%) followed by silt (14.8%) and clay (10.6%). The granulometric fractionation of sediments showed drastic differences in the admixture of sand, silt and clay fractions. Such differences in texture type were mainly due to the transport of sediments from one place to another and reversal exchange with the tidal currents. In Vembanad lake, granulometric composition of sediments was sandy, except a few locations where silt dominated. Ashtamudi and Vembanad lake sediments were clayey sand to silty sand in texture during January- May (Sujatha *et al.,* 2009). According to Sobha *et al.* (2009) both in the bottom sediment and in the overlying water column, distribution and concentration of carbon, nitrogen and phosphorus was significantly influenced by the textural characteristics of sediments.

2.3.2 Chemical properties of sediments

Evaluation of aquatic pollution and identification of phytoremediators in Vellayani lake was studied by Kamal (2011). She found that season and location had a significant influence on chemical properties of lake sediment. Concentration of nutrients in sediments was the reflection of overlying water column (Balakrishnan *et al.*, 1984). Potassium was naturally occurring constituent in sediment. The major source of potassium in freshwater is weathering of rocks. But the quantity increases in the polluted water due to the disposal of domestic wastes. The potassium content in the sediment sample ranged from 0.88 to 5.32 $\mu g\ g^{-1}$ during post - monsoon and 0.32 to 4.34 $\mu g\ g^{-1}$ during pre - monsoon season (Sobha *et al.*, 2009). Nair *et al.* (1987) also observed a high concentration of potassium during post-monsoon season.

Calcium is one of the most abundant elements existing in different forms in the natural water and soil. Being present in high concentration in the rock it is leached from the rock to contaminate the water. Disposal of sewage and industrial wastes also contributes to the content of calcium and has a great affinity to be absorbed on the soil particles which in turn affects the soil texture. In the sediment samples, the calcium value ranged from 0.08 to 0.76 $\mu g\ g^{-1}$ during post monsoon to 0.08 to 0.68 $\mu g\ g^{-1}$ during pre-monsoon season (Sobha *et al.*, 2009).

Characteristics of sediments of Vembanad lake were studied by Murty and Veerayya (1981). They reported that organic carbon was higher along the surficial sediments than bottom layer. Sediment characteristics in Paravur- Kappil backwater system of Kollam was studied by Santhosh (2002). He found that there was wide variation in organic matter content and it ranged from 0.29 per cent to 6.5 per cent. But in most of the sites in Karamana river, organic matter content was higher than 6.5 per cent (Krishnakumar, 2002).

2.3.3 Heavy metal content in sediments

A large portion of metallic substances discharged into the aquatic environment was ultimately incorporated into the sediment. The heavy metal content in sediments of the Vembanad estuary was reported to be above the critical limits (Varma *et al.,* 2007). Sabitha and Sitaram (2007) also reported severe qualitative degradation of sediments in wetlands of Kerala.

Accumulation of heavy metals in sediments may be source of water pollution in case of environmental condition change (Chen *et al.,* 1996). Concentration of iron was more in Kerala rivers. The waste from industries, domestic waste and fertilizers were the important wastes in sediments of estuaries. Iron was mainly derived from these sources (Nair *et al.,* 1987). Concentration of iron in sediments varied from 8690.6 to 88741.2 µg g^{-1} during post-monsoon and its concentration ranged from 15855 to 17840.4 µg g^{-1} during pre-monsoon season (Sobha *et al.,* 2009).

Zinc is an essential element required in traces to sustain life, but its large concentration is proved to be lethal. It is a common contaminant in industrial effluent (Dean *et al.,* 1972). The concentration of zinc varied from 0.4 to 18.6 µg g^{-1} during post-monsoon seasons and from 1.0 to 2.2 µg g^{-1} during pre-monsoon season (Sobha *et al.,* 2009).

The content of copper in aquatic environment is mainly from copper mining, agricultural chemicals and paints. Other sources such as sewage, industrial effluent and wastes from electric generating plants also contributed copper. During post-monsoon season copper content in aquatic system of Thiruvananthapuram district was 335.2 µg g^{-1}. In some locations of Thiruvananthapuram district, copper content was found to be below detectable level (Sobha *et al.*, 2009). Copper sulphate was widely used in agricultural practices and it might be one of the reasons for higher concentration of copper.

Abbasi *et al.* (1998) reported that lead is ranking as 36th element in the order of abundance because its estimated concentration in the earth crust was 12.5 ppm. Mining, smelting and refining works contributed major portion of lead in surface water. Lead reaches the aquatic sediments through precipitation, erosion and leaching of soil as well as municipal and industrial wastes. The concentration of lead ranged from 21.2 to 99.4 µg g^{-1} during postmonsoon and 0.4 to 29.4 µg g^{-1} during pre-monsoon (Sobha *et al.*, 2009).

The metal chromium mainly arises from the sources like electroplating, dyes, explosives, paints, ceramic, paper industries etc. Mishra (1990) found that the domestic input of chromium into the water bodies caused a sharp drop in the dissolved oxygen content with hydrogen iodide production.

Like mercury, cadmium is also a hazardous metal. Presence of cadmium in the environment is harmful. Cadmium is not essential for plants and animals. In sediments, the average concentration of cadmium is 0.2 ppm (Abbassi *et al.*, 1998). During the post-monsoon season, cadmium was almost nil in aquatic system of Thiruvananthapuram district (Sobha *et al.*, 2009).

Due to increased anthropogenic activities the concentration of mercury is estimated to have increased up to five times. Once mercury enters into the aquatic systems, it began to react with various components in the water and a portion of it precipitated into the sediments (Ruiz *et al.*, 2005). Sediments were considered as the major sink and source of mercury (Shi *et al.*, 2005). Mohan *et al.* (2014) studied the surface sediment samples of Vembanad lake and nearshore areas and the samples were seasonally analysed for total mercury and methyl mercury concentration. The results revealed that the northern part of the lake was more contaminated with mercury than the southern part. In the subsurface sediment, the mercury concentration was relatively high, which indicated the possibility of historic industrial mercury deposition. A decreasing trend was also observed towards the surface.

The metal fraction of surficial and core sediments of Achenkovil river basin was examined by Prasad *et al.* (2006). They found that the heavy metals in Achenkovil basin were influenced by both natural and anthropogenic effects. Iron and and Copper were the dominant metals in surficial and core sediments. Distribution of heavy metals in the core sediments of a tropical wetland system was studied by Harikumar *et al.* (2009). They found that in lake, rate of deposition of heavy metals increased with time. The order of abundance of heavy metals followed a trend of Fe > Mn > Zn > Ni > Cu > Pb > Cr > Cd > Hg. According to sediment quality guideline, Vembanad lake sediment was moderately polluted with copper, moderately to highly polluted with zinc and nickel and non polluted to moderately polluted with lead. Sasidharan *et al.* (2013) reported that content wise, heavy metals in Vembanad lake sediments were in the order of Fe > Al > Mn > Zn >Cu >Cr> As > Pb > Hg > Ni > Cd on the basis of their abundance. Gao *et al.* (2016) studied heavy metals in sediments, soils and aquatic plants in China. They found that sediments accumulated more metals compared to soils and aquatic plants.

2.4 Heavy metal accumulation in aquatic macrophytes

In aquatic ecosystems, macrophytes are known as good indicators of heavy metal contamination and they accumulate metals from the surroundings and thereby act as biological filters (Vardanyan and Ingole, 2006). Macrophytes are important component of aquatic communities due to their roles in oxygen production, nutrient cycling, controlling water quality, sediment stabilization and providing habitat and shelter for aquatic life (Gibbons *et al.*, 1994 and Ravera *et al.*, 2003). Aquatic macrophytes have great potential to accumulate heavy metals inside their plant bodies. These plants can accumulate heavy metals up to 100,000 times greater than the amount in the associated water. Therefore, these macrophytes have been used for heavy metal removal from a variety of sources (Mishra and Tripathi, 2008).

2.4.1 Phytoremediation potential of aquatic macrophytes

Phytoremediation, a plant based green technology, has received increasing attention after the discovery of hyperaccumulating plants which are able to accumulate, translocate and concentrate high amount of certain toxic elements in their above ground or harvestable parts (Rahman, 2011). Techniques of phytoremediation include "*phytoextraction, phytodegradation, rhizofiltration, phytostabilization* and *phytovolatilization*" (Salt *et al.*, 1998).

Aquatic macrophytes have phytoremedial capacity and it is a cost effective green technology based on the use of specially selected metal accumulating plants. Due to frequent abundance in aquatic ecosystems, low cost and easy handling, wetland plants are preferred more than other plants (Raj, 2008). This process was not creating any disturbance to landscape and it was cost effective (Itanna and Coulman, 2003). Based on the physiological mechanisms, plants used for phytoremediation were grouped under excluders, accumulators and indicators (Baker, 1981).

Biomonitoring in terms of hyperaccumulator plants was done by Thampatti *et al.* (2007). They found that plants like *Hydrilla verticillate, Eichhornia crassipes* and *Cyperus pangorci* were found to possess hyper accumulation capacity for iron, manganese, zinc, copper and aluminum in the wetlands of Kuttanad. Sasidharan *et al.* (2013) conducted a study on phytoremedial capability of water hyacinth at Regional Agricultural Research Station, Kumarakom. They found that the concentration of heavy metals and other minerals in water hyacinth were Fe (33038 mg kg^{-1}), Al (13075 mg kg^{-1}), Ca (2234.80 mg kg^{-1}), Mn (1440.1 mg kg^{-1}), Mg (1608.3 mg kg^{-1}), Zn (77.08 mg kg^{-1}), Cu (49.80 mg kg^{-1}), Cr (23.37 mg kg^{-1}), As (5.276 mg kg^{-1}), Pb (0.531 mg kg^{-1}) and Hg (0.151 mg kg^{-1}). Chaohua *et al.* (2007)

reported that *E. crassipes* had strong ability to remove Cu from contaminated water bodies.

Gomati *et al.* (2014) reported that *Eichhornia crassipes* accumulated higher amount of copper compared to cadmium and could be used to treat waste water contaminated with Cu and Cd. Mishra *et al.* (2008) reported that among the three macrophytes (water lettuce, duckweed and water hyacinth), water hyacinth was most effective for removal of heavy metals like as Fe, Zn, Cu, Co and Cd. Phytoremediation capability of *Eichhornia crassipes* for removing heavy metals were studied by Odjegba and Fasidi (2007). They reported that concentration of heavy metals in tissues and the bioconcentration factors (BCF) were equal to the initial concentration of individual metal in the growth medium and the duration of exposure. They concluded that natural water bodies and/or wastewater contaminated with low amount of Zn, Cr, Cu, Cd, Pb, Ag and Ni could be effectively remediated using *E. crassipes.*

Kumar *et al.* (2006) monitored some selected freshwater macrophytes to assess trace element contamination in the lake situated in Nal Sarovar Bird Sanctuary of India. They assessed trace element contamination in certain aquatic macrophytes as biomonitors, in comparison with the sediments (abiotic monitor) for heavy metal pollution. The results showed significant differences in accumulation rate of some metals like Zn, Cu and Ni in different plant organs. It also showed more accumulation in roots than stem and leaves. They reported high positive correlation between combinations of different metal pairs in either plant's root, stem or leaf system.

Valitutto *et al.*(2006) studied the elemental concentrations in four free floating aquatic macrophytes (*S. auriculata, P. stratiotes, E. crassipes and E. azurea*) growing in two water reservoirs which received inputs from the polluted Paraıba do Sul river of Brazil. The highest accumulation was observed in *E. crassipes* in which concentration decreased in the following sequence: Mn > Ce > Zn > La > Fe > Ti > Pb > Cr > Mo > Cu. Heavy metal accumulation in aquatic macrophytes of Sevan (Armenia) and Carambolim (India) lake systems was studied by Vardanyan and Ingole (2006). They found that aquatic macrophytes helped in reducing heavy metal concentration and suggested that the macrophyte community of the Sevan lake area needed to be protected and restored on a priority basis.

Phytoremediation of arsenic and lead using alligator weed was studied by Simmons *et al.* (2007). They found that root portion showed highest metal concentration followed by stem and leaf. They also observed that plant tissues showed a metal concentration, which was equals to the metal concentration in aqueous phase. Govind Ballabh Pant Sagar, an anthropogenic lake affected by coal mining effluents and its heavy metal concentration was studied by Mishra *et al.* (2008). They observed high amount of heavy metals such as Cu, Cd, Mn, Pb and Hg. Heavy metals in water and in aquatic macrophytes showed a strong positive correlation. Metals in sediments and in macrophytes also showed a positive correlation. All these results showed the possibility of macrophytes for heavy metal monitoring.

2.5 Mangroves- bioindicators of heavy metals

Mangroves are those plants which have the ability to grow in inter-tidal areas. Mangrove forests are the utmost biologically productive ecosystem and these plants have well developed adaptation during extreme conditions (Kathiresan and Bingham, 2001).

There are different types of mangroves and they exhibited variation in the levels of heavy metal tolerance. Compared to other mangroves, the grey mangroves, *Avicennia marina* had a relatively higher tolerance level (Burchett, 2003). Based on the type of tissues, bioconcentration of various metals in mangroves were different. Lower levels of metals were accumulated in leaves compared with roots. So root tissue was the most commonly used bioindicator for heavy metal pollution with high reliability and accuracy (Defew *et al.*, 2005). Naidoo *et al.* (2014) studied ecophysiological responses of the mangrove *Avicennia marina* to trace metal contamination. They found that with the increasing metal concentration, concentration of all trace metals were increased in plant organs and accumulation was more in roots than in shoots. Compared with mercury and lead, concentration of Cu and Zn were higher.

Chakraborty *et al.* (2013) studied heavy metal pollution and phytoremediation potential of *Avicennia officinalis* L. in the southern coast of the Hoogly estuarine system. They reported that compared to surrounding sediments, *A. officinalis* accumulated lower amount of metals. The extent of mobility of different metals to the above ground part was different. Based on translocation factor, non essential metals like Pb and Cr to leaves showed restricted mobility. Greater mobility was showed by essential metals like Zn and Cu. The results confirmed that *A. officinalis* had the ability to manage the uptake of essential metals for meeting the requirement of their metabolism and it restricted the mobility of non essential metals and thereby reduced toxicity. Thus mangroves played a major role in reducing the heavy metal pollution.

Cheng *et al.* (2014) conducted a study to identify the metal uptake and tolerance by mangroves in relation to root anatomy and lignifications/ suberization. They found that among the six species of mangroves, *Bruguiera gymnorrhiza* (L.), *Kandelia obovata* and *Rhizophora stylosa* could tolerate higher metals compared to *Avicennia marina*, *Acanthus ilicifolius* and *Aegiceras corniculatum.* Thick exodermis with lignifications and suberization was observed in mangroves with high metal tolerance

Materials and methods

3. MATERIALS AND METHODS

An investigation on "Accumulation of heavy metals in Typic Sulfaquents of Kuttanad ecosystem" was carried out by collecting soil, sediment, water and plant samples from different acid sulphate soil series and analyses were done in the Department of Soil Science and Agricultural Chemistry, College of Horticulture, Vellanikkara during 2014-2016. The details of the research work and methodologies followed are given in this section.

3.1 Description of site

Kuttanad is a unique tropical ecosystem among the rice agricultural ecosystems. It is located in the southern coastal part of Kerala State and spread across the districts of Alappuzha, Kottayam and Pathanamthitta. The region extends from 9°20'N to 9°50' N and 76° 20'E to 76° 30'E and consists of the deltaic alluvium of four major rivers flowing through it together with the area in and around Vembanad lake.

Kuttanad is subdivided into six agro-ecological zones based on soils, geomorphology and salinity intrusion. They are i) Kayal lands ii) Lower Kuttanad iii) Upper Kuttanad iv) Vaikom kari v) North Kuttanad and vi) Purakkad kari. The acid sulphate soil series identified in the region were Ambalapuzha, Purakkad, Thotapally, Thuravur, Kallara and Thakazhi constituting a total area of 14,277.51 ha (Beena, 2005).

3.2 Cultivation practices

Paddy is the main crop cultivated in this region. Paddy cultivation in this region has some unique characteristics. Based on flood and saline water intrusion in the area, two crops of paddy are mainly grown in the *karappadam* (upper basin) and one or two crops are cultivated in lower Kuttanad (middle basin) and single crop of paddy is cultivated in the *kayal* lands (lower basin). The traditional crop in Kuttanad is known as *punja* crop and during earlier times paddy cultivation in Kuttanad was known as *punja* cropping since 80 per cent of paddy cultivation was done during this season. Bunding of the field boundaries and bailing out of water from field was carried out before cropping. The season for *punja* crop is from September- October to January- February. Only *punja* crop is taken in some areas. The areas where second crop is not raised are kept under submerged condition for most part of the year. In some areas, paddy cultivation is taken up during *virippu* season also.

3.3 Climate

The climatic parameters were collected from Rice Research Station (RRS), Moncompu. The climate of the study area is humid tropical climate. Southwest monsoon (June- September) and northeast monsoon (October- November) are the two rainy seasons. The average maximum and minimum temperature recorded in the area were 32.91^{0} C and 23.85^{0} C respectively. The average wind speed was 2.92 km h^{-1} and sunshine hours was 6.67 h. The detailed climatic data of the region during study the period is shown in appendix I.

3.4 Soil

Kuttanad soil is a mixture of sand and clay in varying proportions. Presence of decayed organic matter including decayed parts of logs of wood has been reported in some parts of the Kuttanad. Soils of the low lying areas of Kuttanad are highly acidic and contain toxic salts. Poorly drained soils having high content of pyrite is known as potential acid sulphate soils. Based on morphological conditions, these soils can be classified into *kayal* lands, *karappadam* and *kari* lands (Chattopadhyay and Sidharthan, 1985). Acid sulphate soils are locally known as *kari* soils which spread over an area of 14,227 ha. These soils are grouped under the order- Entisol, suborder- Aquent, great group- Sulfaquent and sub group- Typic Sulfaquents (Beena, 2005). *Kari* soils contain high amount of organic matter and these soils are black in colour. *Kayal* soils are reclaimed from Vembanad lake. *Karappadam* soils are mainly seen in inland waterways and rivers.

Acid sulphate soils differ from normal soils, when these soils are exposed to air upon drainage; it oxidizes to sulphuric acid (H_2SO_4) and this lead to formation of actual acid sulphate soils. Low pH, high aluminium, iron and sulphate concentrations are the main characteristics of acid sulphate soils (Breemen and Pons, 1978). Salinity problem in these areas is mainly due to salt water intrusion.

3.5 Sampling location

Sampling was done from six acid sulphate series of Kuttanad namely Ambalapuzha, Thakazhi, Kallara, Thuravur, Purakkad and Thottapally series. Study area can be depicted from Fig.1.

3.6 Collection of samples

Soil, sediment, water, weed and mangrove samples were collected from six acid sulphate series of Kuttanad region.

3.6.1 Soil samples

Soil samples were collected during summer months of 2015 (March and April) from six soil series. From each series, twenty georeferenced soil samples were collected using the GPS (Model No-VX 140, Brand - MAPMYINDIA). Sampling depth was 0-20 cm (Plate. 2). These wet samples were kept in polythene bags, properly labeled and analysed for physical property like texture and chemical properties such as pH, EC, organic carbon, available N, P, K, Ca, Mg, S, Fe, Al, Mn, Zn, Cu, Pb, Cd, Cr and Hg. Necessary moisture correction was done by estimation of soil moisture by gravimetric method. Details of methodology adopted for soil analysis are given in table 1.

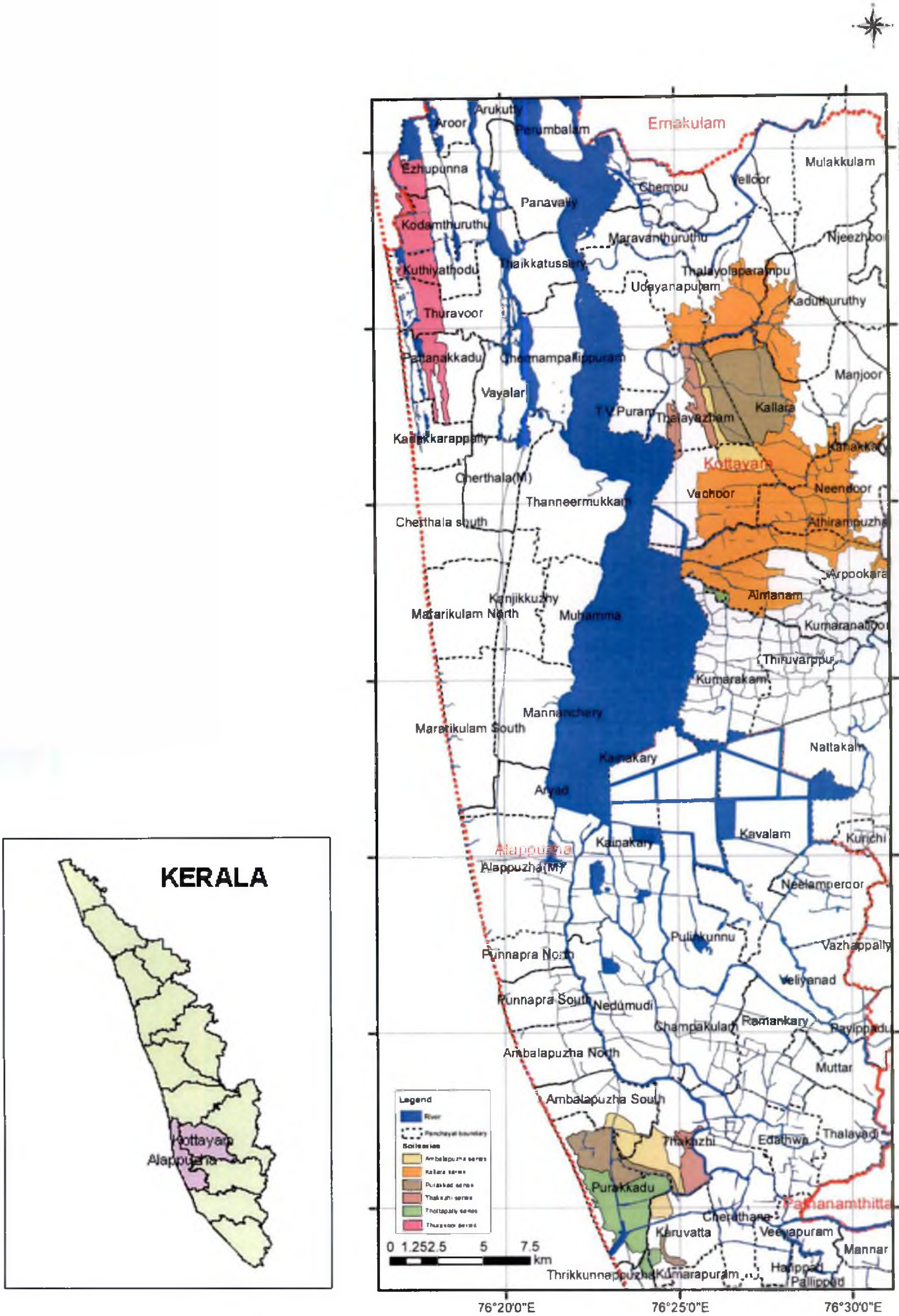

Fig. 1 Acid sulphate soil series of Kuttanad region

Plate 1. Paddy fields in Kuttanad

Plate 2. Collecting soil samples from acid sulphate soils of Kuttanad

Table 1. Standard procedures followed in soil analysis

Parameters	Methods	References
pH	1:2.5 soil water suspension, potentiometric method using pH meter	Jackson (1958)
EC	1:2.5 soil water suspension using conductivity meter	Jackson (1958)
Soil texture	International pipette method	Robinson (1922)
Organic carbon	Wet digestion method	Walkley and Black (1934)
Available nitrogen	Alkaline permanganate method	Subbiah and Asija (1956)
Available phosphorus	Extraction using Bray-1 and reduced molybdate ascorbic acid blue colour method using spectronic-20 spectrophotometer	Bray and Kurtz (1945) Watanabe and Olsen (1965)
Available potassium	Neutral normal ammonium acetate estimation using flame photometer and	Jackson (1958)
Available calcium and magnesium	Neutral normal ammonium acetate and estimation using Atomic Absorption Spectrophotometer(AAS)	Jackson (1958)
Available sulphur	0.15% $CaCl_2$ extraction and estimation by turbidimetric method using Spectronic-20 spectrophotometer	Williams and Steinbergs (1959)
Fe, Mn, Zn, Cu, Pb, Cd, Cr, Hg and Al	0.1 M HCl (Sims and Johnson, 1991)	ICP–OES (Model: Optima 8000)

Plate 3. Van-Veen Grab used for sediment collection

Plate 4. Collecting sediment samples from canals using Van- Veen Grab

Plate 5. Collection of sediments in polythene cover

3.6.2 Sediment samples

The sediment samples were collected from adjoining canals/lakes of six series, (from twenty locations each) using Van- Veen Grab (Plate. 3, 4 and 5). Samples were packed in air- tight pre- labeled polyethylene bags and kept for analysis. Wet analysis was carried out with proper moisture correction. The collected samples were characterized for physical properties like texture and chemical properties such as pH, EC, organic carbon, available N, P, K, S, Ca, Mg, Fe, Al, Mn, Zn, Cu, Pb, Cd, Cr and Hg. The procedures adopted for chemical analysis of sediments were same as that of soil analysis.

3.6.3 Water samples

Twenty representative water samples were collected from the adjoining canals and lakes of each series and stored in plastic bottles for further analysis (Plate. 7). For determination of Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), the samples were collected in BOD bottles. The water samples were characterized for physical properties like colour, temperature, turbidity, suspended solids, electrochemical properties such as pH, EC and chemical properties like total N, P, K, S, Fe, Al, Mn, Zn, Cu, Pb, Cd, Cr and Hg. Total nutrient content of water samples were estimated by evaporating the water samples in water bath for complete dryness and after that digested using di- acid (nitric acid and perchloric acid in the ratio 9:4). The procedures followed for analysis of water samples are given below.

Plate 6. View of Vembanad lake

Plate 7. Collection of water samples from the site

Plate 8.Collection of weed samples from the site

Table 2. Standard procedures followed in water analysis

Physical properties		
Parameters	Methods	References
Colour	Florel- Ule colour scale method	Gupta, 1999
Temperature	Thermometer	
Turbidity	Turbidimetry	
Suspended solids	Filtration method	
Chemical properties		
pH	pH meter	Gupta, 1999
EC	Conductivity meter	Gupta, 1999
Biological Oxygen Demand (BOD)	Winkler method	American Public Health Association (APHA), 1992
Chemical Oxygen Demand (COD)	Titration	American Public Health Association (APHA), 1992
NH_4-N and NO_3-N	Micro-Kjeldahl distillation	A.O.A.C. 1950
Phosphates	Spectrophotometry	Murphy and Riley, 1962
Potassium	Flame photometry	American Public Health Association (APHA),1989
Sulphates	Turbidimetric method	Chesnin and Yien, 1951
Fe, Mn, Zn, Cu, Pb, Cd, Cr, Hg and Al	Nitric- perchloric acid (9:4) digestion (Hesse, 1971) and estimation using ICP- OES (Model: Optima 8000)	

3.6.3.1 Biological Oxygen Demand (BOD)

The BOD was estimated by following Winkler method. Water samples were collected using BOD bottles and stoppered immediately to avoid entrapment of air. An orange brown precipitate was formed after adding a series of reagents. This colour indicated the presence of oxygen in water samples and proper shaking was done to dissolve the precipitate after adding H_2SO_4. The whole content was transferred to conical flask and titrated immediately against sodium thiosulphate solution and reading at the end point was noted for estimating the initial dissolved oxygen content. Simultaneously, another set of sample was incubated at 20°C for five days to determine the final dissolved oxygen (DO). The BOD was calculated from the difference between initial and final DO (APHA, 1992).

3.6.3.2 Chemical Oxygen Demand (COD)

It was measured for the oxygen requirement of organic matter content of a water sample. The organic matter in water sample was oxidized by strong chemical oxidant. Potassium dichromate and sulphuric acid along with silver sulphate as catalyst was used as oxidant. A known amount of water sample was refluxed in a COD reflux unit with a known amount of potassium dichromate in sulphuric acid medium and excess of dichromate was titrated against ferrous ammonium sulphate. A blank was also carried out. Colour change was noticed from yellow through green to brown and the end point was noted. The amount of dichromate consumed was proportional to the COD. It was expressed in milligrams of oxygen consumed per litre of sample.

3.6.4 Weed population study

A survey was conducted in the experimental area to identify the major weed species. Weed population was studied by placing a quadrat of 1x1m at different locations. Number of weeds per square meter was counted and recorded. Dominant weeds present in the locality were identified by calculating relative density, relative frequency and summed dominance ratio.

$$\textbf{Relative density (RDe)} = \frac{\text{Total no. of individuals of the given species} \times 100}{\text{Total no. of individuals of all the species}}$$

$$\textbf{Relative frequency (RF)} = \frac{\text{No. of occurrence of a species X 100}}{\text{No. of occurrence of all the species}}$$

$$\textbf{Summed dominance ratio (SDR)} = \frac{\text{IVI of the given species}}{\text{No. of parameters used to work out IVI}}$$

IVI- Where, IVI is the Importance value index

3.6.4.1 Collection and processing of weed samples

Dominant weeds present in each series were collected and labeled properly from the field itself (Plate.8). Collected weed samples were transported to lab for further analysis. The samples were washed thoroughly with deionised water, dried at room temperature and oven dried at a temperature of 70^0C. The oven dried samples were ground and sieved through 0.2 mm sieve. From this fine powder, 0.5g samples were taken and digested using diacid mixture (nitric acid and perchloric acid in the ratio of 9:4) and N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Pb, Cd, Cr, Hg and Al were estimated by following standard procedures (Table 3).

3.6.5 Collection of samples from mangroves

Mainly three mangroves species were identified in the area. They were 1) *Avicennia officinalis* (Plate. 15) 2) *Rhizophora mucronata* (Plate. 16) and 3) *Bruguiera gymnorrhiza* (Plate. 17). Leaves, shoot and roots were collected separately from these mangrove species. The roots were carefully collected after removing the sediments. All samples were properly packed, labeled in the field itself and transported to laboratory. Samples of plant parts were thoroughly washed with deionised water to remove any adhering sediment and dirt.

3.6.5.1 Processing of mangrove samples

Collected leaves, shoot and root samples were dried at room temperature. After partial drying it was oven dried at a temperature of 70^0C for three days to achieve a constant weight. Samples were ground to fine powder using mixer grinder and 0.5 g was weighed and digested using diacid mixture (nitric acid and perchloric acid in the ratio of 9:4) and used for estimating N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Pb, Cd, Cr, Hg and Al. The details of procedure followed for analysis of plant samples are given in table 3.

Table 3. Standard procedures followed in plant analysis

Parameters	Methods	References
Nitrogen	Micro kjeldahl method and distillation	Piper (1966)
Phosphorus	Nitric-perchloric acid (9:4) digestion and estimation by yellow colour method and estimation using spectronic-20 spectrophotometer	Piper (1966)
Potassium	Nitric-perchloric acid (9:4) digestion and estimation using flame photometer	Piper (1966)
Calcium and magnesium	Nitric-perchloric acid (9:4) digestion and estimation using ICP-OES (Model:Optima 8000)	Piper (1966)
Sulphur	Nitric-perchloric acid (9:4) digestion and turbidimetric method and estimation using spectronic-20 spectrophotometer	Chesnin and Yien (1951)
Fe, Mn, Zn, Cu, Pb, Cd, Cr, Hg and Al	Nitric-perchloric acid (9:4) digestion and estimation using ICP- OES (Model: Optima 8000)	Hesse (1971)

Table 4. Major weed species identified in the study area

Sl.no	Common name	Scientific name	Family	Exotic or Native (E or N)
1	Chinese water chesnut	*Eleocharis dulcis*	Cyperaceae	N
2	Pickerel weed	*Monochoria vaginalis*	Pontederiaceae	N
3	Alligator weed	*Alternanthera philoxeroides*	Amaranthaceae	E
4	Rhyncospora	*Rhyncospora corymbosa*	Cyperaceae	N
5	Weedy rice	*Oryza sativa* f. spontanea	Poaceae	N
6	Common barnyard grass	*Echinocloa crusgalli*	Poaceae	N
7	Red sprangletop	*Leptochloa chinensis*	Poaceae	N
8	Salvinia/kariba weed	*Salvinia molesta*	Salviniaceae	E
9	Water hyacinth	*Eichhornia crassipes*	Pontederiaceae	E

Table 5. List of mangroves identified in the study area

Sl.No.	Scientific name	Family
1	*Avicennia officinalis*	Avicenniaceae
2	*Rhizophora mucronata*	Rhizophoraceae
3	*Bruguiera gymnorrhiza*	Rhizophoraceae

Plate 9. View of aquatic weed infestation in waterways of Kuttanad

Plate10. *Eichhornia crassipes*

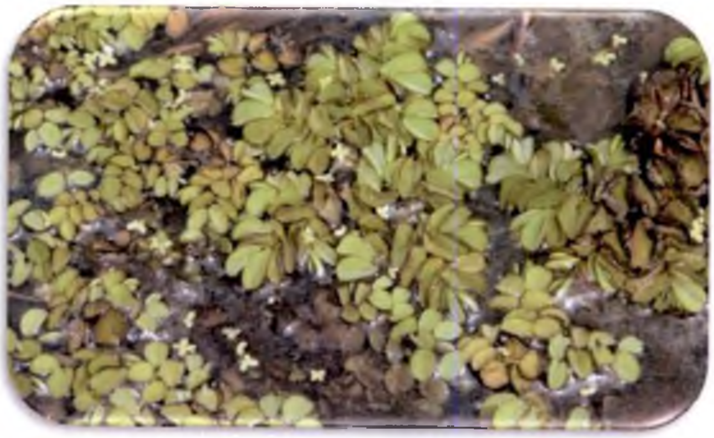

Plate11. *Salvinia molesta*

Plate12. *Eleocharis dulcis*

Plate13. *Monochoria vaginalis*

Plate14. *Alternanthera philoxeroides*

Plate15. *Avicennia officinalis*

Plate16. ***Bruguiera gymnorrhiza***

Plate17. ***Rhizophora mucronata***

3.7 Preparation of maps

From six soil series, soil, sediment and water samples were collected and geographical co-ordinates of all locations were recorded using GPS (Model No-VX 140, Brand - MAPMYINDIA). . Extent of distribution of different parameters like pH, organic carbon, micronutrients and heavy metals in soil, sediment and water samples in six acid sulphate soil series were depicted in different maps. The GIS software used for the purpose was ArcGIS ArcMap version 10 of Environmental System Research Institute (ESRI). GTS (toposheets) maps of 1:50,000 scale were used as base image for map preparation. Google services like google earth were also used for locating and aligning natural features

3.8 Statistical analysis

Statistical analysis was done using Statistical Package for the Social Sciences (SPSS). Analysis of Variance (ANOVA) with Duncan's Multiple Range Test (DMRT) was used to compare the significance of difference among the six series.

Results

4. RESULTS

The results generated from the characterization of soil, sediment and water samples and assessing heavy metal accumulation and phytoextraction capability of macrophytes from six acid sulphate soil series of Kuttanad are presented in this chapter.

4.1 Characterization of acid sulphate soils from six series

Soil samples were collected from six series (20 locations from each series) belonging to acid sulphate soils namely Ambalapuzha, Kallara, Thakazhi, Purakkad, Thottapally and Thuravur. Soil samples were taken and analysed for physical properties like texture, electrochemical properties such as pH, EC, chemical properties like organic carbon, available N, P, K, Ca, Mg, S, Fe, Al, Mn, Zn, Cu, Pb, Cd, Cr and Hg. The results of the analyses carried out are presented here under.

4.1.1 Physical properties

Among the soil physical properties, textural analysis revealed that sand, silt and clay content showed high variation among the different series. Soils collected from Thuravur series showed the highest clay content (50.63%). The highest sand content (54.72 %) was found in Thottapally series and was followed by Purakkad series (49.35 %). Soils from Ambalapuzha series showed highest silt content (43.88 %) followed by Thottapally series (41.81 %). Purakkad and Thakazhi series showed sandy clay loam texture. Kallara series exhibited clay loam texture and sandy loam texture was observed in Thottapally series. Ambalapuzha series was silty loam in texture and clayey texture was observed in Thuravur series (Table 6).

Table 6. Textural classes of soil samples collected from six acid sulphate soil series of Kuttanad

Soil series	Sand	Silt	Clay	Textural class
	(%)			
Ambalapuzha	14.43	43.88	24.60	Silty loam
Kallara	25.98	33.06	28.88	Clay loam
Thakazhi	46.1	19.1	29.11	Sandy clay loam
Purakkad	49.35	18.83	28.23	Sandy clay loam
Thottapally	54.72	41.81	14.85	Sandy loam
Thuravur	22.08	35.74	50.63	Clayey

4.1.2 Electrochemical properties

4.1.2.1 pH

Soil samples collected from all series showed extremely acidic pH. The soil pH varied from 2.9 to 3.9 in the six series (Table 7). Significantly lowest pH was observed in Purakkad series whereas significantly higher pH was noticed in Ambalapuzha and Thottapally series (Fig. 2).

4.1.2.2 Electrical conductivity (EC)

The EC of soil samples collected from the six series were in the range of 0.42 to 1.02 dS m^{-1}. The highest EC value was observed in Purakkad series. Ambalapuzha series showed the lowest EC value (Table 7).

Table 7. Electrochemical properties of soil samples collected from six acid sulphate soil series of Kuttanad

Soil series	pH (Range)	EC (dS m^{-1}) (Range)
Ambalapuzha	3.9^{a} (2.11-4.13)	0.42^{c} (0.13-1.4)
Kallara	3.7^{a} (2.23-4.79)	0.66^{bc} (0.05-1.13)
Thakazhi	3.5^{a} (2.44-4.24)	0.87^{ab} (0.15- 1.70)
Purakkad	2.9^{b} (2.10-4.90)	1.02^{a} (0.25- 1.81)
Thottapally	3.9^{a} (2.30-5.20)	0.73^{ab} (0.13-1.6)
Thuravur	2.9^{b} (2- 4.20)	0.96^{ab} (0.24- 1.81)

4.1.3 Chemical properties

4.1.3.1 Organic carbon

The organic carbon content of the soil samples collected from six soil series were high and ranged from 1.73 to 6.20 per cent (Table 8). The highest organic carbon content was recorded in Kallara series and the lowest in Ambalapuzha series. Kallara series showed significantly higher content of organic carbon compared with other series (Fig. 3).

4.1.3.2 Available nitrogen

Available nitrogen content in the soil samples were low to medium and varied between 61.15 to 310.01 kg ha^{-1}. Significantly lower available N was recorded in

Ambalapuzha series. Kallara series showed significantly higher available N content and was on par with Purakkad and Thuravur (Table 8).

Table 8. Available nutrient status of soil samples collected from six acid sulphate soil series of Kuttanad

Soil series	OC (Range)	N (Range)	P (Range)	K (Range)	Ca (Range)	Mg (Range)	S (Range)
	(%)	(kg ha^{-1})			(mg kg^{-1})		
Ambalapuzha	1.73^{d} (0.47-3.01)	61.15^{b} (42.91-107.28)	10.12^{b} (4.26-11.29)	156.91^{de} (98.93-241.64)	206.04^{d} (68.06-518.57)	93.60^{e} (89.20-99.77)	228.95^{b} (67.36-605.54)
Kallara	6.20^{a} (4.93-7.62)	310.01^{a} (70.69-464.51)	12.41^{ab} (3.87-14.27)	202.83^{cd} (91.84-452.48)	367.98^{bc} (167.25-665.64)	131.62^{b} (126.70-138.70)	320.98^{b} (23.62-707.76)
Thakazhi	2.95^{bc} (1.01-4.32)	79.31^{b} (55.45-126.90)	9.25^{b} (4.21-10.11)	116.99^{e} (33.59-247.90)	204.04^{d} (38.91-395.38)	92.79^{e} (89.39-97.96)	319.55^{b} (50.23-868.76)
Purakkad	3.20^{b} (1.13-4.56)	299.12^{a} (85.83-656.55)	13.67^{a} (5.64-14.21)	252.56^{c} (120.40-351.40)	287.44^{cd} (96.88-510.00)	104.39^{d} (93.75-109.06)	356.26^{b} (159.51-952.59)
Thottapally	3.48^{b} (1.14-4.90)	108.08^{b} (59.22-207.27)	10.07^{b} (2.67-11.64)	313.48^{b} (167.98-480.88)	437.45^{b} (203.49-766.53)	123.53^{c} (113.23-129.04)	502.62^{a} (27.28-753.58)
Thuravur	2.47^{c} (1.59-5.38)	263.03^{a} (143.98-454.08)	11.93^{ab} (6.24-14.25)	388.36^{a} (202.31-848.98)	584.05^{a} (423.36-852.57)	141.06^{a} (136.68-144.35	550.48^{a} (211.33-1081.63)

4.1.3.3 Available phosphorus

The available P content of the six soil series are presented in table 8. The available phosphorus content of the soil samples collected from six series was low and varied from 9.25 to 13.67 kg ha^{-1}. The significantly lowest content was observed in Thakazhi series while significantly highest content of available phosphorus was recorded in Purakkad series.

4.1.3.4 Available potassium

The available potassium content of the soil samples collected from six series was medium to high. The significantly lowest content of available potassium (116.99 kg ha^{-1}) was recorded in Thakazhi series (Table 8). Among the six different series, significantly higher available potassium (388.36 kg ha^{-1}) was observed in Thuravur series.

4.1.3.5 Available calcium

Available calcium content of the soils from six different series ranged from 204.04 to 584.05 mg kg^{-1}. Significantly lower available calcium content was found in Thakazhi series and was on par with Ambalapuzha series. Significantly higher available calcium was recorded in Thuravur series (Table 8).

4.1.3.6 Available magnesium

The available magnesium content of the soil samples collected from six soil series are presented in table 8. Significantly lower Mg content (92.79 mg kg^{-1}) was recorded in Thakazhi series and was on par with Ambalapuzha series. Significantly higher value of available Mg (141.06 mg kg^{-1}) was noticed in the soil samples from Thuravur series.

4.1.3.7 Available sulphur

In the samples collected from six soil series, available sulphur content was high and ranged from 228.95 to 550.48 mg kg^{-1}(Table 8). The lowest value was observed in Ambalapuzha series which was on par with Kallara, Thakazhi and Purakkad series. The highest available sulphur was observed in Thuravur series and was found to be significant.

4.1.4 Micronutrients and heavy metals

4.1.4.1 Available iron

Available iron content in the selected six soil series was high and ranged between 1452.82 and 3039.48 mg kg^{-1} (Table 9). Significantly higher value for iron was recorded in Thuravur series whereas the significantly lowest content in Ambalapuzha series. Available iron content of Ambalapuzha series was on par with Thotapally series (Fig. 4).

4.1.4.2 Available manganese

The available Mn content was high and ranged from 6.25 to 15.58 mg kg^{-1} in the six soil series. Significantly lowest available Mn was observed in Purakkad series and significantly highest available Mn was noticed in Kallara series (Table 9).

Table 9. Available micronutrient status of soil samples collected from six acid sulphate soil series of Kuttanad

Soil series	Fe (Range)	Mn (Range)	Zn (Range)	Cu (Range)
(mg kg^{-1})				
Ambalapuzha	1452.82^{b} (169.53-4491.90)	11.86^{ab} (8.45-18.66)	11.09^{ab} (3.05-15.51)	1.33^{b} (0.03-5.45)
Kallara	2965.04^{a} (542.20-3879.74)	15.58^{a} (3.08-19.96)	8.68^{b} (2.60-12.24)	0.29^{c} (002-2.04)
Thakazhi	2036.68^{ab} (440.11-3460.04)	11.68^{ab} (2.1-19.65)	13.57^{a} (2.34-16.43)	2.62^{a} (0.01-4.32)
Purakkad	1793.56^{b} (433.30-3570.00)	6.25^{b} (2.67-11.38)	3.85^{c} (1.18-9.15)	0.27^{c} (0.04-0.91)
Thottapally	2238.34^{ab} (160.08-4908.3)	10.92^{ab} (4.59-17.10)	4.24^{c} (2.31-5.34)	0.24^{c} (.02-0.84)
Thuravur	3039.48^{a} (866.29-11217.91)	6.63^{b} (1.48-7.76)	8.38^{b} (2.34-12.44)	0.56^{c} (0.11-0.88)

4.1.4.3 Available zinc

Available Zn content of the soil samples collected from six soil series are given in table 9 and found that the available zinc content ranged from 3.85 to 13.57 mg kg^{-1}. The significantly lowest available Zn was recorded in Purakkad series and the significantly highest Zn content in Thakazhi series.

4.1.4.4 Available copper

Available copper was deficient in soil samples collected from all series and ranged from 0.24 to 2.62 mg kg^{-1}. The available copper content was significantly low in Thuravur series. The significantly higher available Cu was seen in soil samples taken from Thakazhi series (Table 9).

4.1.4.5 Available lead

The available lead content ranged from 0.22 to 1.03 mg kg^{-1}(Table 10). The lowest value was reported in Ambalapuzha series, which was on par with Purakkad series. Significantly highest value was reported in Thakazhi series (Fig. 6).

Table 10. Available heavy metal status of soil samples collected from six acid sulphate soil series of Kuttanad

Soil series	Pb (Range)	Cr (Range)	Hg	Al (Range)	Cd
(mg kg^{-1})					
Ambalapuzha	0.22^{c} (0.01-0.41)	0.67^{b} (0.26-1.32)	BDL	265.35^{c} (97.37-433.25)	BDL
Kallara	0.86^{ab} (0.13-0.84)	1.41^{a} (0.20-3.21)	BDL	549.90^{a} (118.84- 973.00)	BDL
Thakazhi	1.03^{a} (0.46-2.68)	0.45^{b} (0.04-0.83)	BDL	422.03^{b} (188.35-726.99)	BDL
Purakkad	0.38^{c} (0.02-0.89)	0.28^{b} (0.02-1.16)	BDL	154.24^{d} (72.96-263.81)	BDL
Thottapally	0.50^{bc} (0.04-1.54)	0.62^{b} (0.04-1.56)	BDL	147.79^{d} (105.20235.20)	BDL
Thuravur	0.81^{ab} (0.02-2.21)	1.41^{a} (0.48-2.97)	BDL	153.90^{d} (78.83-259.53)	BDL

BDL-Below detectable level

4.1.4.6 Available chromium

The available chromium content ranged from 0.28 to 1.41 mg kg^{-1} (Table 10). The lowest available chromium was recorded in Purakkad series. Available chromium content of Purakkad series was on par with Ambalapuzha, Thakazhi and Thotapally series. The highest value was observed in Kallara series (Fig. 7).

4.1.4.7 Available mercury

Available mercury content of soils was below detectable level in all the six soil series (Table 10).

4.1.4.8 Available aluminium

The available aluminium content showed a range from 147.79 to 549.90 mg kg^{-1}. Thottapally series showed the lowest value for available aluminium while the highest content was observed in Kallara series (Table 10 and Fig. 5)

4.1.4.9 Available cadmium

Available cadmium content of soils was below detectable level in all the six soil series (Table 10).

4.1.5 Correlation coefficient between soil properties and heavy metals

The correlation between soil properties and heavy metal status in soils of six series of Kuttanad is given in the table 11. The pH had significant positive correlation with Al (0.181*), and significant negative correlation with N (-0.189*) and K (-0.185*). Available N was found to have significant positive correlation with EC (0.220*), K (0.488**), Ca (0.414**), Mg (0.372**) and S (0.244**). The Zn (-0.367**), Cu (-0.343**) and Al (-0.459**) had significant negative correlation with available N. Organic carbon had significant positive correlation with Ca (0.207*), Mg (0.389**), Fe (0.238**) and Al (0.433**). Potassium showed significant positive correlation with Ca (0.422**), Mg (0.556**), S (0.331**), Fe (0.200*) and Cr (0.193*) and significant negative correlation with Mn (-0.249**), Zn (-0.210*), Cu (-0.378**) and Al (-0.354**). Magnesium (0.689**), S (0.252**), Fe (0.365**) and Cr (0.217*) showed significant positive correlation with Ca. Ca had a significant negative correlation with Cu (-0.266**) and Al (-0.221*). Magnesium showed significant positive correlation with S (0.336**), Fe (0.318**) and Cr (0.291**). Zn (-0.204*) and Cu (-0.389**) showed significant negative correlation with Mg. Iron showed significant positive correlation with Cr (0.232*) and significant negative correlation with Cu (-0.218*). Manganese was found to have significant positive correlation with Zn (0.307**), Pb (0.279**) and Al (0.325**).

Table 11.Correlation coefficient between soil properties and heavy metals

	pH	EC	N	OC	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	Pb	Cr	Al
pH	1															
EC	-0.101	1														
N	-0.189*	0.220*	1													
OC	0.016	0.044	0.010	1												
P	-0.136	-0.006	0.150	-0.049	1											
K	-0.185*	0.155	0.488**	-0.037	-0.029	1										
Ca	-0.177	0.092	0.414**	0.207*	0.001	0.422**	1									
Mg	-0.120	0.112	0.372**	0.389**	-0.074	0.556**	0.689**	1								
S	-0.152	0.162	0.244**	0.066	0.018	0.331**	0.252**	0.336**	1							
Fe	-0.108	0.089	0.165	0.238**	-0.123	0.200*	0.365**	0.318**	0.067	1						
Mn	0.089	-0.139	-0.174	0.126	-0.156	-0.249**	0.069	0.009	-0.131	0.043	1					
Zn	0.120	-0.125	-0.367**	-0.079	-0.161	-0.210*	-0.135	-0.204*	-0.124	0.126	0.307**	1				
Cu	0.136	-0.037	-0.308**	-0.181*	0.046	-0.325**	-0.266**	-0.389**	0.118	-0.218*	0.003	0.287**	1			
Pb	-0.031	-0.070	-0.123	0.103	0.150	-0.090	0.088	0.145	0.006	-0.164	0.279**	0.290**	0.191*	1		
Cr	0.004	-0.101	-0.007	0.121	-0.064	0.193*	0.217*	0.291**	-0.042	0.232*	0.052	-0.022	-0.120	0.041	1	
Al	0.181*	-0.086	-0.459**	0.433**	-0.128	-0.354**	-0.221*	-0.055	-0.169	0.072	0.325**	0.476**	0.307**	0.299**	0.273**	1

*- Significant at 5% level

**- Significant at 1% level

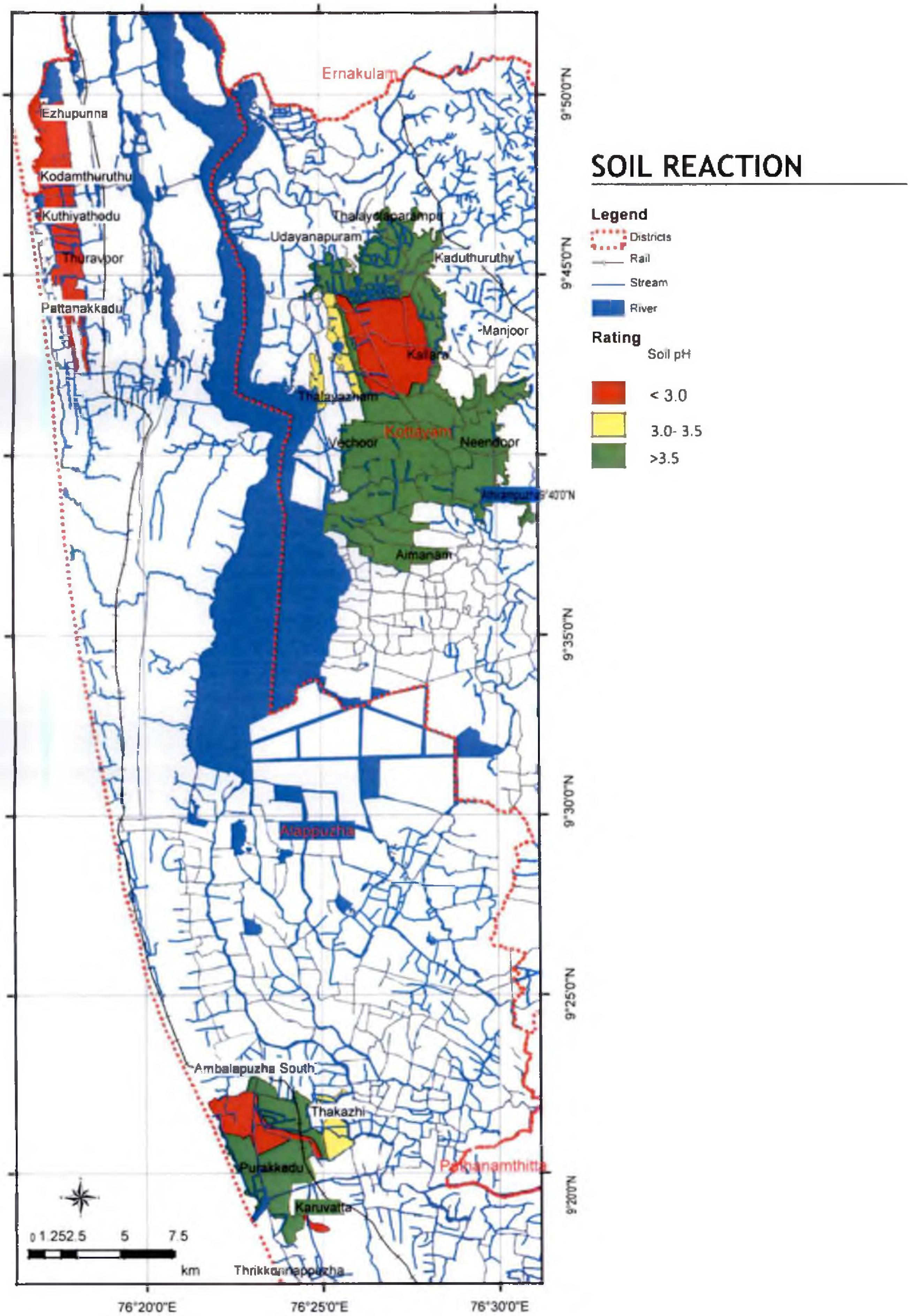

Fig.2 pH of acid sulphate soils

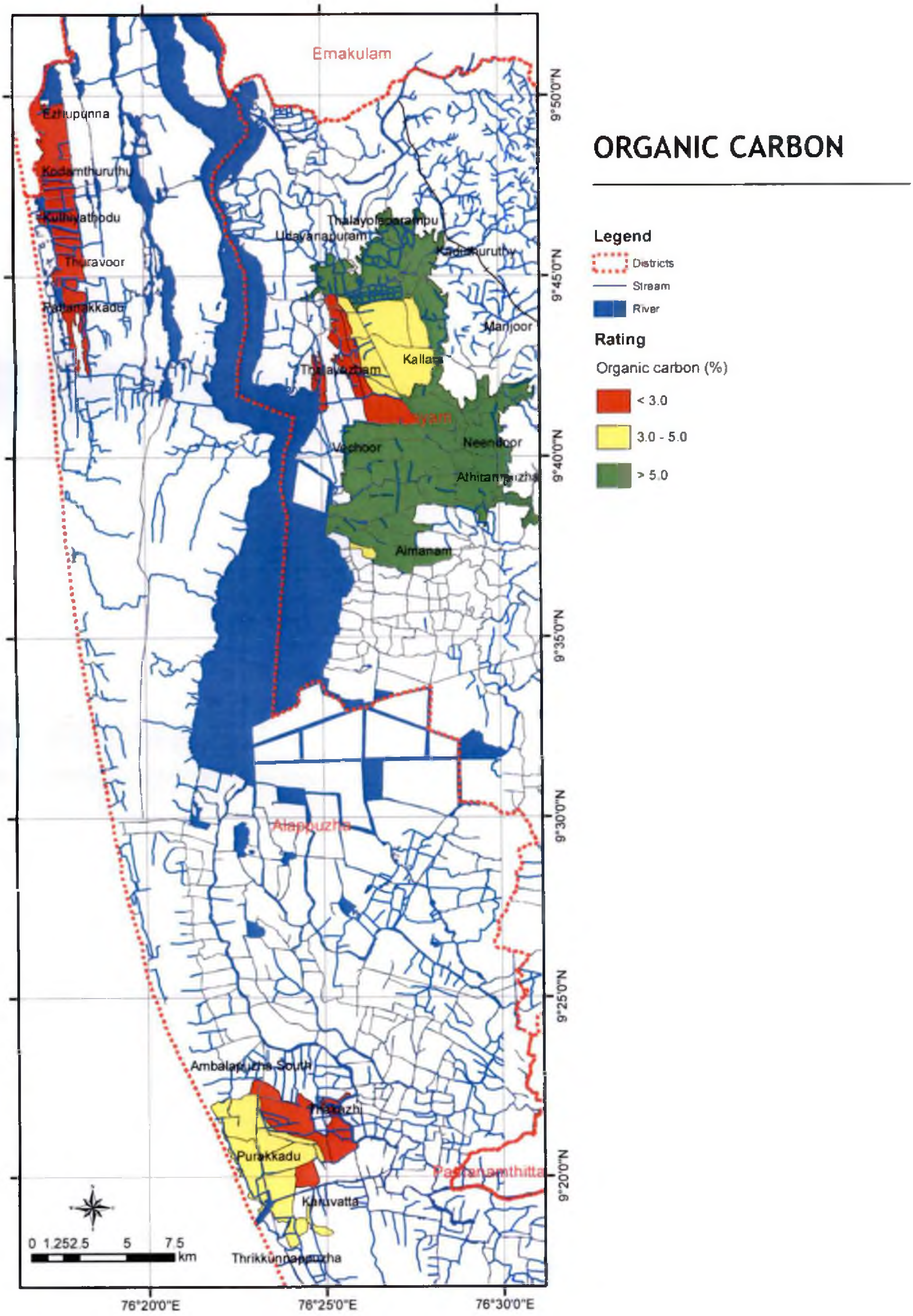

Fig. 3 Organic carbon of acid suphate soils

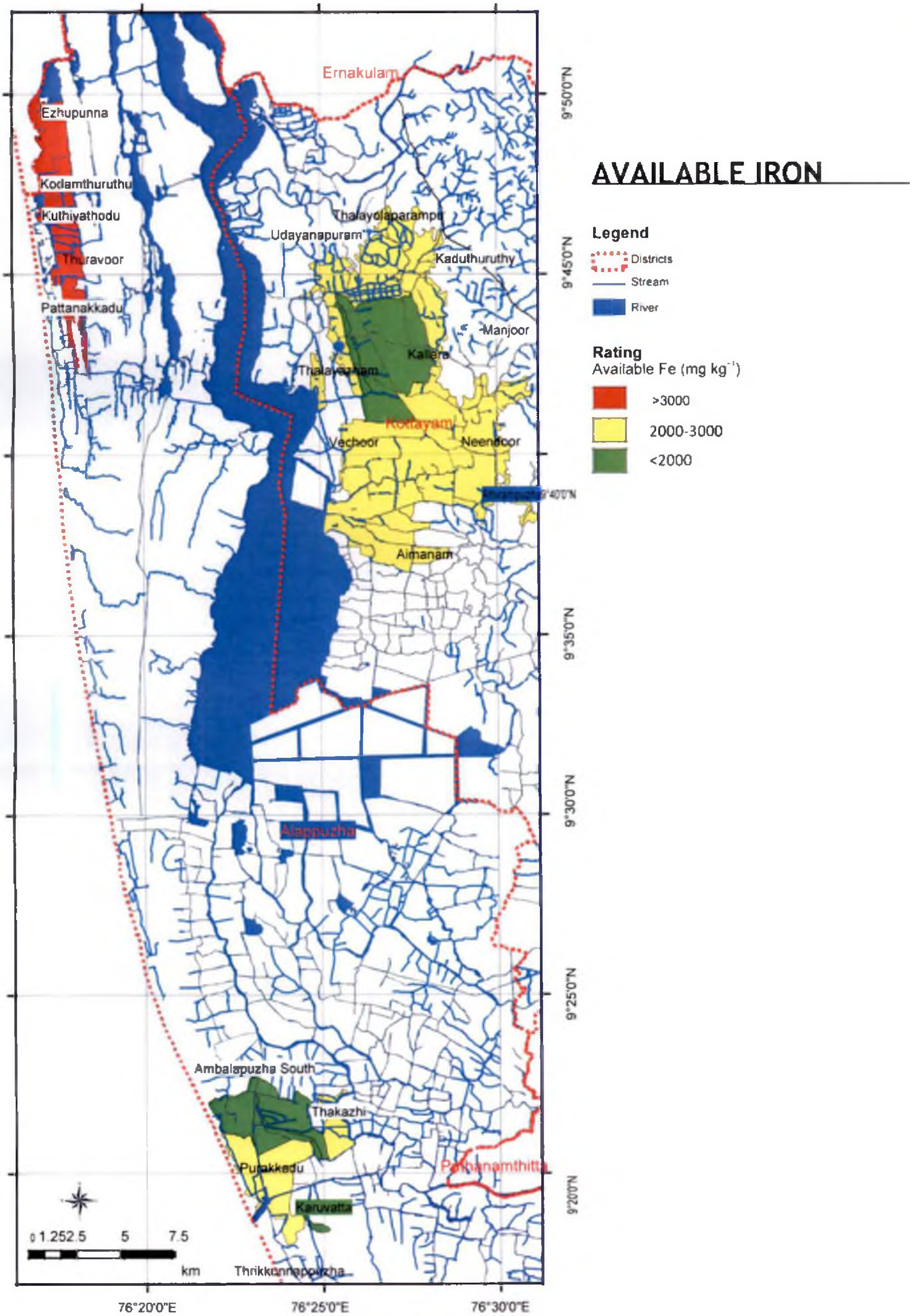

Fig. 4 Available iron of acid sulphate soils

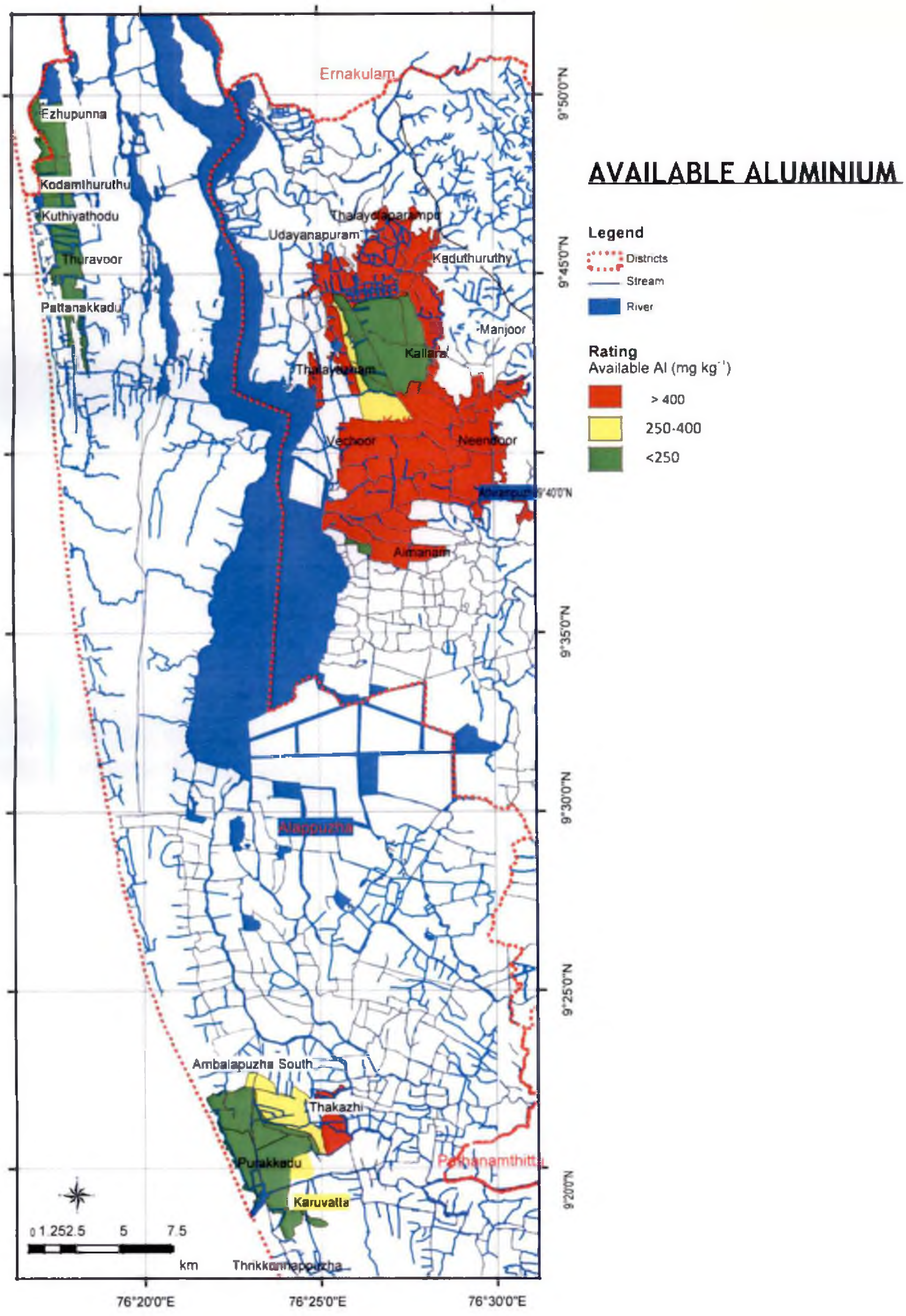

Fig. 5 Available aluminium of acid sulphate soils

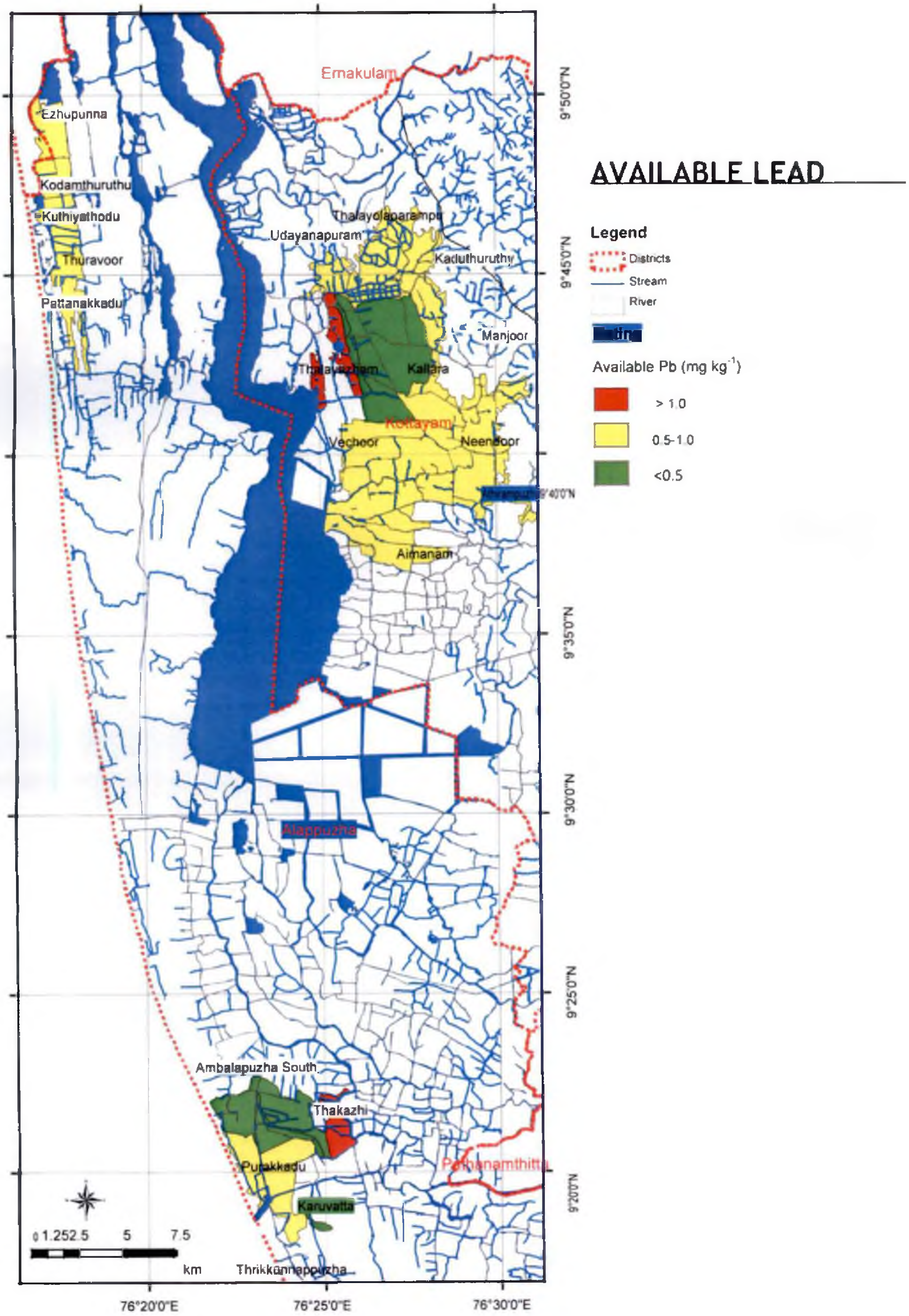

Fig. 6 Available lead of acid sulphate soils

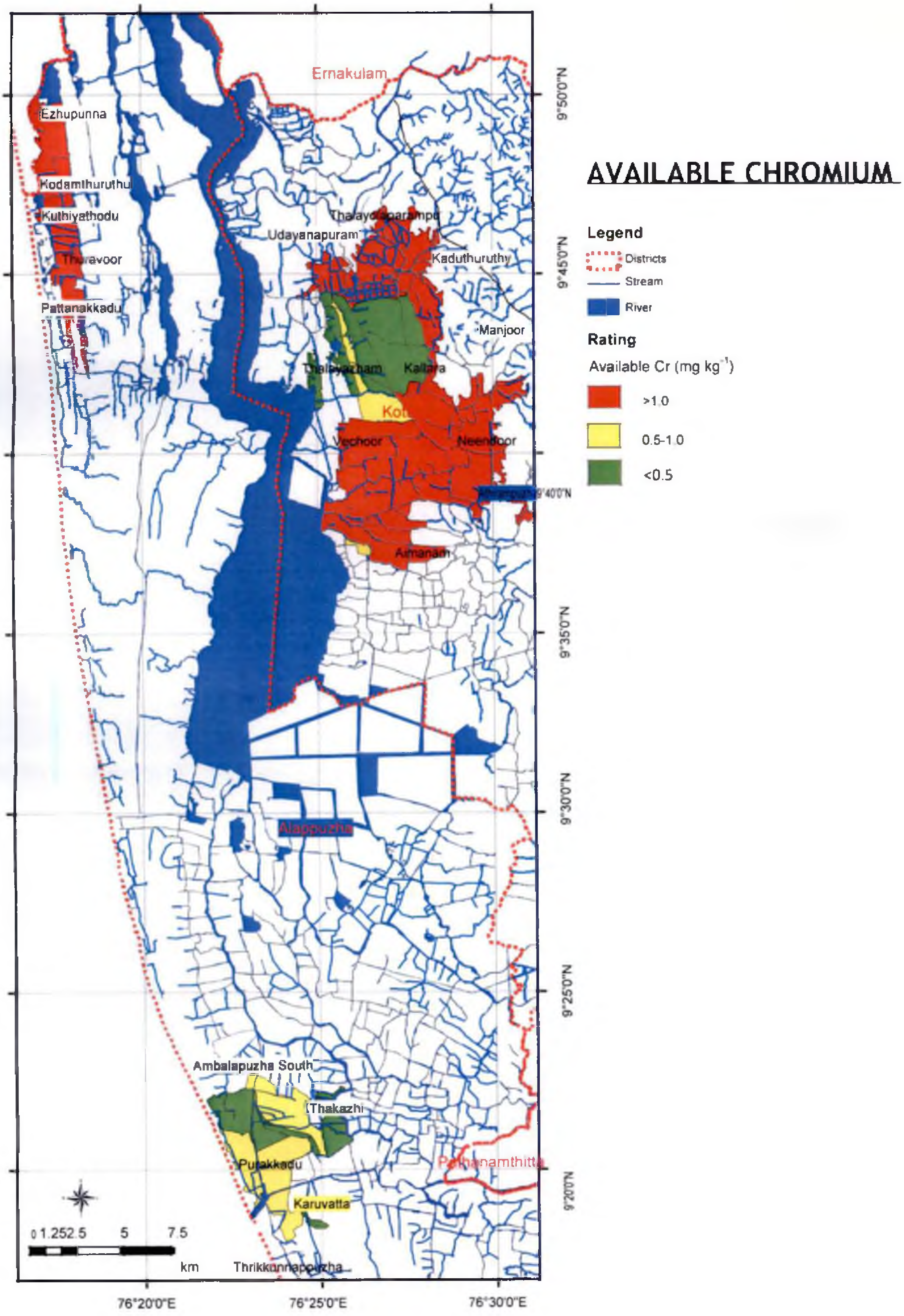

Fig.7 Available chromium of acid sulphate soils

Zinc had significant positive correlation with Cu (0.287**), Pb (0.290**) and Al (0.476**). Cu showed significant positive correlation with Pb (0.191*) and Al (0.307**). Al (0.273**) had significant positive correlation with Pb.

4.2 Characterization of sediment samples

Sediment samples were collected from adjoining canals/lakes of six soil series (20 numbers from each series) and characterized for physical properties like texture, electrochemical properties like pH, EC and chemical properties like organic carbon, available N, P, K, Ca, Mg, S, Fe, Al, Mn, Zn, Cu, Pb, Cd, Cr and Al. The analytical data regarding physical properties are presented in table 12.

Table 12. Textural classes of sediments collected from six acid sulphate soil series of Kuttanad

Soil series	Sand	Silt	Clay	Textural class
	(%)			
Ambalapuzha	84.25	4.95	9.65	Loamy sand
Kallara	59.50	25.2	10.25	Sandy loam
Thakazhi	61.62	6.00	27.06	Sandy clay loam
Purakkad	64.39	8.57	23.97	Sandy clay loam
Thottapally	65.00	21.85	8.48	Sandy loam
Thuravur	71.95	7.10	20.25	Sandy clay loam

From table 12, it is clear that Ambalapuzha series showed highest content of sand (84.25%) followed by Thuravur (71.95%). Silt content was highest in the sediment collected from canals of Kallara series (25.20%). Clay content was highest in the sediments collected from Thakazhi series (27.06%) followed by sediments collected from Purakkad series (23.97%). The dominant texture found in these areas was sandy clay l

4.2.1 Electrochemical properties

4.2.1.1 pH

The pH of sediment samples collected from six soil series were strongly acidic and it ranged from 4.4 to 5.5 (Table 13). Significantly lowest pH was recorded from sediments of Thottapally series and significantly highest value was observed in Ambalapuzha series. The pH of Ambalapuzha series was on par with Thakazhi, Kallara and Purakkad series.

4.2.1.2 Electrical conductivity

The electrical conductivity of the sediments collected from six soil series ranged from 0.3 to 0.68 dS m^{-1} (Table 13). The data revealed that there was no significant difference in EC for all the six soil series.

Table 13. Electrochemical properties of sediments collected from six acid sulphate soil series of Kuttanad

Series	pH (Range)	EC (dS m^{-1}) (Range)
Ambalapuzha	5.5^{a} (3.57-6.46)	0.68^{a} (0.17-1.42)
Kallara	5.4^{a} (3.89-6.38)	0.51^{a} (0.12-1.79)
Thakazhi	5.4^{a} (4.04-6.80)	0.48^{a} (0.13-1.81)
Purakkad	5.0^{ab} (3.36-6.28)	0.63^{a} (0.32-1.95
Thottapally	4.4^{c} (2.62-5.60)	0.57^{a} (0.11-0.98)
Thuravur	4.9^{bc} (3.50-6.25)	0.32^{a} (0.23-5.66)

4.2.2 Chemical properties

4.2.2.1 Organic carbon

The organic carbon content of the sediments collected from six acid sulphate soil series was high and ranged from 2.22 to 6.77 per cent in the six soil series (Table 14). Significantly lowest value was recorded in sediments collected from Thuravur series which was on par with organic carbon content of sediments collected from Ambalapuzha series. Sediments collected from Kallara series recorded significantly higher organic carbon content (Fig. 8).

4.2.2.2 Available nitrogen

Available nitrogen content in sediments collected from all series were low and it ranged from 45.27 to 222.27 mg kg^{-1} (Table 14). Sediments from Kallara series showed significantly higher value and the lowest value were obtained in sediments from Thottapally series.

4.2.2.3 Available phosphorus

The data from table 14 indicated that available P content in sediments collected from all series was low to medium. The sediments from Kallara series showed significantly lowest available phosphorus content (8.72 mg kg^{-1}). Significantly the highest value of available phosphorus (28.70 mg kg^{-1}) was obtained from sediments of Thuravur series.

4.2.2.4 Available potassium

Available potassium content ranged from 61.58 to 343.29 mg kg^{-1} (Table 14). Significantly higher value of potassium was noticed from sediments of Thuravur series, whereas the sediments from Thakazhi series recorded the lowest value which was on par with available potassium content of Kallara series.

Table 14. Available nutrient status of sediments collected from six acid sulphate soil series of Kuttanad

Series	OC (Range)	N (Range)	P (Range)	K (Range)	Ca (Range)	Mg (Range)	S (Range)
	(%)	(mg kg^{-1})					
Ambalapuzha	2.23^{c} (0.75-3.62)	148.92^{b} (57.10-471.50)	20.03^{b} (6.89-24.12)	74.67^{cd} (35.96-124.53)	257.72^{c} (210.92-316.86)	91.01^{d} (65.79-109.65)	628.74^{bc} (279.08-1069.90)
Kallara	6.77^{a} (4.55-9.27)	222.27^{a} (101.25-417.25)	8.72^{c} (3.13-10.87)	61.58^{d} (28.32-75.48)	305.30^{c} (96.76-457.38)	132.21^{c} (96.15-168.27)	548.27^{c} (86.37-2705.43)
Thakazhi	2.92^{b} (1.45-4.41)	167.02^{b} (101.22-215.10)	17.30^{b} (5.98-20.04)	68.63^{d} (43.32-104.12)	312.62^{c} (251.90-415.66)	126.22^{c} (98.04-147.05)	571.93^{bc} (199.02-1826.90)
Purakkad	2.63^{bc} (1.37-5.63)	69.62^{cd} (11.60-154.14)	23.01^{ab} (12.13-26.34)	105.07^{b} (67.21-172.75)	744.06^{a} (402.09-929.17)	162.56^{a} (157.08-167.77)	768.33^{abc} (216.79-1518.35)
Thottapally	2.76^{bc} (1.86-4.13)	45.27^{d} (10.12-76.24)	16.97^{b} (4.25-18.12)	98.79^{bc} (69.56-120.01)	530.71^{b} (356.04-6466.66)	144.66^{b} (140.00-158.98)	955.09^{a} (559.45-1721.06)
Thuravur	2.22^{c} (0.54-3.50)	92.79^{c} (45.24-101.32)	28.70^{a} (14.36-32.20)	343.29^{a} (275.57-403.24)	675.13^{a} (383.77-967.12)	161.19^{a} (156.65-165.20)	844.70^{ab} (306.93-1674.26)

4.2.2.5 Available calcium

The available Ca content ranged from 257.72 to 744.06 mg kg^{-1}. Sediments from Ambalapuzha series showed least value for available Ca and was on par with available Ca content of sediments collected from Thakazhi and Kallara series. Significantly higher value was recorded in the sediments from Purakkad series which was on par with that from Thuravur series (Table 14).

4.2.2.6 Available magnesium

The available magnesium content ranged from 91.01 to 162.56 mg kg^{-1} (Table 14). The lowest value was recorded from sediments collected from Ambalapuzha series while the highest value was obtained from samples collected from Purakkad series.

4.2.2.7 Available sulphur

The data from table 14 revealed that available sulphur content in sediments of all series was high and it ranged from 548.27 to 955.09 mg kg^{-1}. Sediments from the waterways of Thakazhi series recorded significantly lowest value of available sulphur while highest value was recorded from Thottapally series.

4.2.3 Micronutrients and heavy metals

4.2.3.1 Available iron

The content of available iron in sediments was high and it ranged from 1054.87 to 4903.21 mg kg^{-1}. Available Fe content of sediments from Thottapally was on par with the available Fe content of sediments from Thuravur series. Significantly higher available Fe content was reported for sediments from Ambalapuzha series (Table 15 and Fig. 9).

4.2.3.2 Available manganese

The available manganese content was high in sediments collected from all series and it ranged from 2.15 to 91.94 mg kg^{-1}. The lowest value was recorded from sediments of Thuravur series which was on par with that from Ambalapuzha, Purakkad and Thottapally series (Table 15). The highest available manganese content was recorded from sediments collected from the canals of Thakazhi series.

Table 15. Available micronutrient status of sediments collected from six acid sulphate soil series of Kuttanad

Series	Fe (Range)	Mn (Range)	Zn (Range)	Cu (Range)
(mg kg^{-1})				
Ambalapuzha	4903.21^{a} (1137.37-6039.91)	24.81^{c} (13.37-35.14)	36.05^{a} (7.25-81.72)	0.50^{a} (0.18-3.47)
Kallara	3553.28^{bc} (660.84-5788.81)	91.94^{a} (28.10-98.76)	26.20^{b} (14.21-56.87)	0.68^{a} (0.00-6.36)
Thakazhi	3013.05^{c} (741.05-5352.21)	53.84^{b} (22.78-130.54)	24.16^{bc} (9.67-48.78)	0.68^{a} (0.10-7.34)
Purakkad	4413.84^{ab} (1234.45-8652.98)	21.79^{c} (6.05-48.31)	17.05^{cd} (4.47-33.08)	0.41^{a} (0.00-3.76)
Thottapally	1054.87^{d} (369.40-3520.00)	14.07^{c} (5.20-25.20)	9.95^{d} (4.36-15.42)	0.27^{a} (0.1-1.34)
Thuravur	1598.49^{d} (590.60-1678.32)	2.15^{c} (0.24-5.86)	11.45^{d} (7.52-21.26)	0.19^{a} (0.00-0.55)

4.2.3.3 Available zinc

The available zinc content was sufficient in sediments collected from all series and it ranged from 9.95 to 36.05 mg kg^{-1}. Significantly lowest available zinc content was recorded from sediments of Thottapally series and significantly highest available Zn content was noticed in sediments of Ambalapuzha series (Table 15).

4.2.3.4 Available copper

The content of available Cu was deficient in sediments collected from all series and it ranged from 0.19 to 0.68 mg kg^{-1} (Table 15). There was no significant difference in available Cu content of sediment samples collected from six soil series.

4.2.3.5 Available lead

The content of available Pb ranged from 0.50 to 2.73 mg kg^{-1} (Table 16). Significantly lower available lead was associated with the sediments from Ambalapuzha series while highest available Pb content from those collected from Thakazhi series (Fig. 11).

Table 16. Available heavy metal status of sediments collected from six acid sulphate soil series of Kuttanad

Series	Pb (Range)	Cr (Range)	Hg	Al (Range)	Cd
(mg kg^{-1})					
Ambalapuzha	0.50^{c} (0.02-1.91)	0.61^{c} (0.02-1.54)	BDL	198.76^{abc} (69.80-456.12)	BDL
Kallara	2.73^{a} (0.01-2.98)	1.83^{b} (0.12-4.85)	BDL	265.55^{a} (153.85-439.26)	BDL
Thakazhi	1.18^{bc} (0.77-3.56)	3.47^{a} (0.04-5.96)	BDL	235.91^{ab} (111.44-509.60)	BDL
Purakkad	2.01^{ab} (0.67-5.51)	2.23^{b} (0.06-4.71)	BDL	229.56^{ab} (72.32-405.69)	BDL
Thottapally	1.61^{b} (1.02-2.44)	0.34^{c} (0.14-0.58)	BDL	142.75^{c} (105.80-204.00)	BDL
Thuravur	0.71^{c} (0.02-2.22)	0.97^{c} (0.04-3.47)	BDL	194.49^{bc} (80.18-320.70)	BDL

BDL- Below detectable level

4.2.3.6 Available chromium

The available chromium content varied from 0.34 to 3.47 mg kg^{-1} (Table 16). Sediments from Thottapally series recorded the lowest value for available chromium content. Content of chromium in Thottapally series was on par with that from Ambalapuzha and Thuravur series. The highest available chromium was reported from sediments of Kallara series.

4.2.3.7 Available mercury

Available Hg content of sediments collected from all the six soil series were below detectable level (Table 16).

4.2.3.8 Available aluminium

The available aluminium content of the sediments collected from six soil series varied from 142.75 to 265.55 mg kg^{-1}. The lowest value was recorded from the sediments of Thottapally series whereas the highest value from Thakazhi series (Table 16 and Fig. 10).

4.2.3.9 Available cadmium

Available Cd content of sediments collected from all the six soil series were below detectable level (Table 16).

Table 17. Correlation coefficient between sediment properties and heavy metals

	Ph	EC	N	OC	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	Pb	Cr	Al
pH	1															
EC	-0.129	1														
N	0.379**	-0.135	1													
OC	0.157	0.003	0.377**	1												
P	0.016	-0.031	-0.220*	-0.140	1											
K	-0.154	-0.062	-0.235**	-0.281**	0.097	1										
Ca	-0.263**	-0.059	-0.360**	-0.203*	0.102	0.427**	1									
Mg	-0.281**	-0.086	-0.350**	-0.084	0.131	0.415**	0.596**	1								
S	-0.293**	0.080	-0.319**	-0.119	0.047	0.221*	0.245**	0.145	1							
Fe	0.171	0.082	0.225*	-0.049	0.087	-0.268**	-0.173	-0.254**	-0.139	1						
Mn	0.225*	-0.074	0.357**	0.151	-0.037	-0.360**	-0.266**	-0.130	-0.335**	0.281**	1					
Zn	0.292**	0.015	0.390**	0.053	-0.087	-0.284**	-0.383**	-0.435**	-0.096	0.460**	0.359**	1				
Cu	-0.088	-0.049	0.054	-0.003	-0.074	-0.022	-0.123	-0.136	-0.037	-0.044	0.040	0.042	1			
Pb	-0.130	0.063	0.044	-0.093	0.069	-0.171	0.070	0.195*	-0.089	0.006	0.326**	0.015	0.106	1		
Cr	0.225*	-0.046	0.330**	0.455**	0.080	-0.230*	-0.104	0.082	-0.239**	0.381**	0.440**	0.179	-0.036	0.093	1	
Al	0.150	0.109	0.234*	0.128	0.170	-0.080	-0.067	-0.040	-0.058	0.208*	0.068	-0.019	0.027	0.113	0.247**	1

*- Significant at 5% level

**- Significant at 1% level

4.2.4 The correlation coefficient between sediment properties and heavy metals

The correlation coefficient between sediment properties and heavy metals in six series of Kuttanad are given in table 17. The pH had significant positive correlation with N (0.379**), Mn (0.225*), Zn (0.292**) and Cr (0.225**). Calcium (-0.263**), Mg (-0.281**) and S (-0.293**) showed significant negative correlation with pH. Nitrogen had significant positive correlation with OC (0.377**), Fe (0.225**), Mn (0.357**), Zn (0.390**), Cr (0.330**) and Al (0.234**). Nitrogen had significant negative correlation with P (-0.220*), Ca (-0.360**), Mg (-0.350**) and S (0.319**). Organic carbon showed significant positive correlation with Cr (0.455**) and significant negative correlation with K (-0.281**) and Ca (-0.203*). Potassium had significant positive correlation with Ca (0.427**), Mg (0.415**) and S (0.221*). Iron (-0.268**), Mn (-0.360**), Zn (-0.284**) and Cr (-0.230*) showed significant negative correlation with K. Calcium had significant positive correlation with Mg (0.596**) and S (0.245**) and significant negative correlation with Zn (0.383**). Lead (0.195*) showed significant positive correlation with Mg. Iron (-0.254**) and Zn (-0.435**) showed significant negative correlation with Mg. Sulphur showed significant negative correlation with Mn (-0.335**) and Cr (-0.239**). Iron showed significant positive correlation with Mn (0.281**), Zn (0.460**), Cr (0.381**) and Al (0.208**). Zinc (0.359**), Pb (0.326**) and Cr (0.440**) showed significant positive correlation with Mn. Chromium showed significant positive correlation with Al (0.247**).

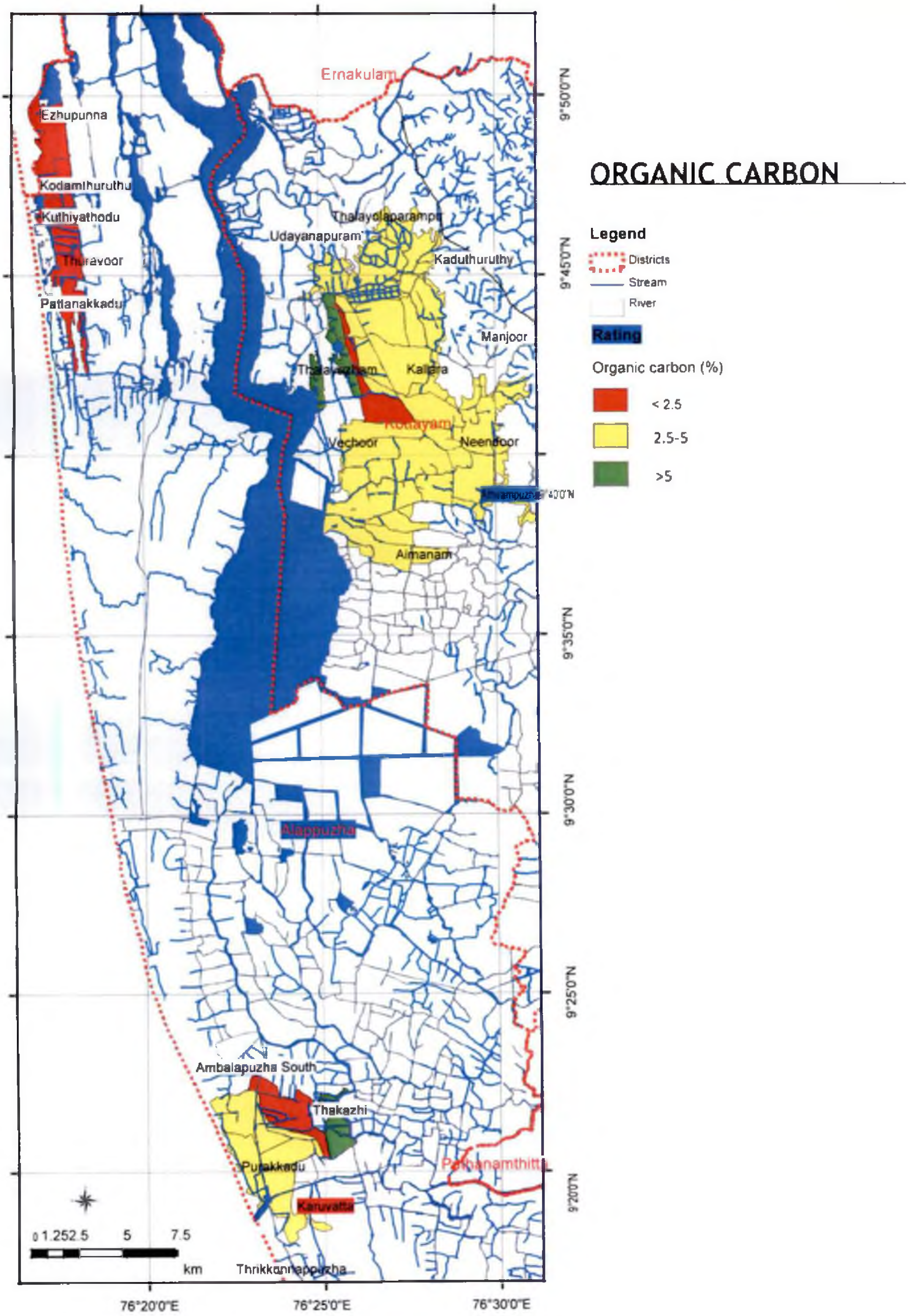

Fig. 8 Organic carbon content in sediments

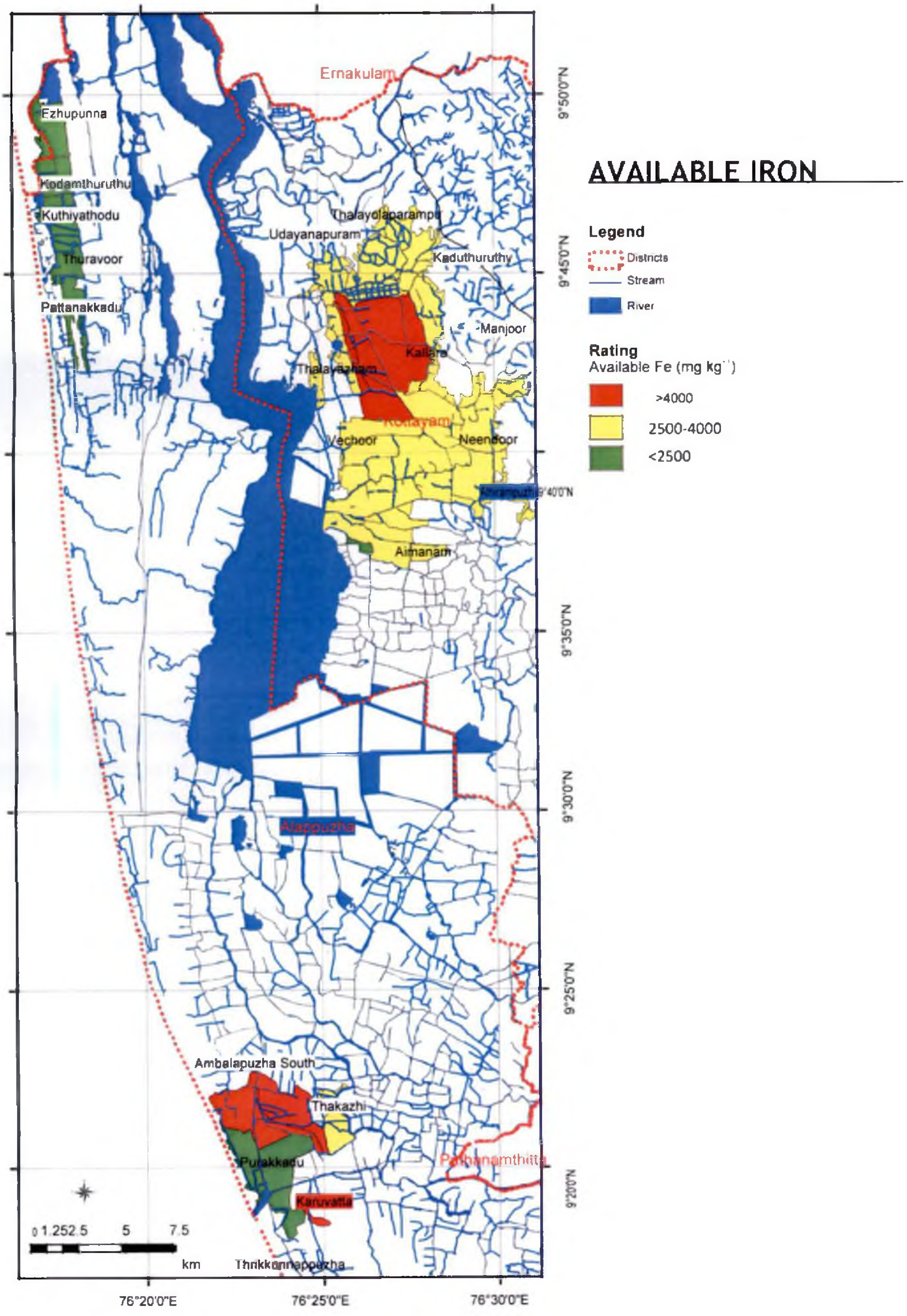

Fig. 9 Available iron content in sediments

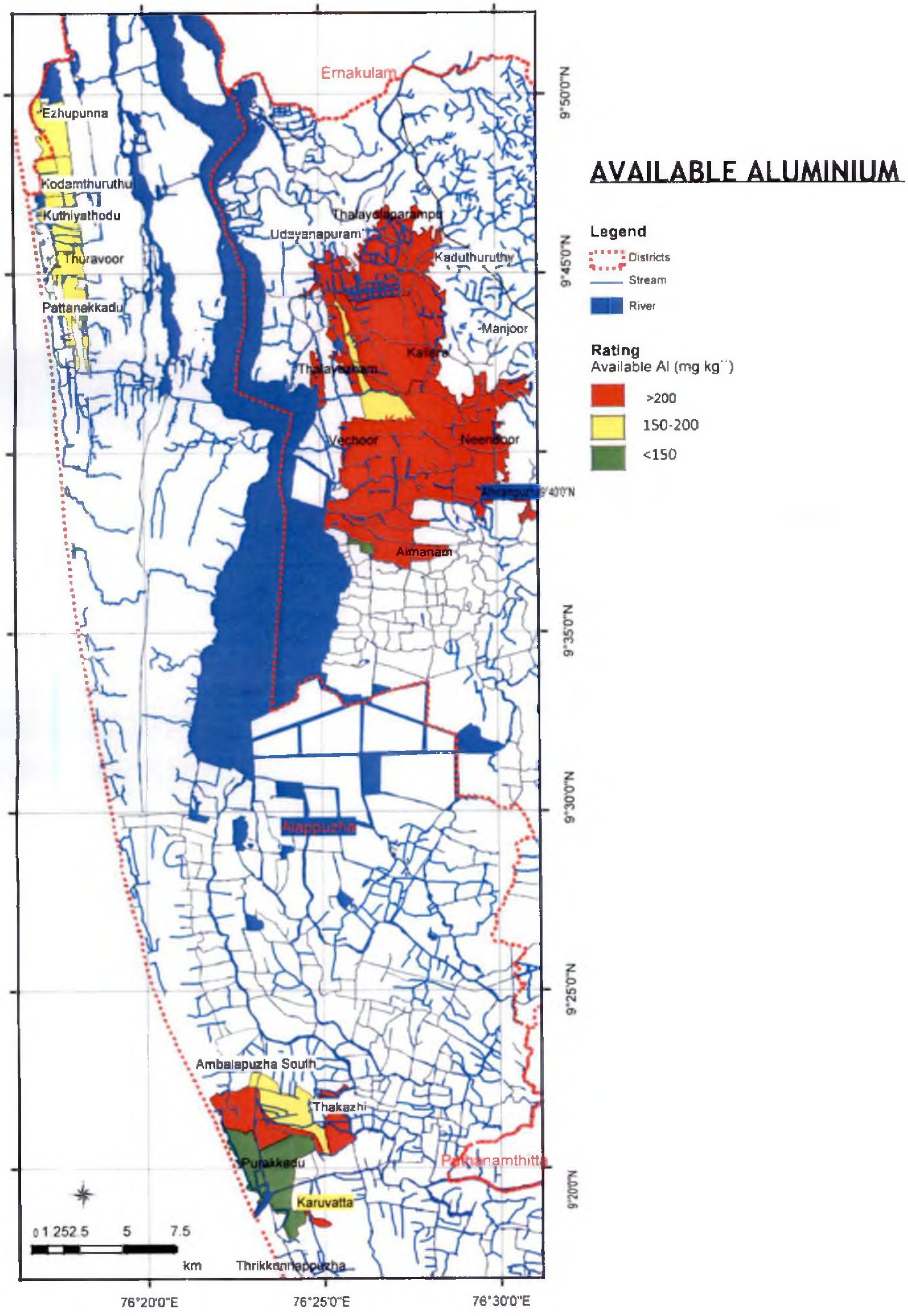

Fig.10 Available aluminium content in sediments

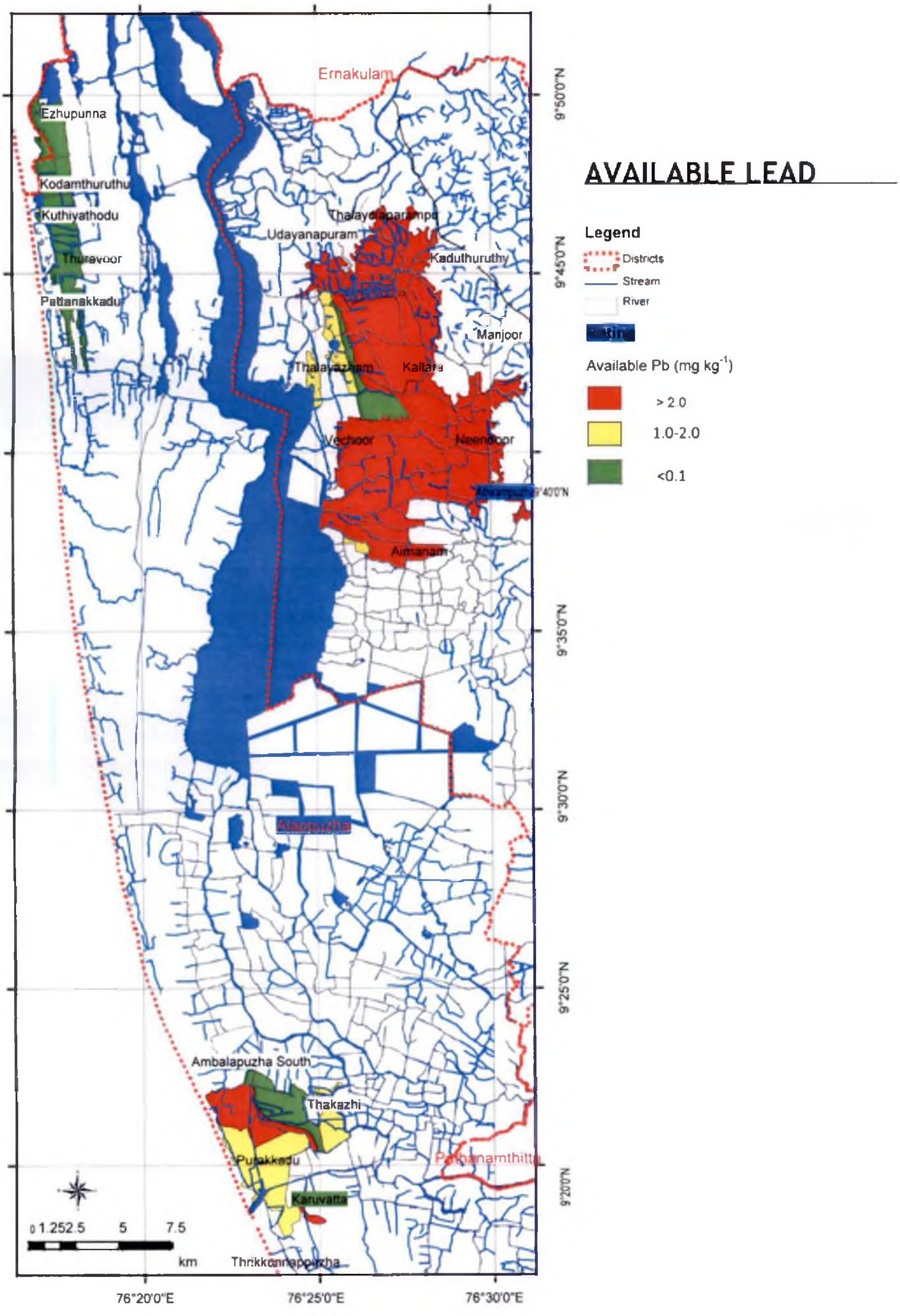

Fig.11 Available lead content in sediments

4.3 Characterization of water samples

Water samples were collected from adjoining canals/ lakes of six soil series (20 locations from each series) and analyzed for physical properties like colour, temperature, turbidity, suspended solids, electrochemical properties like pH, EC, water quality parameters like biochemical oxygen demand (BOD), chemical oxygen demand (COD) and chemical properties like total N, P, K, S, Fe, Al, Mn, Zn, Cu, Pb, Cd, Cr and Hg.

4.3.1 Physical properties

4.3.1.1 Temperature

The temperature of water collected from locations belonging to different series ranged from 31.07^0C to 32.25^0C. The lowest temperature was recorded for water samples from Thuravur series and the highest temperature was recorded in water samples from Thotapally series (Table 18).

4.3.1.2 Turbidity

The turbidity of water samples collected from adjoining canals/lakes from the six soil series varied from 1.61 to 3.39 NTU (Table 18). The lowest turbidity was recorded in the water samples from Thakazhi series whereas the highest value was noted in water samples of Thuravur series.

4.3.1.3 Colour and suspended solids

Water samples collected from all canals showed pale yellow colour and the suspended solids were found to be absent (Table 18).

Table 18. Physical properties of water samples collected from different soil series of Kuttanad

Soil series	Colour	Temperature (Range)	Turbidity (Range)	Suspended solids
		(^{0}C)	(NTU)	(mg L^{-1})
Ambalapuzha	Pale yellow	31.24 ^{bc} (30.1-32.00)	2.27 ^{ab} (1.10-7.20)	NIL
Kallara	Pale yellow	31.15 ^{c} (30.20-32.00)	2.65 ^{ab} (0.40-4.50)	NIL
Thakazhi	Pale yellow	31.12 ^{c} (29.00-33.00)	1.61 ^{b} (0.20-6.10)	NIL
Purakkad	Pale yellow	31.78 ^{ab} (31.00-34.20)	2.87 ^{ab} (0.90-7.90)	NIL
Thottapally	Pale yellow	32.25 ^{a} (31.00-34.00)	2.14 ^{ab} (0.40-4.30)	NIL
Thuravur	Pale yellow	31.07 ^{c} (30.30-32.10)	3.39 ^{a} (0.50-5.50)	NIL

NTU-Nephelometric turbidity unit

4.3.2. Water quality parameters

4.3.2.1 Biochemical oxygen demand (BOD)

The BOD values of water samples collected from different series ranged between 6.69 and 12.75 mg L^{-1}. The lowest BOD was noticed in water samples from canals of Thuravur series. Significantly higher BOD value was observed in water samples of Ambalapuzha series (Table 19).

4.3.2.2 Chemical oxygen demand (COD)

The data from table 19 indicated that COD of water samples collected from different series ranged from 85 to 176 mg L^{-1}. Water samples of Thakazhi series recorded significantly lowest value which was followed by water samples from Thuravur series. Water samples from Thottapally series showed significantly higher COD.

Table 19. Biological oxygen demand (BOD) and chemical oxygen demand (COD) of water samples collected from different soil series of Kuttanad

Soil series	BOD (Range)	COD (Range)
	(mg L^{-1})	
Ambalapuzha	12.75^{a} (1.41-20.61)	130.00^{ab} (60.00-220.00)
Kallara	6.97^{c} (3.45-17.56)	129.00^{ab} (80.00-160.00)
Thakazhi	8.45^{bc} (1.50-15.50)	85.00^{b} (60.00-80.00)
Purakkad	10.70^{ab} (5.50-22.20)	153.00^{a} (80.00-200.00)
Thottapally	7.69^{bc} (2.89-17.10)	176.00^{a} (40.00-380.00)
Thuravur	6.69^{c} (3.3-22.5)	102.00^{b} (60.00-380.00)

4.3.3 Electrochemical properties of water samples

4.3.3.1 pH

The pH of water samples from all the six soil series ranged from 5.4 to 6.6 (Table 20). Significantly lowest and highest pH was recorded from water samples collected from the canals of Purakkad and Kallara series respectively.

4.3.3.2 Electrical conductivity

The electrical conductivity values ranged from 0.02 to 0.74 dS m^{-1} for the 20 water samples collected from all the six soil series (Table 20). Water samples from Thuravur series reported the lowest value of EC, which was on par with EC of Thotapally and Kallara series. The highest EC value was recorded in water samples of Purakkad series.

Table 20. Electrochemical properties of water samples collected from different soil series of Kuttanad

Soil series	pH (Range)	EC (dS m^{-1}) (Range)
Ambalapuzha	6.2^{a} (5.00-7.64)	0.39^{b} (0.24-0.49)
Kallara	6.6^{a} (3.62-7.75)	0.14^{c} (0.05-0.39)
Thakazhi	6.6^{a} (3.60-7.52)	0.39^{b} (0.04-1.06)
Purakkad	5.4^{b} (4.21-5.96)	0.74^{a} (0.02-1.80)
Thottapally	5.4^{b} (4.14-6.28)	0.04^{c} (0.01-0.45)
Thuravur	6.3^{a} (5.88-6.92)	0.02^{c} (0.02-0.64)

4.3.4 Chemical properties of water samples

4.3.4.1 Total nitrogen

The ammoniacal nitrogen content (NH_4-N) was less compared to nitrate nitrogen content (NO_3-N) in all the water samples (Table 21). Ammoniacal nitrogen content ranged from 0.11 to 0.7 mg L^{-1}. The lowest ammoniacal nitrogen content was recorded in water samples collected from Thuravur series, which was on par with the ammoniacal nitrogen content of water samples of Purakkad and Ambalapuzha series. The highest ammoniacal nitrogen content was recorded from water samples from Kallara series. Nitrate nitrogen content of water samples ranged from 3.25 to 5.63 mg L^{-1}. The lowest nitrate nitrogen content was reported in water samples of Purakkad series whereas the highest from Thakazhi series (Table 21).

4.3.4.2 Total phosphorus

The total phosphorus content ranged from 0.17 to 0.25 mg L^{-1} in different series (Table 21). There was no significant difference in total phosphorus concentration of water samples from the six series. The lowest content was reported in water samples from Thuravur series and highest in Thottapally series.

Table 21.Total nutrient content of water samples collected from different soil series of Kuttanad

Soil series	N (Range)		P (Range)	K (Range)	S (Range)
	NH_4-N	NO_3-N			
	(mg L^{-1})				
Ambalapuzha	0.17^{c} (0.00-0.56)	4.84^{ab} (2.24-9.52)	0.20^{a} (0.06-0.49)	5.36^{c} (2.40-9.60)	1.53^{b} (0.11-2.18)
Kallara	0.70^{a} (0.00-1.12)	3.98^{b} (1.68-6.21)	0.18^{a} (0.02-0.54)	6.83^{bc} (2.00-7.80)	0.44^{b} (.03-1.26)
Thakazhi	0.45^{b} (0.00-1.68)	5.63^{a} (1.67-6.16)	0.24^{a} (0.01-0.74)	9.12^{bc} (1.00-10.00)	3.76^{a} (0.04-5.67)
Purakkad	0.17^{c} (0.00-0.56)	3.25^{b} (1.12-5.04)	0.20^{a} (0.08-0.49)	9.09^{bc} (3.40-13.20)	2.46^{b} (0.61-4.93)
Thottapally	0.39^{b} (0.00-0.56)	3.42^{b} (1.12-9.52)	0.25^{a} (0.11-1.08)	15.94^{b} (12.00-18.00)	1.96^{b} (0.22-4.25)
Thuravur	0.11^{c} (0.00-0.56)	3.28^{b} (0.00-6.54)	0.17^{a} (0.02-0.5)	19.27^{a} (8.40-26.00)	1.92^{b} (0.38-5.89)

4.3.4.3 Total potassium

The total potassium content of water samples ranged between 5.36 and 19.27 mg L^{-1}. The lowest total potassium was recorded from water samples of Ambalapuzha series whereas the highest total potassium was observed in water samples collected from Thuravur series (Table 21).

4.3.4.4 Total sulphur

The total sulphur content of water samples ranged from 0.44 to 3.76 mg L^{-1}. The lowest content was recorded in water samples collected from Kallara series and the highest from Thakazhi series (Table 21). Total sulphur content of Kallara serieswas on par with that of Ambalapuzha, Purakkad, Thottapally and Thuravur series.

4.3.5 Total micronutrient content and heavy metals in water

4.3.5.1 Total iron

The iron content ranged from 2.70 to 3.53 mg L^{-1}. Even though there was no significant difference in the total Fe content of water samples collected from the six soil series, the lowest and highest total Fe content was reported in water samples collected from Thakazhi and Kallara series respectively (Table 22).

4.3.5.2 Total manganese

Similar to total Fe content, there was no wide difference in the total Mn concentration in water samples collected from the adjoining waterways of six soil series (Table 22). The total manganese content ranged from 0.05 to 0.27 mg L^{-1}. The highest total Mn content was observed in water samples from Purakkad series.

Table 22.Total micronutrient status of water samples collected from different soil series of Kuttanad

Soil series	**Fe** **(Range)**	**Mn** **(Range)**	**Zn**	**Cu**
	(mg L^{-1})			
Ambalapuzha	2.81^{a} (1.43-5.10)	0.13^{b} (0.01-0.54)	BDL	BDL
Kallara	3.53^{a} (0.28-9.92)	0.10^{b} (0.00-0.28)	BDL	BDL
Thakazhi	2.70^{a} (1.13-5.43)	0.10^{b} (0.00-0.26)	BDL	BDL
Purakkad	3.44^{a} (2.60-5.94)	0.27^{a} (0.04-0.60)	BDL	BDL
Thottapally	2.78^{a} (1.65-5.34)	0.07^{b} (0.02-0.13)	BDL	BDL
Thuravur	3.49^{a} (1.44-6.99)	0.05^{b} (0.01-0.10)	BDL	BDL

BDL- Below detectable level

4.3.5.3 Total lead

Total lead content of water samples ranged from 0.02 to 0.10 mg L^{-1}. The lowest value was obtained from Thuravur series and total lead content of water samples from Thuravur series was on par with total Pb content of Ambalapuzha, Kallara and Thakazhi series (Table 23). The highest value of total Pb was observed in water samples from Thottapally series which was followed by water samples from Purakkad series (Fig. 13).

4.3.5.4 Total chromium

Total chromium content of water samples collected from the six series ranged from 0.11 to 0.25 mg L^{-1}. Water samples from Thakazhi series recorded the lowest chromium content and the highest content in water samples from Purakkad series (Table 23 and Fig. 14).

Table 23. Total heavy metal status of water samples collected from different soil series of Kuttanad

Soil series	Pb (Range)	Cr (Range)	Hg	Al (Range)	Cd
	(mg L^{-1})				
Ambalapuzha	0.04^{b} (0.02-0.09)	0.17^{b} (0.04-0.38)	BDL	0.54^{ab} (0.08-1.87)	BDL
Kallara	0.03^{b} (0.01-0.08)	0.14^{bc} (0.00-0.34)	BDL	0.62^{a} (0.00-1.29)	BDL
Thakazhi	0.03^{b} (0.01-0.05)	0.11^{c} (.02-0.25)	BDL	0.61^{a} (0.07-1.10)	BDL.
Purakkad	0.09^{a} (0.01-0.27)	0.25^{a} (0.08-0.34)	BDL	0.35^{bc} (0.18-0.49)	BDL
Thottapally	0.10^{a} (0.01-0.41)	0.24^{a} (0.17-0.39)	BDL	0.19^{c} (0.01-0.54)	BDL
Thuravur	0.02^{b} (0.00-0.05)	0.18^{b} (0.09-0.37)	BDL	0.63^{a} (0.32-1.23)	BDL

BDL- Below detectable level

4.3.5.5 Total mercury

Total mercury content of water samples collected from different series were found to be below detectable level (Table 23).

4.3.5.6 Total aluminium

The data pertaining to total Al content in water samples from six different soil series are shown in table 23. Total aluminium content in water samples from these series varied between 0.19 and 0.63 mg L^{-1}. The lowest value for total aluminium was recorded from water samples of Thotapally series and the highest value was noticed in the samples of Thuravur series (Fig. 12).

4.3.5.7 Total cadmium

Total cadmium content of water samples collected from different series were found to be below detectable level (Table 23).

Table 24. Correlation between water quality parameters and heavy metals

	pH	EC	N	P	K	S	Fe	Mn	Pb	Cr	Al
pH	1										
EC	-0.201*	1									
N	0.153	-0.028	1								
P	-0.010	0.036	0.009	1							
K	-0.234*	-0.151	-0.118	-0.112	1						
S	-0.125	-0.091	-0.148	-0.048	0.525**	1					
Fe	-0.032	-0.051	0.064	-0.151	0.067	-0.145	1				
Mn	-0.075	0.425**	0.061	-0.108	-0.182*	-0.102	0.297**	1			
Pb	-0.273**	-0.078	-0.078	-0.015	-0.002	-0.104	0.162	0.094	1		
Cr	-0.270**	0.173	-0.012	0.105	0.074	-0.017	0.291**	0.325**	-0.017	1	
Al	0.256**	-0.052	0.083	-0.092	0.043	0.053	0.367**	0.127	-0.105	-0.097	1

*- Significant at 5% level

**- Significant at 1% level

4.3.6 Correlation between water quality parameters and heavy metals

The correlation between water quality parameters and heavy metals in six soil series are given in table 24. The pH had significant positive correlation with Al (0.256**) and negative correlation with EC (-0.201*), K (-0.234*), Pb (-0.273**) and Cr (-0.270**). Electrical conductivity showed significant positive correlation with Mn (0.425**). Potasssium had significant positive correlation with S (0.525**) and significant negative correlation with Mn (-0.182*). Iron had significant positive correlation with Mn (0.297**), Cr (0.291**) and Al (0.367**). A significant positive correlation was observed between Mn and Cr (0.35**).

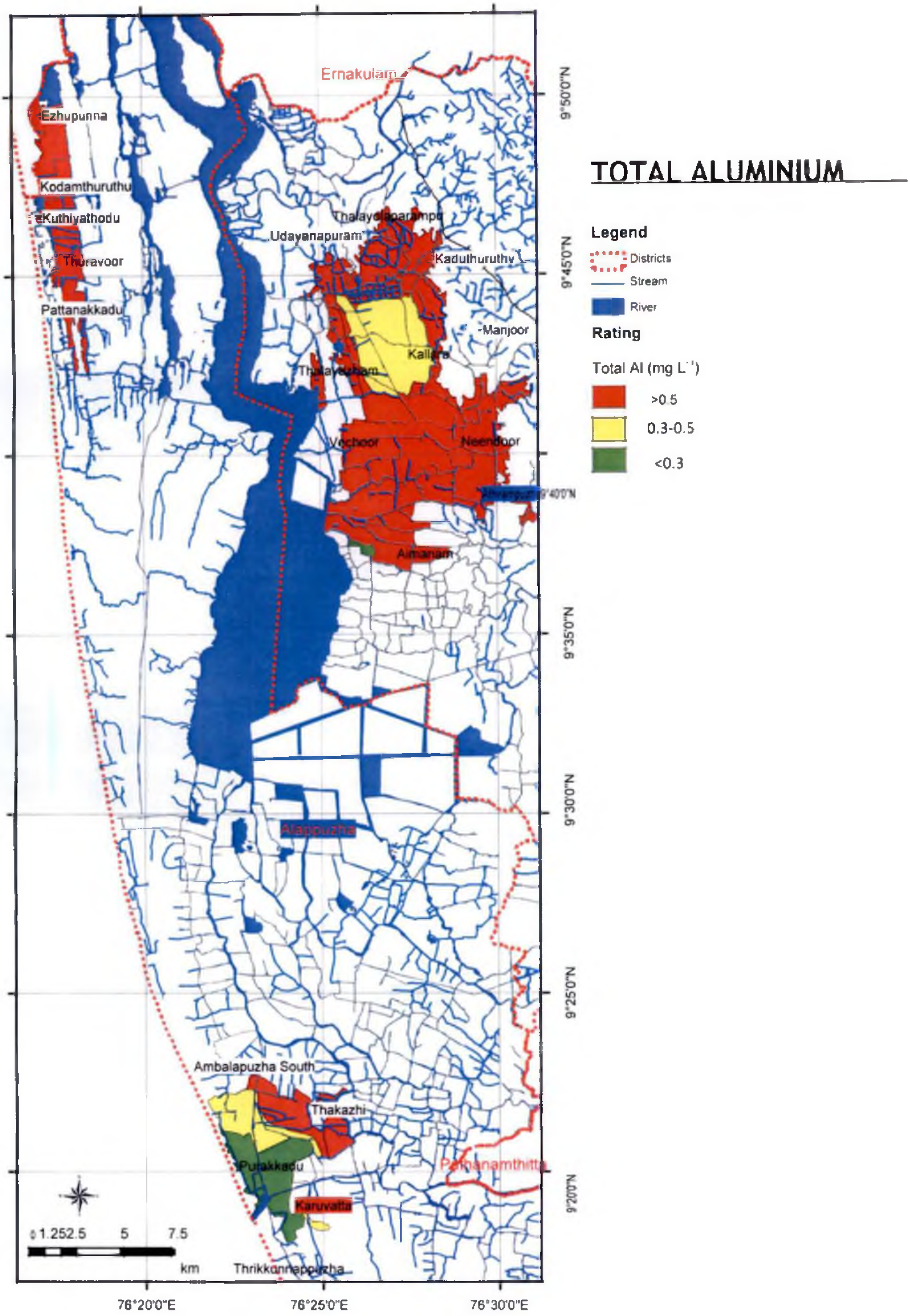

Fig.12 Total aluminium content in water

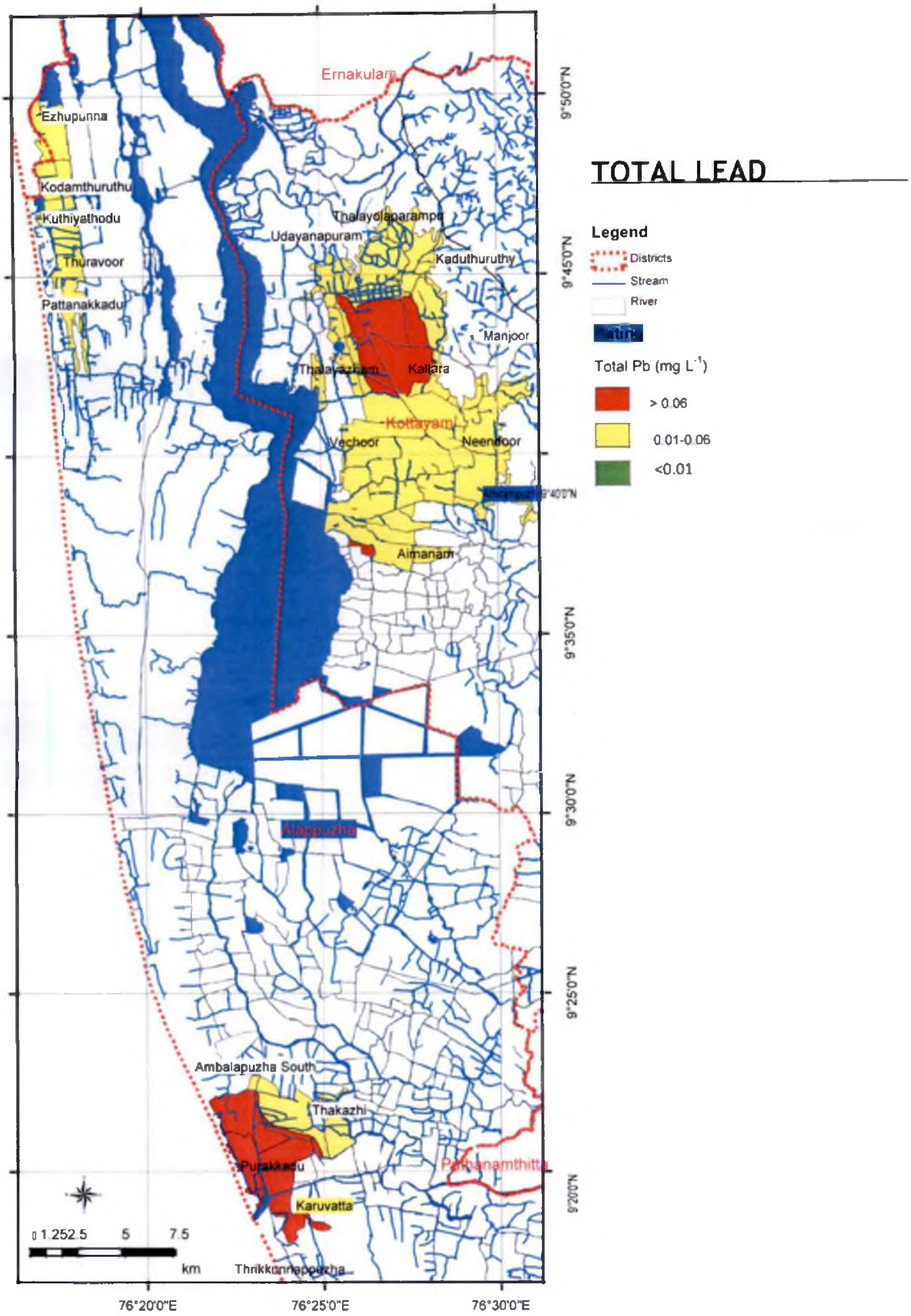

Fig. 13 Total lead content in water

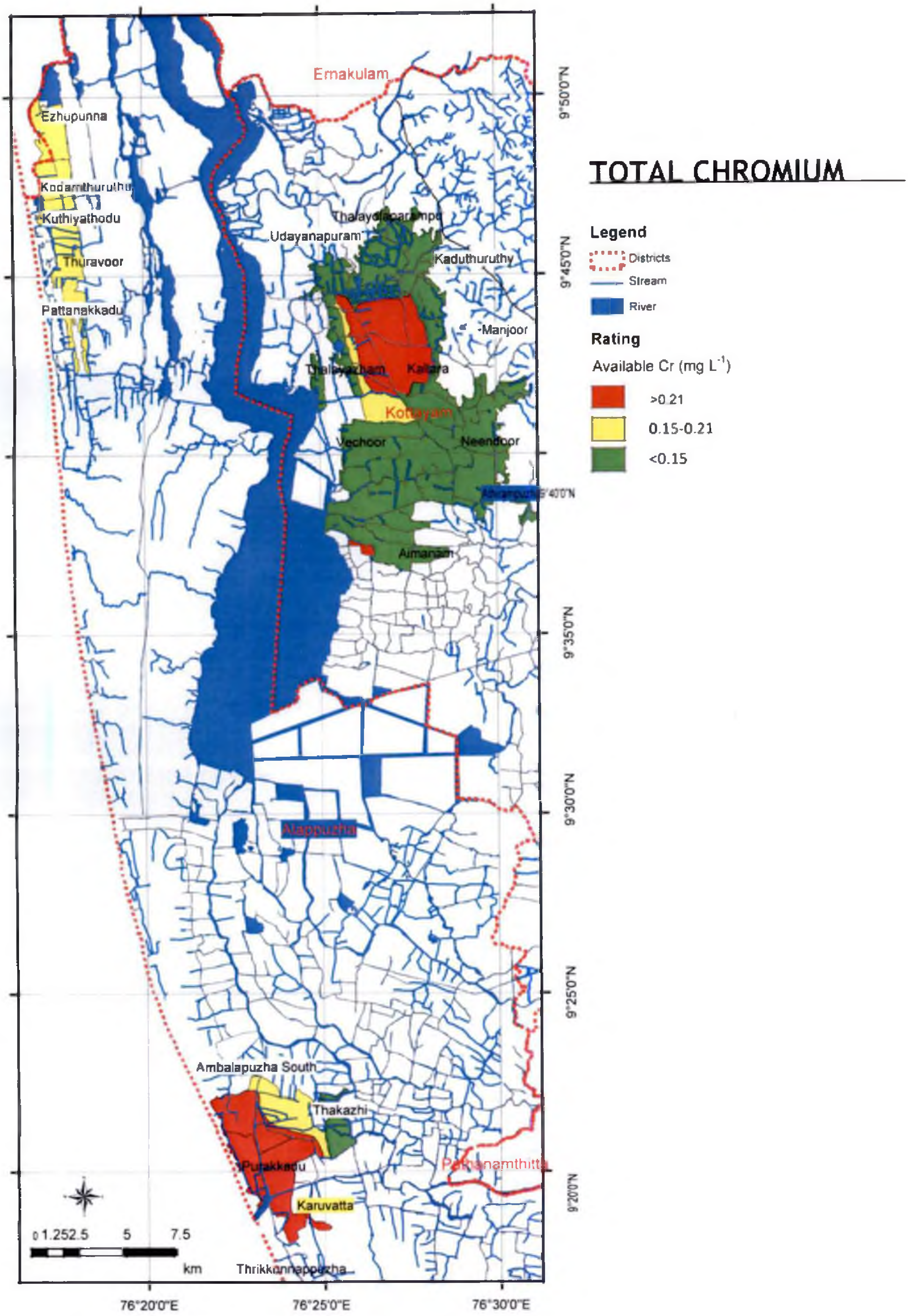

Fig.14 Total chromium content in water

Table 25. Distribution of dominant macrophytes in six series of Kuttanad

Weed species	Relative density (RDe)	Relative frequency (RF)	Summed dominance ratio (SDR)
Ambalapuzha			
Echinochloa crusgalli	31.3	25.64	28.47
Eleocharis dulcis	19.35	20.51	19.93
Leptochloa chinensis	15.2	17.94	16.57
Monochoria vaginalis	14.74	12.82	13.78
Oryza sativa f. spontanea	7.83	10.2	9.01
Rhyncospora corymbosa	5.99	7.92	6.95
Alligator weed	5.53	5.12	5.32
Kallara			
Echinochloa crusgalli	22.82	24.24	23.53
Oryza sativa f. spontanea	22.82	21.21	22.01
Leptochloa chinensis	20.65	18.18	19.41
Eleocharis dulcis	11.95	15.15	13.55
Monochoria vaginalis	15.21	12.12	13.66
Rhyncospora corymbosa	6.52	9.09	7.81
Thakazhi			
Echinochloa crusgalli	29.37	27.58	28.47
Oryza sativa f. spontanea	26.25	20.68	23.46
Monochoria vaginalis	17.5	17.24	17.37
Leptochloa chinensis	12.5	13.79	13.14
Eleocharis dulcis	10	10.34	10.17
Rhyncospora corymbosa	4.37	10.34	7.35
Purakkad			
Echinochloa crusgalli	20.31	22.41	21.36
Oryza sativa f. spontanea	20.31	22.41	21.36
Monochoria vaginalis	15.41	16.22	15.81
Eleocharis dulcis	14.34	9.82	12.08
Rhyncospora corymbosa	7.82	3.22	5.52
Thottapally			
Echinochloa crusgalli	22.31	23.24	22.77
Oryza sativa f. spontanea	22.13	17.25	19.69
Monochoria vaginalis	15.43	20.21	17.82
Eleocharis dulcis	15.21	14.24	14.74
Rhyncospora corymbosa	11.92	10.86	11.39
Thuravur			
Echinochloa crusgalli	27.29	28.19	27.74
Eleocharis dulcis	22.21	23.13	22.67
Monochoria vaginalis	14.23	15.11	14.67
Oryza sativa f. spontanea	9.25	11.31	10.28
Rhyncospora corymbosa	6.82	7.94	7.38

Dominant weed species present in paddy field and waterways were collected for analysis and calculated its relative frequency (RF), relative density (RD) and summed dominance ratio (SDR). The data on population study are presented in table 25.

Among all the six series, summed dominance ratio was the highest for *Echinochloa crusgalli* followed by *Eleocharis dulcis* in Ambalapuzha and Thuravur series and *Oryza sativa* f. *spontanea* in Kallara, Thakazhi, Purakkad and Thottapally series. *Eichhornia crassipes* and *Salvinia molesta* were the dominant weed species along the waterways of all six series (Table 25).

4.4 Nutrient composition in dominant macrophytes of acid sulphate soil series

Dominant macrophytes present in six acid sulphate series were *Echinochloa crusgalli, Monochoria vaginalis, Eleocharis dulcis, Leptochloa chinensis, Alternanthera philoxeroides, Eichhornia crassipes and Salvinia molesta.* The results of nutrient content in dominant macrophytes are presented here.

Table 26. Nutrient content in dominant macrophytes of Ambalapuzha series

Weed species	N	P	K	S	Ca	Mg
	(%)					
Echinochloa crusgalli	1.45	0.29	0.98	0.34	0.38	0.32
Eleocharis dulcis	2.27	0.10	0.94	0.31	0.09	0.12
Leptochloa chinensis	1.12	0.18	1.76	0.34	0.3	0.13
Monochoria vaginalis	3.18	0.43	1.13	0.76	0.8	0.49
Eichhornia crassipes	1.74	0.23	0.42	0.35	0.32	0.20
Salvinia molesta	1.88	0.44	0.53	0.64	0.21	0.20

The data on nutrient content in dominant macrophytes of Ambalapuzha series are given in table 26. Nitrogen content was high in *Monochoria vaginalis.* High content of P was observed in *Salvinia molesta* (0.44 %). *Leptochloa chinensis* showed high content of K (1.76 %). The S, Ca and Mg contents were high in *Monochoria vaginalis* (0.76, 0.80 and 0.49 % respectively). *Eleocharis dulcis* showed low content of P, S, Ca and Mg (0.1, 0.31, 0.09 and 0.12 % respectively). The lowest content of K was observed in *Salvinia molesta* (0.53 %).

Table 27. Micronutrients and heavy metal content in dominant macrophytes of Ambalapuzha series

Weed species	Fe	Mn	Zn	Cu	Pb	Cr	Al
	(mg kg^{-1})						
Echinochloa crusgalli	572.60	94.20	30.20	4.80	3.80	23.20	61.40
Eleocharis dulcis	551.00	24.00	3.00	5.80	1.20	6.00	58.60
Leptochloa chinensis	754.80	61.80	6.00	3.60	3.80	20.40	92.60
Monochoria vaginalis	2318.00	134.80	76.40	8.40	1.80	15.00	308.20
Eichhornia crassipes	4316.00	916.20	98.20	2.10	5.20	23.30	316.20
Salvinia molesta	8400.00	928.00	147.50	9.20	2.10	25.70	1708.00

The data on micronutrients and heavy metal content indominant macrophytes of Ambalapuzha series are given in table 27. Among the weed species, Fe, Mn, Zn, Cu and Al were highest in *Salvinia molesta* (8400, 928, 147.5, 9.20 and 1708 mg kg^{-1} respectively). *Eichhornia crassipes* showed the highest content of Pb (5.20 mg kg^{-1}). Higher Cr content was observed in *Salvinia molesta* (25.70 mg kg^{-1}). *Eleocharis dulcis* showed the lowest content of Fe, Mn, Zn, Cr and Al (551.00, 24.00, 3.00, 6.00 and 58.60 mg kg^{-1} respectively). *Eichhornia crassipes* showed low content of Cu (2.10 mg kg^{-1}).

Table 28. Nutrient content in dominant macrophytes of Kallara series

Weed species	N	P	K	S	Ca	Mg
	(%)					
Echinochloa crusgalli	2.38	0.30	0.91	0.55	0.26	0.33
Oryza sativa f. spontanea	1.99	0.29	1.16	0.34	0.31	0.32
Leptochloa chinensis	1.10	0.18	1.34	0.29	0.19	0.13
Eleocharis dulcis	1.01	0.28	1.08	0.31	0.13	0.14
Eichhornia crassipes	1.70	0.18	0.42	0.38	0.16	0.38
Salvinia molesta	1.82	0.38	0.70	0.67	0.30	0.37

Data pertaining to nutrient content in dominant macrophytes of Kallara series are presented in table 28. *Echinochloa crusgalli* showed high content of nitrogen (2.38 %). *Salvinia molesta* recorded high content of P and S (0.38 and 0.67 % respectively). *Oryza sativa* f. *spontanea* showed high content of Ca (0.31 %) and Mg content was high in *Eichhornia crassipes*. Highest content of K (1.34 %) was noticed in *Leptochloa chinensis*. Both *Eichhornia crassipes* and *Leptochloa chinensis* showed lower amount of P (0.18 %). Low content of Mg and S was noticed in *Leptochloa chinensis* (0.13 and 0.29 % respectively). The content of K was lowest in *Eichhornia crassipes* (0.42 %). *Eleocharis dulcis* showed low content of Ca (0.13 %).

Table 29. Micronutrients and heavy metal content in dominant macrophytes of Kallara series

Weed species	Fe	Mn	Zn	Cu	Pb	Cr	Al
	(mg kg^{-1})						
Echinochloa crusgalli	864.00	27.80	39.60	5.40	2.20	24.00	85.60
Oryza sativa f. spontanea	523.00	83.60	56.00	5.20	3.80	15.10	68.10
Leptochloa chinensis	652.00	65.20	8.90	2.80	4.10	20.60	52.80
Eleocharis dulcis	1566.20	166.00	9.00	4.60	2.00	9.40	177.60
Eichhornia crassipes	2926.00	738.00	124.30	5.40	4.20	20.62	186.20
Salvinia molesta	9632.00	734.00	94.50	8.10	0.89	30.45	2282.00

Data on micronutrients and heavy metal content in dominant macrophytes of Kallara series are given in table 29. *Salvinia molesta* contained highest amount of Fe, Cu, Cr and Al (9632, 8.10, 30.45 and 2282 mg kg^{-1} respectively). The highest content of Mn and Zn was noticed in *Eichhornia crassipes* (738.00 and 124.30 mg kg^{-1} respectively). *Eichhornia crassipes* showed high content of Pb (4.20 mg kg^{-1}). Fe content was lowest in *Oryza sativa* f. *spontanea* (523.00 mg kg^{-1}). *Echinochloa crusgalli* contained low amount of Mn (27.80 mg kg^{-1}). Zn, Cu and Al contents were found to be the lowest in *Leptochloa chinensis* (8.90, 2.80 and 52.80 mg kg^{-1} respectively). Low content of Pb was noticed in *Salvinia molesta* (0.89 mg kg^{-1}). *Eleocharis dulcis* showed low content of Cr (9.40 mg kg^{-1}).

Table 30. Nutrient content in dominant macrophytes of Thakazhi series

Weed species	N	P	K	S	Ca	Mg
	(%)					
Echinochloa crusgalli	1.21	0.29	1.00	0.44	0.32	0.32
Oryza sativa f. *spontanea*	1.89	0.31	1.12	0.32	0.36	0.32
Monochoria vaginalis	2.27	0.53	0.52	0.43	0.32	0.23
Alternanthera philoxeroides	2.94	0.29	7.22	0.37	0.44	0.54
Eichhornia crassipes	1.71	0.16	0.23	0.44	0.23	1.62
Salvinia molesta	1.79	0.32	0.63	0.85	1.18	0.52

Nutrient content indominant macrophytes of Thakazhi series are given in table 30. *Salvinia molesta* showed highest content of Ca and S (1.18 and 0.85 % respectively). Highest P content was noticed in *Monochoria vaginalis* (0.53 %). *Alternanthera philoxeroides* showed highest amount of N and K (2.94 and 7.22 % respectively). The highest content of Mg was noticed in *Eichhornia crassipes* (1.62 %). Nutrients such as P, K and Ca registered the lowest value in *Eichhornia crassipes* (0.16, 0.23 and 0.23 % respectively). *Oryza sativa* f. *spontanea* showed low S content (0.32 %). *Monochoria vaginalis* contained the lowest amount of Mg (0.23%).

Table 31. Micronutrients and heavy metal content in dominant macrophytes of Thakazhi series

Weed species	Fe	Mn	Zn	Cu	Pb	Cr	Al
	(mg kg^{-1})						
Echinochloa crusgalli	718.30	61.00	34.90	5.10	2.30	20.60	73.50
Oryza sativa f. spontanea	633.00	78.40	58.00	4.40	3.00	14.40	65.00
Monochoria vaginalis	2689.00	173.00	30.60	4.40	0.90	8.80	135.80
Alternanthera philoxeroides	1952.00	190.80	6.00	0.60	1.80	20.80	669.40
Eichhornia crassipes	4203.00	928.20	132.60	5.70	4.89	24.38	308.90
Salvinia molesta	9457.00	894.00	126.90	10.20	2.10	41.80	3903.00

Data on micronutrients and heavy metal content in dominant macrophytes of Thakazhi series are given in table 31. Highest content of Fe, Cu, Cr and Al was observed in *Salvinia molesta* (9457, 10.20, 41.80 and 3903 mg kg^{-1} respectively). The content of Mn, Zn and Pb were highest in *Eichhornia crassipes* (928, 132.6 and 4.89 mg kg^{-1} respectively). *Oryza sativa* f. *spontanea* showed lowest content of Fe and Al (633 and 65 mg kg^{-1} respectively). Low Mn content was noticed in *Echinochloa crusgalli* (61 mg kg^{-1}). The low content of Zn and Cu were reported in *Alternanthera philoxeroides* (6.00 and 0.6 mg kg^{-1} respectively). *Monochoria vaginalis* contained the lowest content of Pb and Cr (0.98 and 8.80mg kg^{-1} respectively).

Table 32. Nutrient content in dominant macrophytes of Purakkad series

Weed species	N	P	K	S	Ca	Mg
	(%)					
Echinochloa crusgalli	1.53	0.28	1.10	0.23	0.37	0.57
Oryza sativa f. *spontanea*	1.98	0.30	2.66	0.33	0.30	0.34
Monochoria vaginalis	2.53	0.41	1.11	0.42	0.29	0.37
Eichhornia crassipes	1.73	0.20	0.34	0.45	1.42	1.73
Salvinia molesta	1.85	0.32	0.87	0.69	1.50	0.54

Data regarding nutrient contents in dominant macrophytes of Purakkad series are presented in Table 32. *Monochoria vaginalis* showed highest content of N and P (2.53 and 0.41% respectively). Highest content of K was noticed in *Oryza sativa* f. *spontanea* (2.66 %). The content of S and Ca were highest in *Salvinia molesta* (0.69 and 1.50 % respectively).. *Eichhornia crassipes* showed high content of Mg (1.73 %). The low P and K content were observed in *Eichhorniacrassipes* (0.20 and 0.34 % respectively). S content was the lowest in *Echinochloa crusgalli* (0.23 %). The lowest content of Ca (0.29 %) and Mg (0.34 %) was noticed in *Monochoria vaginalis* and *Oryza sativa* f. *spontanea* respectively.

Table 33. Micronutrients and heavy metal content in dominant macrophytes of Purakkad series

Weed species	Fe	Mn	Zn	Cu	Pb	Cr	Al
	(mg kg^{-1})						
Echinochloa crusgalli	865.20	53.20	23.60	0.40	2.80	17.80	59.60
Oryza sativa f. spontanea	578.00	76.00	57.00	2.10	3.90	14.75	66.55
Monochoria vaginalis	4842.00	164.20	67.80	4.60	2.20	17.20	501.80
Eichhornia crassipes	3481.00	729.00	192.20	1.98	4.82	24.20	196.80
Salvinia molesta	8864.00	540.00	142.00	7.20	1.40	45.20	2856.00

Micronutrients and heavy metal contents in dominant macrophytes of Purakkad series are given in table 33. High content of Fe, Cr and Al was noticed in *Salvinia molesta* (8864, 45.20 and 2856 mg kg^{-1} respectively). The content of Mn, Zn and Pb were high in *Eichhornia crassipes* (729, 192.20 and 4.82 mg kg^{-1} respectively). The highest content of Cu was noticed in *Monochoria vaginalis* (4.60 mg kg^{-1}). The content of Fe and Cr were the lowest in *Oryza sativa* f. *spontanea* (578 and 14.75 mg kg^{-1} respectively). *Monochoria vaginalis* showed low content of Mn (64.20 mg kg^{-1}). The content of Mn, Zn, Cu and Al were the lowest in *Echinochloa crusgalli* (53.20, 23.60,0.40 and 59.60 mg kg^{-1} respectively). *Salvinia molesta* showed low content of Pb (1.40 mg kg^{-1})

Table 34. Nutrient content in dominant macrophytes of Thottapally series

Weed species	N	P	K	S	Ca	Mg
	(%)					
Echinochloa crusgalli	1.43	0.41	0.88	0.48	0.29	0.37
Oryza sativa f. *spontanea*	1.92	0.33	2.10	0.29	0.35	0.32
Monochoria vaginalis	2.26	0.47	7.61	0.43	0.30	0.30
Eichhornia crassipes	1.74	0.21	0.44	0.29	1.44	1.62
Salvinia molesta	1.86	0.33	0.39	1.01	0.85	0.49

Nutrient contents in dominant macrophytes of Thottapally series are shown in table 34. The highest content of N, P and K was noticed in *Monochoria vaginalis* (2.26, 0.47 and 7.61 %). *Salvinia molesta* showed high content of S (1.01 %). Ca and Mg concentrations were highest in *Eichhornia crassipes* (1.44 and 1.62 % respectively). The content of P recorded the lowest value in *Eichhornia crassipes* (0.21 %), K was the lowest in *Salvinia molesta* (0.39 %). Both *Oryza sativa* f. *spontanea* and *Eichhornia crassipes* showed lowest S content (0.29 %). Among all the macrophytes, the content of Ca was lowest in *Echinochloa crusgalli* (0.29 %) and *Monochoria vaginalis* showed low content of Mg (0.30 %).

Table 35. Micronutrients and heavy metal content in dominant macrophytes of Thottapally series

Weed species	Fe	Mn	Zn	Cu	Pb	Cr	Al
	(mg kg^{-1})						
Echinochloa crusgalli	842.00	53.60	67.80	4.60	2.20	16.80	301.60
Oryza sativa f. spontanea	871.00	89.98	68.90	1.20	1.10	13.25	72.80
Monochoria vaginalis	4265.50	118.60	49.20	4.50	2.05	13.00	218.80
Eichhornia crassipes	3016.00	746.20	157.00	6.60	3.40	21.20	293.20
Salvinia molesta	9845.00	839.40	109.60	7.80	2.00	38.40	2950.00

Data on micronutrients and heavy metal content in dominant macrophytes of Thottapally series are given in table 35. Highest content of Fe, Mn, Cu, Cr and Al were noticed in *Salvinia molesta* (9845, 839.40, 7.80, 38.40 and 2950 mg kg^{-1} respectively).The content of Zn and Pb were the highest in *Eichhornia crassipes* (157 and 3.40 mg kg^{-1} respectively). The content of Fe, Cu, Pb and Al was the lowest in *Oryza sativa* f. *spontanea* (871, 1.20, 1.10 and 72.80 mg kg^{-1} respectively). *Echinochloa crusgalli* showed the lowest content of Mn (53.60 mg kg^{-1}). The Zn and Cr content were lowest in *Monochoria vaginalis* (49.20 and 13 mg kg^{-1} respectively).

Table 36. Nutrient content in dominant macrophytes of Thuravur series

Weed species	N	P	K	S	Ca	Mg
	(%)					
Echinochloa crusgalli	1.88	0.19	1.21	0.32	0.27	0.30
Eleocharis dulcis	1.89	0.19	0.31	0.35	0.11	0.13
Monochoria vaginalis	2.29	0.44	0.49	0.41	0.33	0.29
Eichhornia crassipes	1.61	0.27	0.35	0.31	0.24	1.73
Salvinia molesta	1.76	0.44	0.72	0.89	0.43	0.52

Nutrient contents of dominant macrophytes of Thuravur series are given in table 36. *Monochoria vaginalis* showed highest content of N and P (2.29 and 0.44 % respectively). *Echinochloacrusgalli* showed higher K content (1.21 %). Contents of S and Ca were highest in *Salvinia molesta* (0.89 and 0.43 respectively). *Eichhornia crassipes* showed highest content of Mg (1.73 %). Both *Echinochloa crusgalli* and *Eleocharis dulcis* showed the lowest content of P (0.19 %). The K, Ca and Mg contents were the lowest in *Eleocharis dulcis* (0.31, 0.11 and 0.13 % respectively). *Eichhornia crassipes* showed lowest S content (0.31 %).

Table 37. Micronutrients and heavy metal content in dominant macrophytes of Thuravur series

Weed species	Fe	Mn	Zn	Cu	Pb	Cr	Al
	(mg kg^{-1})						
Echinochloa crusgalli	689.00	58.90	29.92	2.20	4.90	13.21	66.90
Eleocharis dulcis	1058.60	95.00	6.00	5.20	1.60	7.70	118.10
Monochoria vaginalis	3875.00	167.00	26.50	2.60	1.60	9.40	143.20
Eichhornia crassipes	4289.10	892.80	98.60	6.90	6.80	26.21	526.20
Salvinia molesta	8110.00	789.10	117.20	2.40	1.90	35.20	2295.00

Fe, Zn, Cr and Al contents were highest in *Salvinia molesta* (8110, 117.2, 35.2 and 2295mg kg^{-1} respectively). *Eichhornia crassipes* showed highest content of Mn, Cu and Pb (892.8, 6.90 and 6.80 mg kg^{-1} respectively). The lowest content of Fe, Mn, Cu and Al was noticed in *Echinochloa crusgalli* (689, 58.9, 2.20 and 66.90 mg kg^{-1} respectively). *Eleocharis dulcis* showed lowest content of Zn and Cr (6 and 7.70 mg kg^{-1} respectively). The content of Pb was lowest in both *Monochoria vaginalis* (0.60 mg kg^{-1}) and *Eleocharis dulcis* (0.60 mg kg^{-1}) (Table 37).

4.5 Phytoextraction capability of mangrove species

Three mangrove species (*Avicennia officinalis, Bruguiera gymnorrhiza, Rhizophora mucronata)* were collected from Kuttanad region and different parts of mangrove plants were analysed for nutrients and heavy metal content. The data generated on chemical analysis of mangrove plants are presented in table 38.

Table 38. Nutrient content in different parts of mangrove species

Species	Plant parts	N	P	K	S	Ca	Mg
		(%)					
Avicennia officinalis	Root	1.76	0.06	0.44	0.15	2.09	1.27
	Shoot	1.51	0.06	0.35	0.13	3.15	1.28
	Leaf	2.27	0.14	0.45	0.33	4.04	2.77
Bruguiera gymnorrhiza	Root	1.00	0.09	0.47	0.32	0.78	1.10
	Shoot	0.76	0.06	0.49	0.33	3.28	1.92
	Leaf	1.51	0.10	0.48	0.19	5.27	3.70
Rhizophora mucronata	Root	1.00	0.13	0.41	0.08	0.69	0.96
	Shoot	1.76	0.09	0.30	0.06	4.06	1.39
	Leaf	2.27	0.08	0.50	0.70	3.85	5.13

4.5.1 Nutrient contents in root, shoot and leaves of different mangrove species

4.5.1.1 Nutrient content in root of mangroves

The data on nutrient contents in mangrove plants is shown in Table 38. It was found that among the three mangrove species, P content (0.13 %) was more in root of *Rhizophora mucronata.* The K (0.47 %) and S (0.32 %) were accumulated more in root of *Bruguiera gymnorrhiza.* The roots of *Avicennia officinalis* showed highest content of N, Ca and Mg (1.76, 2.09 and 1.27 per cent respectively) than the other two species.

4.5.1.2 Nutrient content in shoot of mangroves

The concentration of N and P was more in shoots of *Rhizophora mucronata* (1.76 and 0.09 % respectively). *Bruguiera gymnorrhiza* showed highest content of K and S (0.49 and 0.33 per cent respectively). Ca content was more in the shoots of *Rhizophora mucronata* (4.06 %). Shoots of *Bruguiera gymnorrhiza* showed highest content of Mg (1.92%).

4.5.1.3 Nutrient content in leaves of mangroves

Among the three mangrove species, N content (2.27 %) was more in leaves of *Avicennia officinalis* and *Rhizophora mucronata.* P content was more in the leaves of *Avicennia officinalis* (0.14 %). Concentration of K and S were more in leaves of *Rhizophora mucronata* (0.50 and 0.70 % respectively). Ca content in the leaves of *Bruguiera gymnorrhiza* (5.27 %) was higher compared to other species. The leaves of *Rhizophora mucronata* showed highest amount of Mg (5.13 %).

Table 39. Micronutrient content in different parts of mangrove species

Species	Plant parts	Fe	Mn	Zn	Cu
		(mg kg^{-1})			
Avicennia officinalis	Root	336.10	111.70	BDL	1.61
	Shoot	137.30	86.60	BDL	1.60
	Leaf	209.30	270.60	BDL	3.35
Bruguiera gymnorrhiza	Root	470.50	18.60	BDL	3.40
	Shoot	132.50	34.70	BDL	5.75
	Leaf	132.70	101.50	BDL	2.70
Rhizophora mucronata	Root	197.35	13.45	BDL	1.15
	Shoot	192.30	63.50	BDL	3.50
	Leaf	133.20	57.70	BDL	1.30

BDL- Below detectable level

4.5.2 Micronutrient content in the roots, shoots and leaves of different mangrove species

4.5.2.1 Micronutrient content in root of mangroves

Data on micronutrient content of different parts of three mangrove species are presented in table 39. It is clear from the data that among the three mangrove species, Fe and Cu was more accumulated in roots of *Bruguiera gymnorrhiza*

(470.50 and 3.40 mg kg^{-1} respectively), and more Mn was accumulated in roots of *Avicennia officinalis* (111.70 mg kg^{-1}).

4.5.2.2 Micronutrient content in shoot of mangroves

Shoots of *Rhizophora mucronata* showed highest content of Fe (192.30 mg kg^{-1}). Content of Mn was more in shoots of *Avicennia officinalis* (86.6 mg kg^{-1}). More Cu (5.75 mg kg^{-1}) was accumulated in the shoots of *Bruguiera gymnorrhiza.*

4.5.2.3 Micronutrient content in leaves of mangroves

Micronutrient contents in the leaves of different mangroves showed that accumulation of Fe, Mn and Cu were highest in the leaves of *Avicennia officinalis* (209.30, 270.60 and 3.35 mg kg^{-1} respectively). Zn content was below detectable level in all the parts of different mangrove species.

Table 40. Heavy metal content in different parts of mangrove species

Species	**Plant parts**	**Pb**	**Cd**	**Cr**	**Hg**	**Al**
		(mg kg^{-1})				
Avicennia officinalis	Root	1.41	BDL	9.00	BDL	34.50
	Shoot	1.30	BDL	7.10	BDL	21.30
	Leaf	0.98	BDL	6.50	BDL	17.30
Bruguiera gymnorrhiza	Root	1.10	BDL	9.30	BDL	45.00
	Shoot	1.00	BDL	8.95	BDL	41.50
	Leaf	0.59	BDL	8.10	BDL	11.90
Rhizophora mucronata	Root	1.15	BDL	7.55	BDL	25.85
	Shoot	1.00	BDL	6.50	BDL	22.50
	Leaf	1.00	BDL	5.50	BDL	21.10

BDL- Below detectable level

4.5.3 Heavy metal content in root, shoot and leaves of different mangrove species

4.5.3.1 Heavy metal content in root of mangroves

Table 40 showed heavy metal accumulation in root, shoot and leaves of different mangroves. Among three mangrove species, Pb accumulation was more in the roots of *Avicennia officinalis* (1.41 mg kg^{-1}). Accumulation of Cr and Al was highest in the roots of *Bruguiera gymnorrhiza* (9.30 and 45.00 mg kg^{-1} respectively).

4.5.3.2 Heavy metal content in shoot of magroves

Among the three mangrove species, shoots of *Avicennia officinalis* accumulated more amount of Pb (1.30 mg kg^{-1}). The heavy metals like Cr and Al were more accumulated in the shoots of *Bruguiera gymnorrhiza* (8.95 and 41.50 mg kg^{-1} respectively).

4.5.3.3 Heavy metal content in leaves of mangroves

Rhizophora mucronata accumulated more amounts of Pb and Al in leaf portions (1.00 and 21.10 mg kg^{-1} respectively). Highest Cr was accumulated in the leaves of *Bruguiera gymnorrhiza* (8.10 mg kg^{-1}).

The heavy metals like Cd and Hg were below detectable level in all the mangrove species under study.

Discussion

5. DISCUSSION

Acid sulphate soils have low pH, high sulphur, iron and aluminium concentrations. Oxidation of metallic sulphide compound present in these soils enhances the chances of heavy metal availability. Soil contamination due to heavy metal poses threat to vegetation and quality of ground water. The discussion pertaining to the study entitled "Accumulation of heavy metals in Typic of Kuttanad ecosystem" is given in this chapter.

5.1 Characterisation of acid sulphate soil

5.1.1 Electrochemical properties

Acid sulphate soils are extremely acidic with a pH ranging from 2.9 to 3.9 (Fig.15). The extreme acidity of this soil is due to the formation of sulphuric acid. Oxidation of reduced sulphur compounds in pyritic mud releases sulphuric acid which results in a dramatic drop of pH in acid sulphate soils. Another reason is due to production of organic acids during the anaerobic decomposition of organic matter or due to release of H^+ ions during hydrolysis of Fe and Al hydroxides. In acid sulphate soils, acidity was contributed by presence of pyrite (Ponnamperuma *et al.*, 1973; Iyer, 1989). The results were in agreement with the findings of Beena and Thampatti (2013) who reported that the pH of acid sulphate soils of Kuttanad ranged from 3 to 5.2.

Generally soils of Kuttanad show acid saline nature. This is mainly due to the intrusion of sea water. From the present study, it was observed that the EC of the selected six soil series ranged from 0.42 to 1.02 dS m^{-1} (Fig. 16). The observed value was low compared to earlier reports. This may be due to the construction of Thannermukkom bund, which prevents the intrusion of saline water from sea. Similar results were reported by Thampatti and Jose (1999).

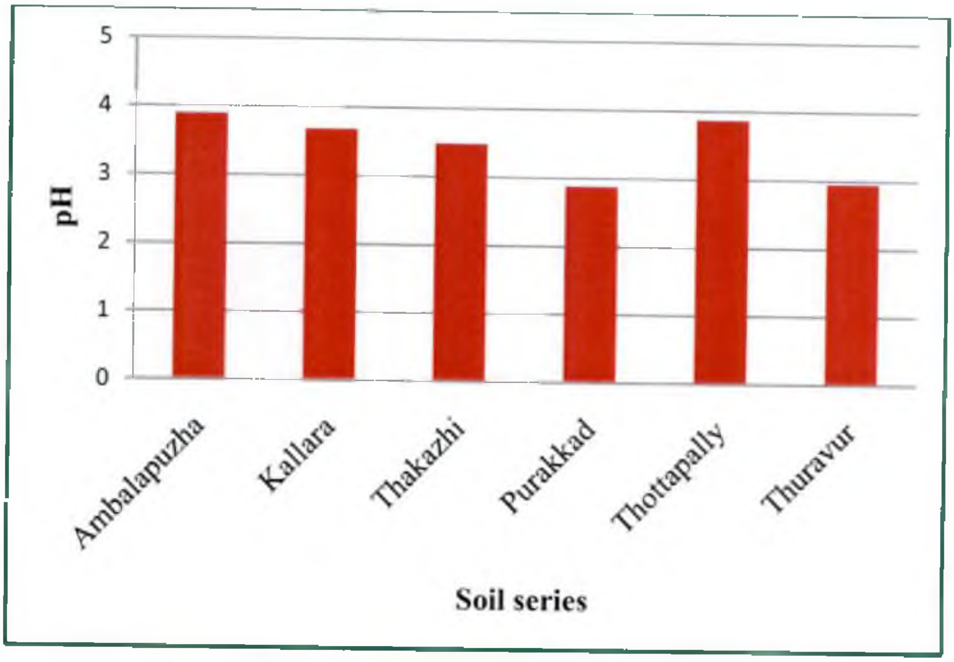

Fig.15 pH of different soil series of Kuttanad

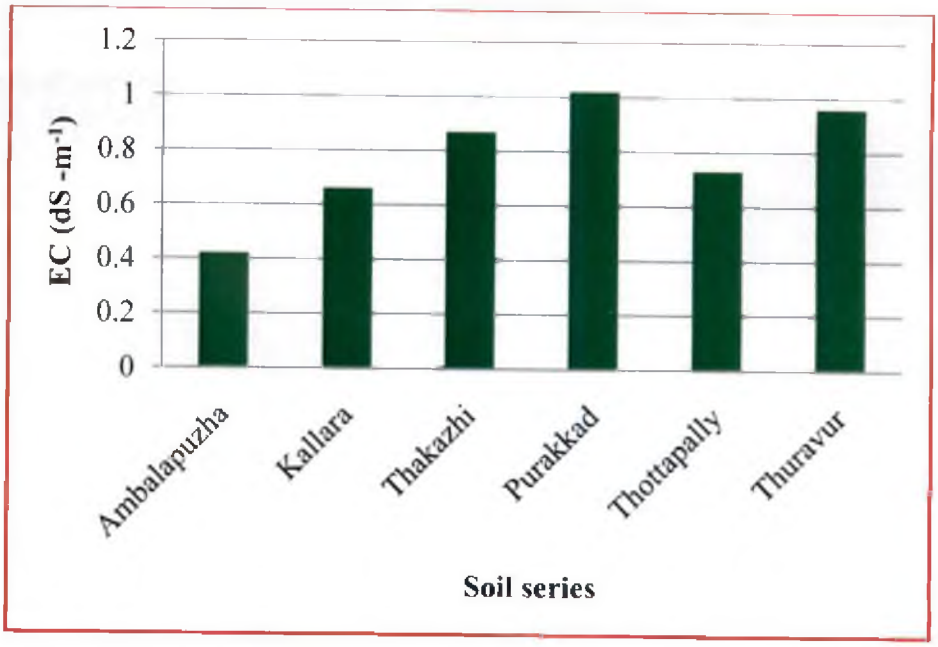

Fig.16 Electrical conductivity of different soil series of Kuttanad

They found that EC values of Kuttanad soils showed a considerable reduction in post barrage period compared to pre barrage period. From table 7 it is clear that there are variations in pH and EC among the different sites of study. An inverse relationship was existed between these two parameters. For example, the Ambalapuzha soil which recorded the pH of 3.9 and EC 0.42 dS m^{-1} and Purakkad soil with the pH 2.9 and EC 1.02 dS m^{-1}. This may be due to the proximity of Purakkad area to sea when compared to Ambalapuzha series. So the link between sea water intrusion and the electrochemical properties of the soil became clear.

5.1.2 Chemical properties

5.1.2.1 Organic carbon

Generally Kuttanad soils are rich in organic matter due to the presence of decomposed, partially decomposed and undecomposed organic matter. Among different acid sulphate soil series, Kallara, Purakkad and Thuravur series recorded high organic carbon content (Beena, 2005). Organic carbon content in the study area ranged from 1.73 to 6.2 per cent. Among these six soil series; Kallara series recorded the highest value (6.2 %) (Fig. 17). This may be due to the richness of organic matter debris in this area. Both clay and silt content reported to be high for Kallara series and this might have contributed to the organic matter content in the soil.

5.1.2.2 Available nitrogen

Content of available nitrogen was low to medium range in all series. Among the selected six soil series, Kallara series recorded significantly highest value of available nitrogen (310.01 kg ha^{-1}) (Fig. 18). This is on line with the organic matter status of this series as discussed in section 5.1.2.1. During summer months easily decomposable compounds were released due to rapid decomposition of organic matter or there might be rapid mineralization, which accounts for its high amount of available nitrogen.

Thampatti (1999) also reported that available N content of Kuttanad soils was 284 kg ha^{-1} during rainy season and 324 kg ha^{-1} during summer months. As the organic carbon content is less for Ambalapuzha soil (1.73%), the available nitrogen content is also reported to be the lowest (61.15 kg ha^{-1}).

5.1.2.3 Available phosphorus

Generally Kuttanad soils are deficient in P status due to the high P fixation capacity of these soils. Soil samples collected from six series of acid sulphate soils of Kuttanad showed P content ranging from 9.25 to 13.67 kg ha^{-1} (Fig. 19). Soil samples from different series were deficient in available P. This may be due to the presence of kaolinite clays along with oxides and hydroxides of Fe and Al in these soils which lead to high P fixation. Soil samples from Purakkad series showed the highest value of available P (13.67 kg ha^{-1}) compared to other series. Decomposition of organic matter and solubilisation of Fe compounds occuring during summer might have increased the content of available P. Beena (2005) also opined that due to P fixation, acid sulphate soils were deficient in P.

5.1.2.4 Available potassium

Potassium content of the soil samples from different acid sulphate soil series was in medium to high range and the values ranged from 116.99 to 388.36 kg ha^{-1}. The highest value was reported in Thuravur series (Fig.18) where the textural class was reported as clay. Similar results were reported by Beena (2005). The lowest potassium content was registered for Thakazhi series where almost all the available nutrients were comparatively less which may be due to crop removal. Thampatti and Jose (1999) reported that as the soil depth increased the content of K also increased.

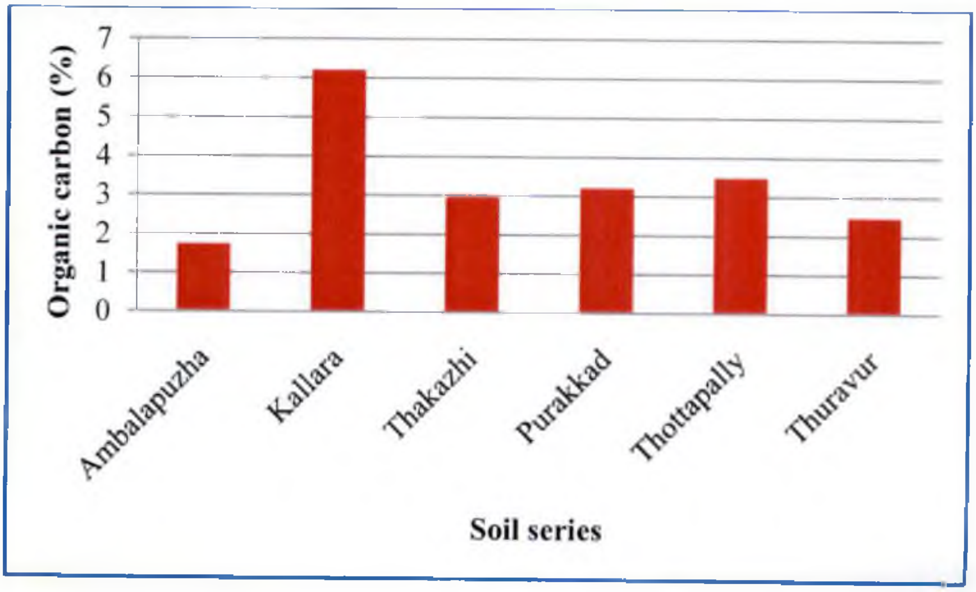

Fig.17 Organic carbon content of different soil series of Kuttanad

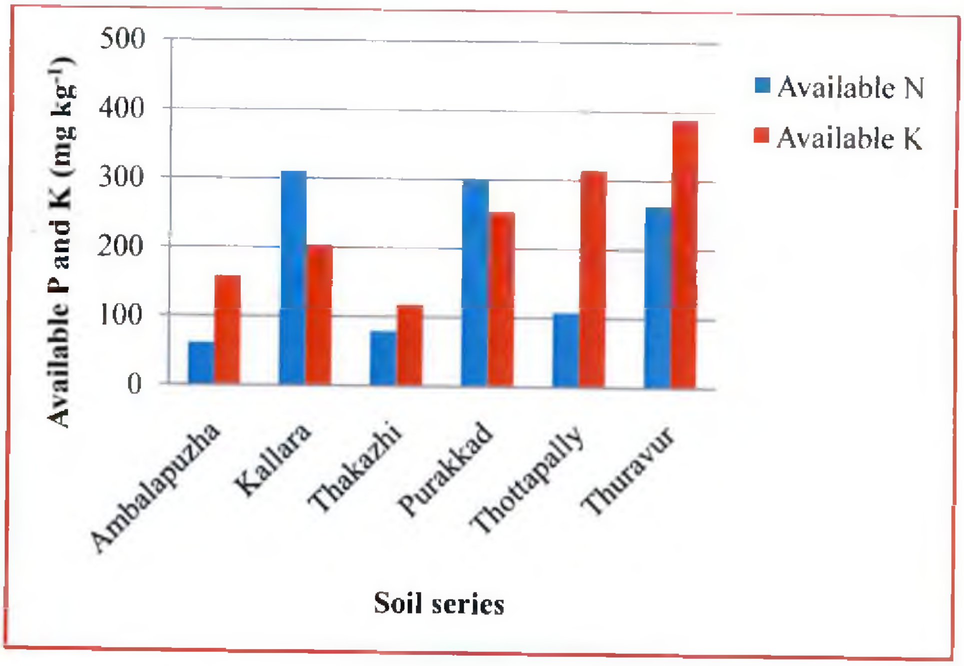

Fig.18 Available N and K content of different soil series of Kuttanad

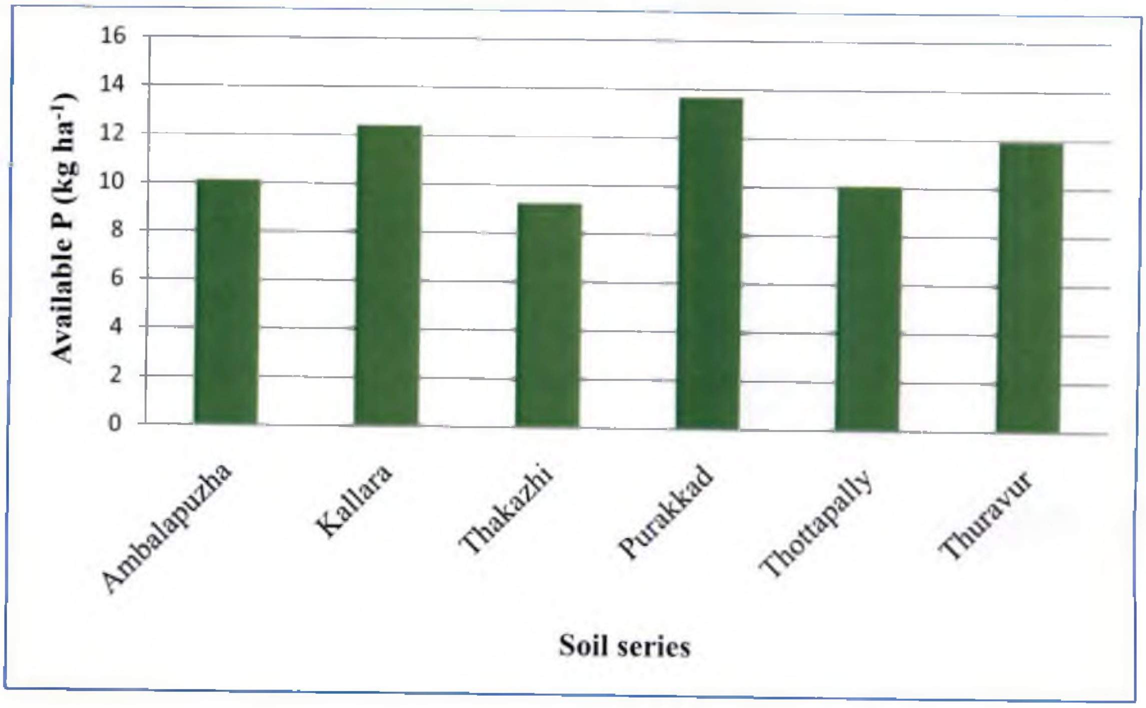

Fig.19 Available P content of different soil series of Kuttanad

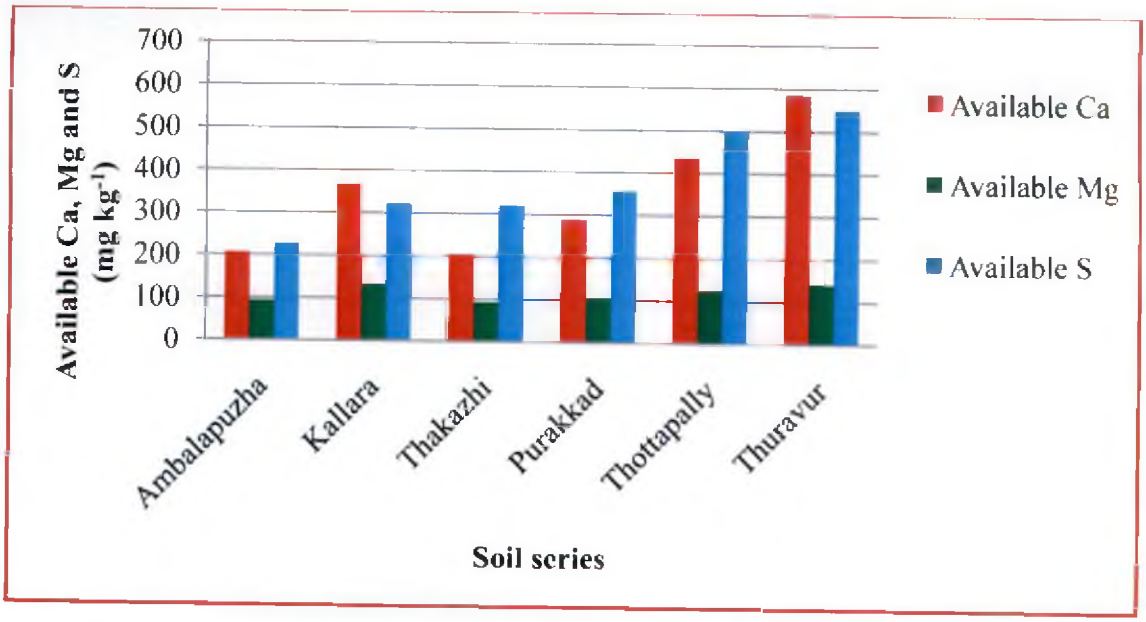

Fig.20 Available Ca, Mg and S content of different soil series of Kuttanad

5.1.2.5 Available calcium, magnesium and sulphur

Soil samples from Thuravur series showed highest calcium and magnesium contents compared to other soil series. Calcium and magnesium contents in the samples from Thuravur series were 584.05 and 141.06 mg kg^{-1} respectively (Fig. 20). The high calcium content in Thuravur series may be due to intrusion of saline water in this area. Another reason is the clay content of the soil series which is comparatively the highest. Available Ca content of surface soils of these series ranged from 514 to 1456 mg kg^{-1} (Beena, 2005). In Typic Sulfaquents of Kuttanad, Ca was the dominant cation in exchange complex (Thampatti, 1997).

High amount of sulphur was noticed in acid sulphate soil due to the presence of sulphur containing minerals. Acid sulphate soils contain iron sulfide minerals (commonly pyrite), if this soils are drained they come into contact with oxygen. The pyrite in the soil reacts with the oxygen and breaks down, this process turns pyrite into suphuric acid. In the present study, available sulphur content varied from 228.95 to 550.48 mg kg^{-1}. Highest available sulphur content was noticed in samples of Thuravur series (Fig. 20). Surface layers of acid sulphate soils of Kuttand showed sulphur content in the range of 80 to 5155 mg kg^{-1} (Beena, 2005).

5.1.3 Influence of soil properties on heavy metal availability

Accumulation of pollutants in Kuttanad soils was reported due to construction of Thannermukkom barrage across the Vembanad lake. Seasonal flooding and dewatering influence the geochemistry of Kuttanad soil. Heavy metals are natural components of soil formed mainly by weathering of rocks or sometimes from volcanic activity (Forstner and Prosi, 1978; Zollar, 1984 and Biney *et al.,* 1991). More toxic forms of heavy metals are available for further transport through food chain and cause great threat to human beings and animals (Wong and Li, 2002). Sorptions of heavy metals are greatly influenced by soil pH as it directly controls the solubilities of metal hydroxides, metal carbonates and phosphates (Appel and Ma, 2002). When the soil pH is lowered, more metal can be found in the solution and metal mobility can be increased due to increased proton concentration (Sherene, 2010). Plants take up available form of heavy metals. So heavy metal concentration in soil solution phase is of major importance. Solubility of heavy metals in soil is mainly controlled by pH and organic carbon. The pH had a major role in solubility and retention of metals in flooded soil and sediments and their availability to plants (Reddy and Patric, 1977).

High content of organic matter generally increased the availability of micronutrients in acid soils (Rulkowska *et al.,* 2014; Li *et al.,* 2007). Acid sulphate soils have high content of iron. Available iron content ranged from 1452.82 to 3039.48 mg kg^{-1}. Thuravur series reported highest available Fe (Fig 21). High content of iron in these series may be due to low soil pH and submerged condition. Under submerged condition, free CO_2 in water can dissolve Fe and it gets solubilised and thereby increases its availability. Iron- bearing minerals such as pyrites and jarosites cause increase in iron content. A significant positive correlation was observed between Fe and soil organic carbon. Iron content increased with increase in soil organic carbon. High amount of organic carbon in soil led to production of more amount of complexing agent which enhanced better extractability of Fe. Similar results were reported by Katyal and Sharma (1991).

A wide fluctuation in total Fe and Mn contents is mainly due to nature of parent material, climatic condition and anthropogenic activities (Behera and Shukla, 2013). The soils contained available Mn in the range of 6.25 to 15.58 mg kg^{-1}. In case of available Mn in soil, toxicity was not reported. Continuous submergence has maintained Mn in soluble form due to soil reduction. Like Fe, availability of Mn increased during submergence, but content of Mn in soil was less compared to iron. Iron and Mn availability to plant was based on soil properties and plant type (Frageria *et al.*, 2002).

Among the soil properties, pH and soil organic carbon were important to improve availability of Fe and Mn. For each unit increase in soil pH from 4 to 9, solubility of Fe showed a 1000 fold decrease and 100 fold decrease was observed for Mn, Zn and Cu (Lindsay, 1979). At pH below 5, almost all the reducible Mn was converted to water soluble and exchangeable forms (Gotoh and Patrick, 1972). In the present study, among the six acid sulphate soil series of Kuttanad, Kallara series showed highest available Mn (Fig. 22). This may be due to high organic carbon content in these series (6.20%). Organic matter enhanced Mn availability to crop. Availability of Mn increased with increasing clay content of the soil and it increased markedly after waterlogging for one month (Mitra and Mandel, 1983). Similar findings were reported by Mokma *et al.* (1979). In Kallara series, texture was clay loam texture, may be this is the reason for high available Mn in this series. Available Zn content ranged from 3.85 to 13.57 mg kg^{-1} (Fig. 22).

Available Cu was deficient in 90 per cent of *kayal*, *kari* and *karappadam* soils (Aiyer *et al.*, 1975). In the present study, available Cu content seemed to be ranging from 0.24 to 2.62 mg kg^{-1}. Soil samples collected from Thuravur series showed low amount of available Cu (Fig. 22). The available lead content ranged from 0.22 to 1.03 mg kg^{-1}. The highest lead availability was reported in Thakazhi series. Available mercury content of soil samples from all the six series were below detectable level. Aluminium content was very high in acid sulphate soil. The soil pH below 4.5 enhanced the extractable and water soluble Al content of these soils (Raju, 1988, KAU, 1994). High content of aluminium in these soils may be due to hydrolysis of clay minerals under low pH condition which releases soluble Al into the soil solution. Significantly higher value of Al was observed in Kallara series (Fig. 23). A significant positive correlation was noticed between Al and organic carbon. This may be due to the production of organic acid due to the decomposition of organic matter which lowers the pH to less than 4 and hence solubilises Al in soil. Organic matter has a major role in release of heavy metals. Sherene (2010) reported that organic matter addition led to release of metals from solids to the soil solution because of the complexation of metals by soluble organic matter.

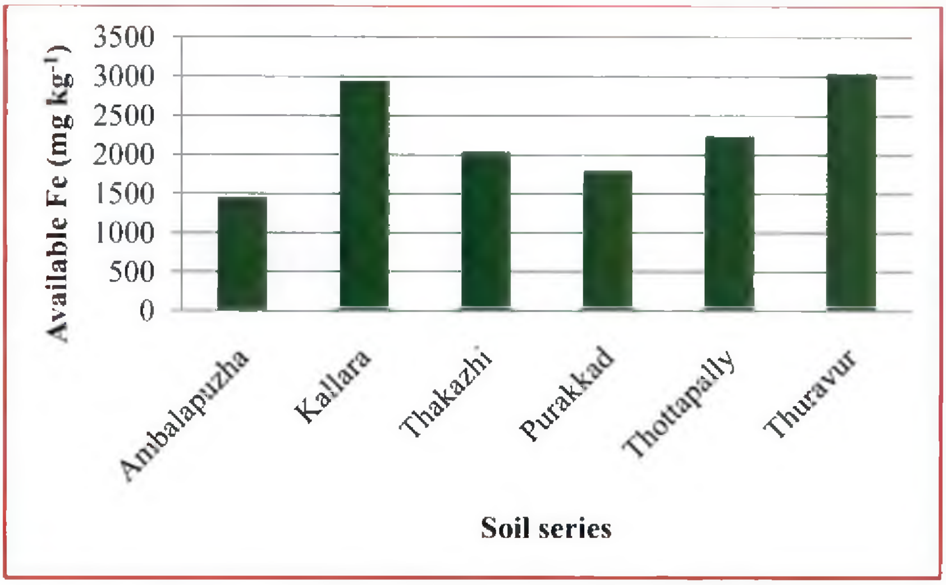

Fig.21 Available Fe content of different soil series of Kuttanad

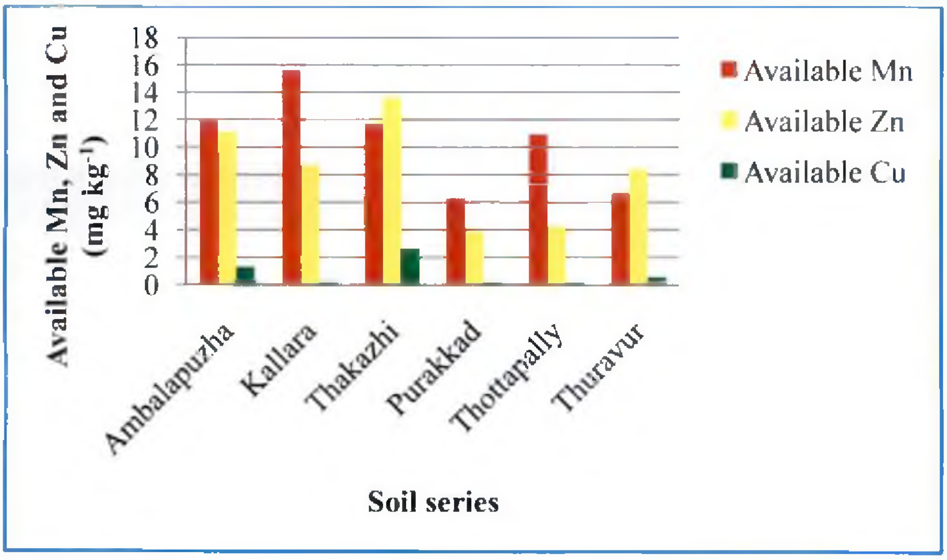

Fig.22 Available Mn, Zn and Cu content of different soil series of Kuttanad

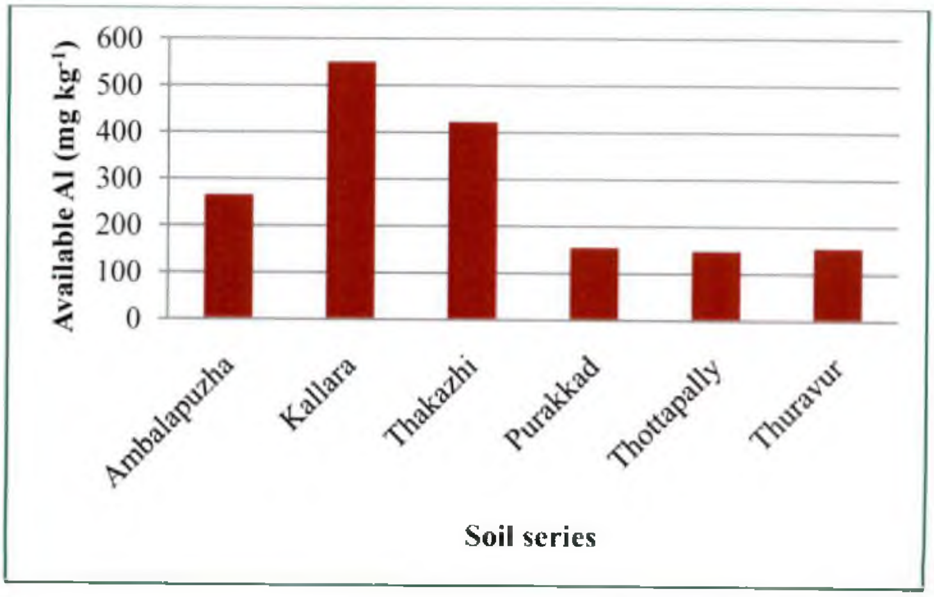

Fig.23 Available Al content of different soil series of Kuttanad

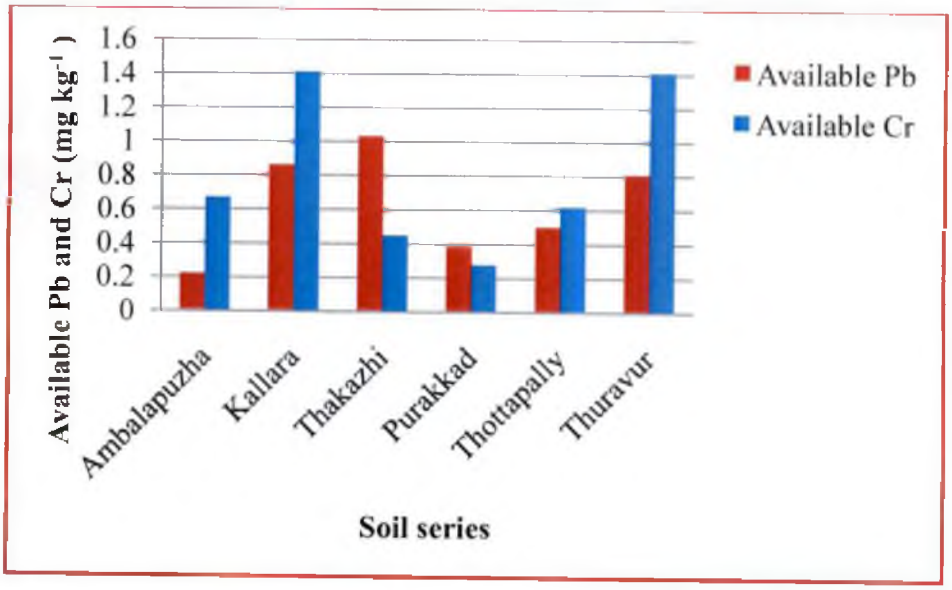

Fig.24 Available Pb and Cr content of different soil series of Kuttanad

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Available Pb content ranged from 0.22 to 1.03 mg kg^{-1} in the present investigation. Significantly higher value was observed in soil samples collected from Thakazhi series (Fig. 24). Phosphatic fertilizers like single super phosphate derived from phosphatic rock are the main sources of Pb (Parameswari *et al.*, 2014). They also found that total and available heavy metal contents were found in top surface layer. Available Cr content ranged from 0.28 to 1.41 mg kg^{-1}. Kallara and Thakazhi series showed significantly higher value of Cr (Fig. 24). Generally major source of chromium pollution in the environment is from wastewater and sludge from dyeing and tanning industries (Sherene, 2010).

5.2 Physico- chemical characteristics of sediment

Sediments act as a store house of nutrients in aquatic environment. It not only acts as a sink but also act as a source of contaminant in aquatic system. So study of characteristics of sediments and its level of contamination is a useful tool for assessment of environmental pollution. Sediment samples were collected from nearby water bodies of acid sulphate soil series such as Ambalapuzha, Kallara, Thakazhi, Thottapally, Purakkad and Thuravur.

5.2.1 Electrochemical properties

Electrochemical properties such as pH and EC exhibited variation among different series. The major factors determining pH of soil includes the concentration of reduced iron, manganese, hydroxides, carbonates, carbonic acid, and humic acid (Patric and Mikkelson, 1971). Low pH was reported in Thottapally series (Fig. 25). The acidic pH of sediments may be due to dumping of waste (Sobha *et al.*, 2009) or may be due to partial decomposition of organic matter accumulated in the sediment. EC ranged from 0.3 to 0.68 dS m^{-1} in the study area (Fig.26).

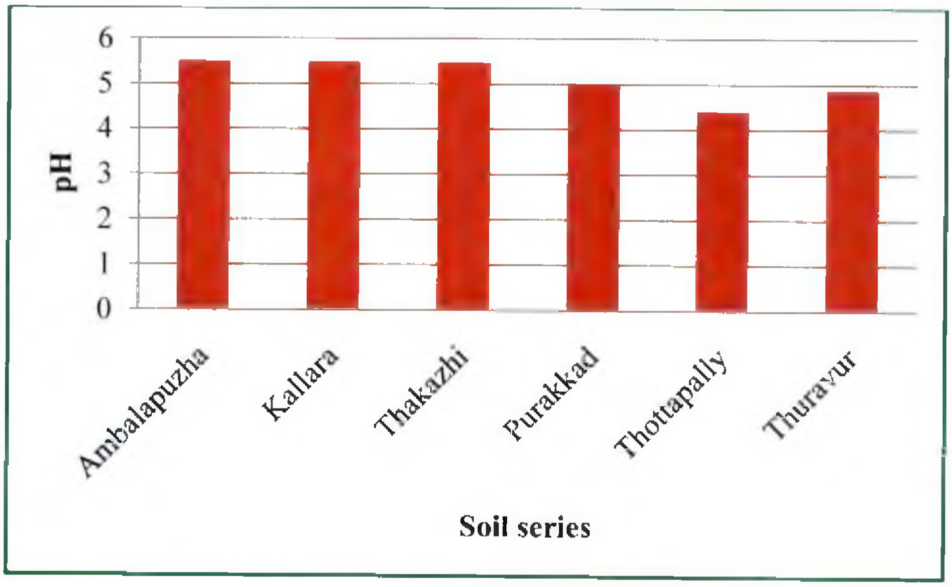

Fig.25 pH of sediments collected from six soil series of Kuttanad

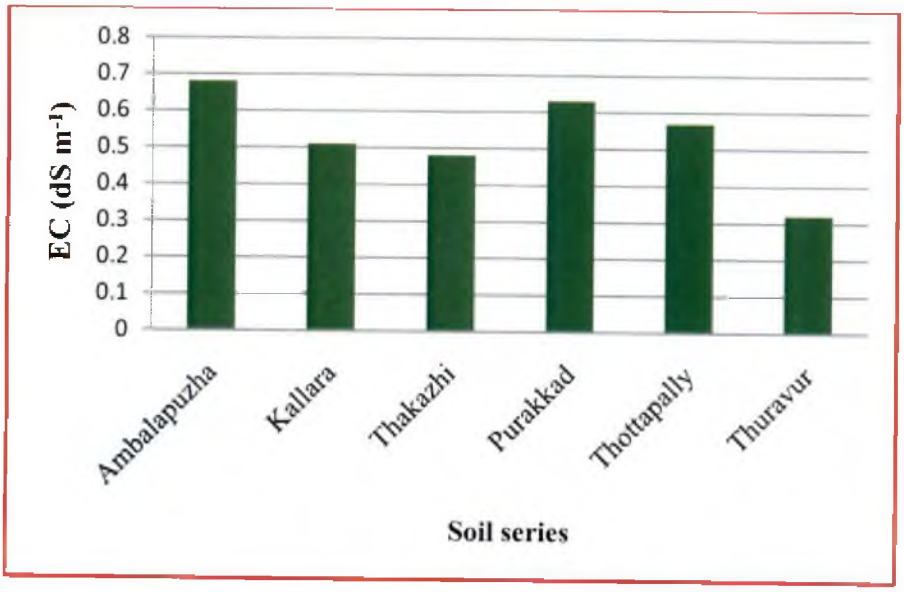

Fig.26 EC of sediments collected from six soil series of Kuttanad

of available P (Fig.28). In Kuttanad, washing of cloths in canals using soaps and detergents is a common practice; this may be the reason for increased P content in sediments (Thomas *et al.*, 2001).

Potassium is the naturally occurring element in the sediment and major source of potassium is weathering of rocks (Sobha *et al.*, 2009). The potassium content ranged from 61.58 to 343.29 mg kg^{-1}. Highest value was observed in sediments collected from canals of Thuravur series (Fig.28). The main reason for high K content in sediment may be due to leaching from nearby paddy field or may be due to presence of primary minerals containing potassium. Ca and Mg content were also high in sediment samples (Fig. 29). Available sulphur also showed higher value in sediment samples, it ranged from 548.27 to 955.09 mg kg^{-1} (Fig.28).

5.2.3 Heavy metals in sediments

All heavy metals are ultimately reaching sediments of aquatic environment. Heavy metals may associate with sediment particle either through absorption or complexation process. Iron is most abundant essential element present in Kerala rivers. Industrial wastes, fertilizers and domestic wastes are the sources of Fe. The concentration of Fe in sediment samples collected from six series ranged from 1054.87 to 4903.21 mg kg^{-1}. The highest value was reported from sediments of Ambalapuzha series (Fig. 30). This may be due to textural characters of sediment. Fine particles like clay was dominant in sediments of all series. Fine particles retained more metals than coarse particles (Fernandez and Jones, 1987). This may be the reason for high content of Fe in sediments.

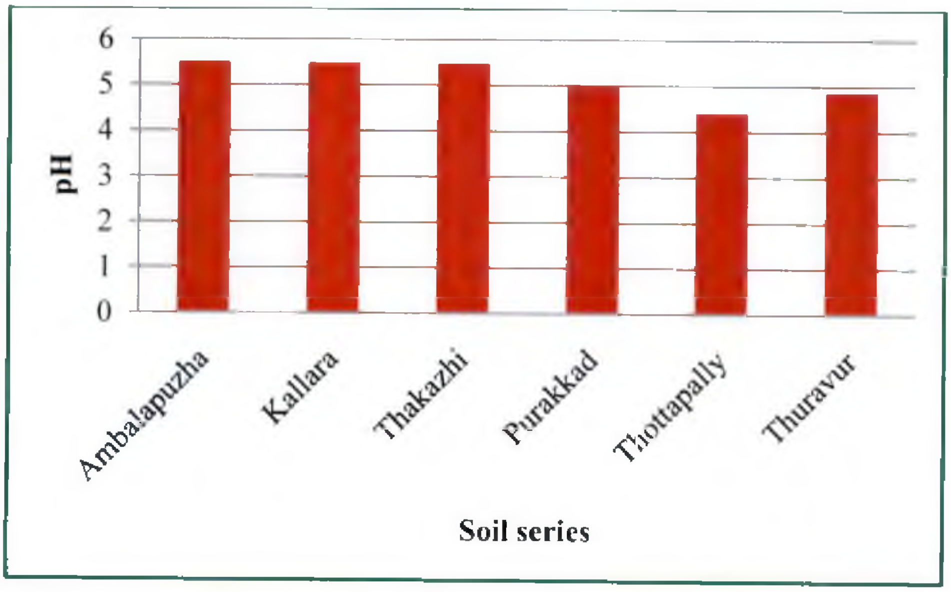

Fig.25 pH of sediments collected from six soil series of Kuttanad

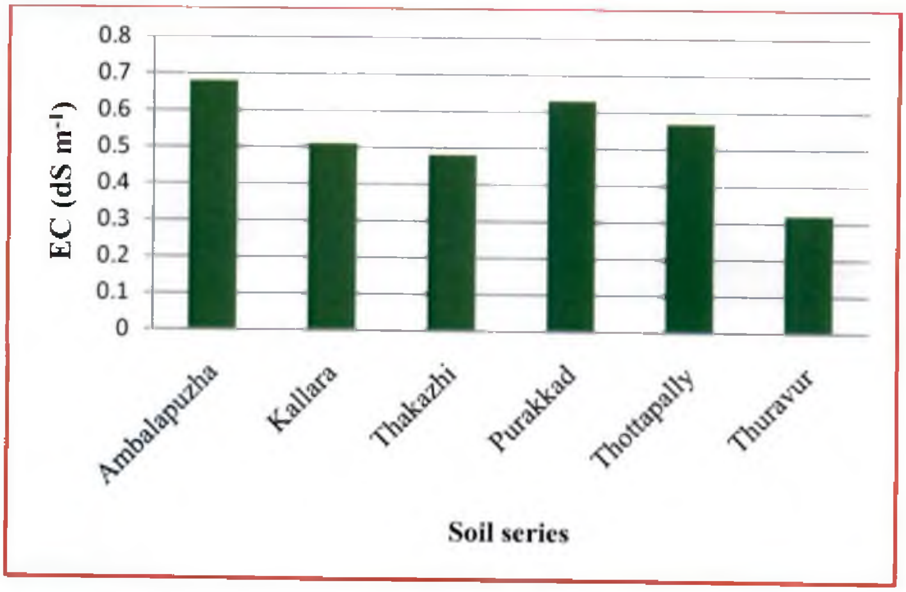

Fig.26 EC of sediments collected from six soil series of Kuttanad

5.2.2 Available nutrients

High organic matter content in soil caused the darkening (Ponnamperuma and Ikekashi, 1979). In the present study, sediments collected from six series showed black colour which itself indicates high organic matter. Organic carbon content of sediments ranged from 2.22 to 6.77 per cent. Higher organic carbon was reported from sediments collected from Kallara series (Fig. 27). This may be due to decaying of aquatic macrophytes. *Eichhornia crassipes* was the dominant aquatic macrophyte in water bodies of this area. *Eichhornia* mats play a major role in increasing organic carbon content of sediments in this area.

Texture of the sediment also had a major role in organic carbon content. Textural pattern determines the selective enrichment of organic carbon. Organic carbon content was high in sediments collected from all series. Sandy loam, loamy sand and sandy clay loam were the dominant texture in sediments under study. Hellen and Pillai (2013) reported that there was a correlation between texture and organic carbon. Fine grained sediments like sandy loam, loamy sand and sandy clay loam showed high content of organic carbon compared to sand. Low organic carbon was observed in areas with sandy texture (Sobha *et al.*, 2009)

Nitrogen was derived primarily from oxidation of nitrogenous organic matter (Sobha *et al.*, 2009). Nitrogen content in the sediment depended on local conditions of rainfall, quanitities of fresh water inflows and biological activity (Kemp, 1971). In the present study, nitrogen content of the sediments ranged from 45.27 to 222.27 mg kg^{-1}. Sediments from Kallara series showed high content of available nitrogen (Fig.28). This may be due to presence of thick mats of *Eichhornia* in these areas. *Eichhornia* contributes nitrogen by organic matter decomposition through absorption and recycling.

Phosphorus is one of the major nutrients in aquatic system (Reddy *et al.,* 1998). The present study revealed that available phosphorus of sediment samples ranged from 8.72 to 28.70 mg kg^{-1}. Sediments from canal system of this series showed high content of available P (Fig.28). In Kuttanad, washing of cloths in canals using soaps and detergents is a common practice; this may be the reason for increased P content in sediments (Thomas *et al.,* 2001).

Potassium is the naturally occurring element in the sediment and major source of potassium is weathering of rocks (Sobha *et al*., 2009). The potassium content ranged from 61.58 to 343.29 mg kg^{-1}. Highest value was observed in sediments collected from canals of Thuravur series (Fig.28). The main reason for high K content in sediment may be due to leaching from nearby paddy field or may be due to presence of primary minerals containing potassium. Ca and Mg content were also high in sediment samples (Fig. 29). Available sulphur also showed higher value in sediment samples, it ranged from 548.27 to 955.09 mg kg^{-1} (Fig.28).

5.2.3 Heavy metals in sediments

All heavy metals are ultimately reaching sediments of aquatic environment. Heavy metals may associate with sediment particle either through absorption or complexation process. Iron is most abundant essential element present in Kerala rivers. Industrial wastes, fertilizers and domestic wastes are the sources of Fe. The concentration of Fe in sediment samples collected from six series ranged from 1054.87 to 4903.21 mg kg^{-1}. The highest value was reported from sediments of Ambalapuzha series (Fig. 30). This may be due to textural characters of sediment. Fine particles like clay was dominant in sediments of all series. Fine particles retained more metals than coarse particles (Fernandez and Jones, 1987). This may be the reason for high content of Fe in sediments.

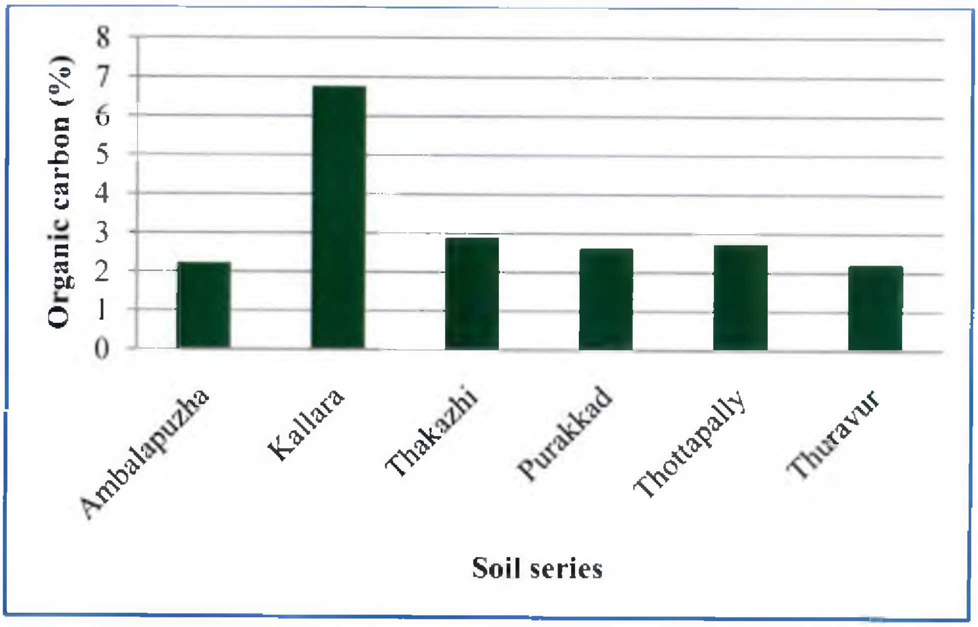

Fig.27 Organic carbon content of sediments collected from six soil series of Kuttanad

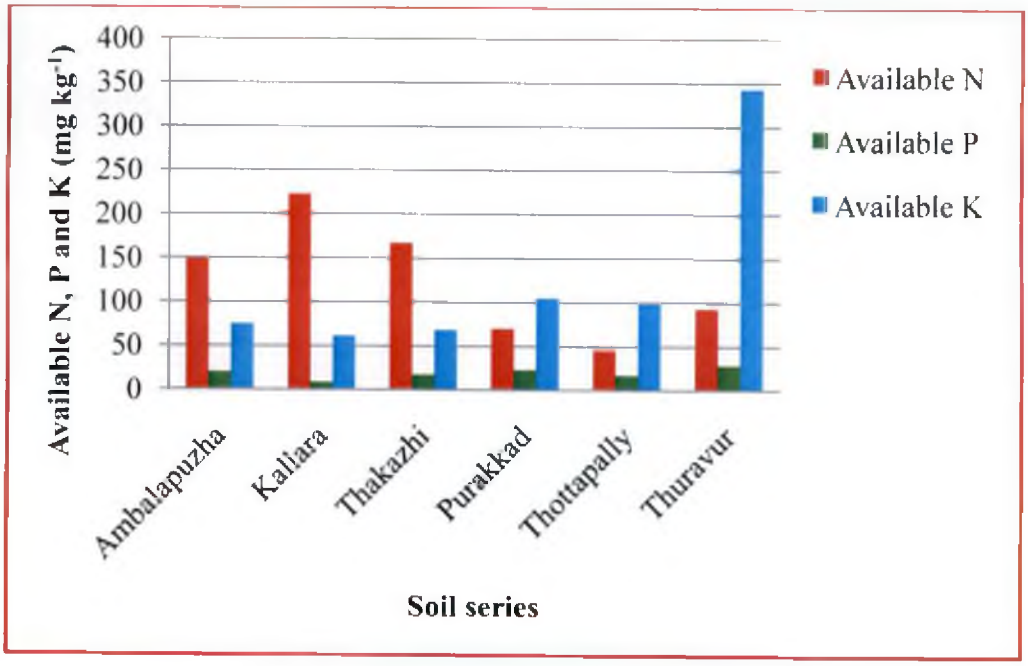

Fig.28 Available N, P and K content of sediments collected from six soil series of Kuttanad

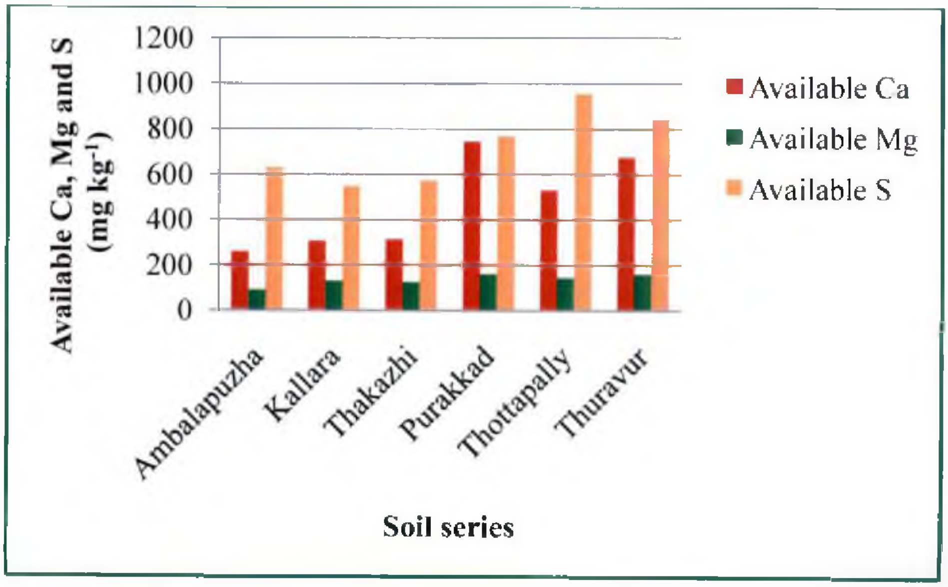

Fig. 29 Available Ca, Mg and S content of sediments collected from six soil series of Kuttanad

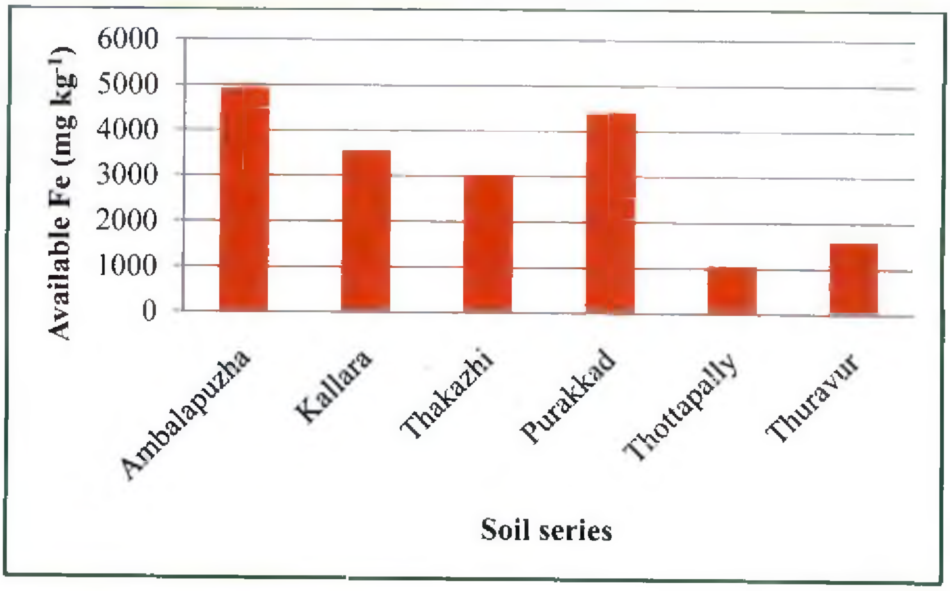

Fig. 30 Available Fe content of sediments collected from six soil series of Kuttanad

Available Mn and Zn were found to be higher in all sediment samples (Fig. 31). Trace quantities of Zn is necessary to sustain biological life, but its large concentration is proved to be lethal. It is a common contaminant in industrial effluents (Dean *et al.*, 1972).

Heavy metals like Hg and Cd were below detectable level. Presence of Cu, Pb, Cr and Al were noticed in sediments. The content of available Cu ranged from 0.19 to 0.68 mg kg^{-1}. There was no significant difference in available Cu content of sediment samples collected from six soil series. Major portion of lead in the surface water is from mining, smelting, refining etc. Lead reaches the aquatic system through precipitation, erosion and leaching from soil or from municipal and industrial wastes (Sobha *et al.*, 2009). Available Pb content in sediment ranged from 0.50 to 2.01 mg kg^{-1} (Fig.32). Available Cr content in sediment ranged from 0.34 to 3.47 mg kg^{-1} (Fig.32). Earlier studies reported that high concentration of metals were present in sediments when compared to plant parts. Metals were adsorbed on ion exchange sites of fine silt/ clay or it was adsorbed within Fe and Mn colloidal oxide compounds (Harbison, 1986). This is the reason for low availability of metals. Another reason is the high organic matter content in sediment, which facilitated complexation with refractory organics (Mac- Farlane *et al.*, 2003).

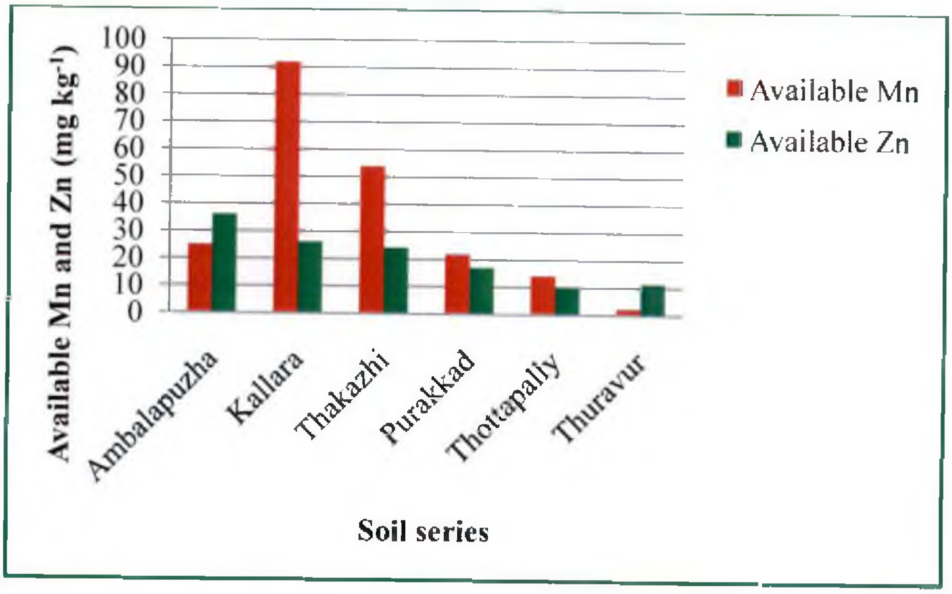

Fig.31 Available Mn and Zn content of sediments collected from six soil series of Kuttanad

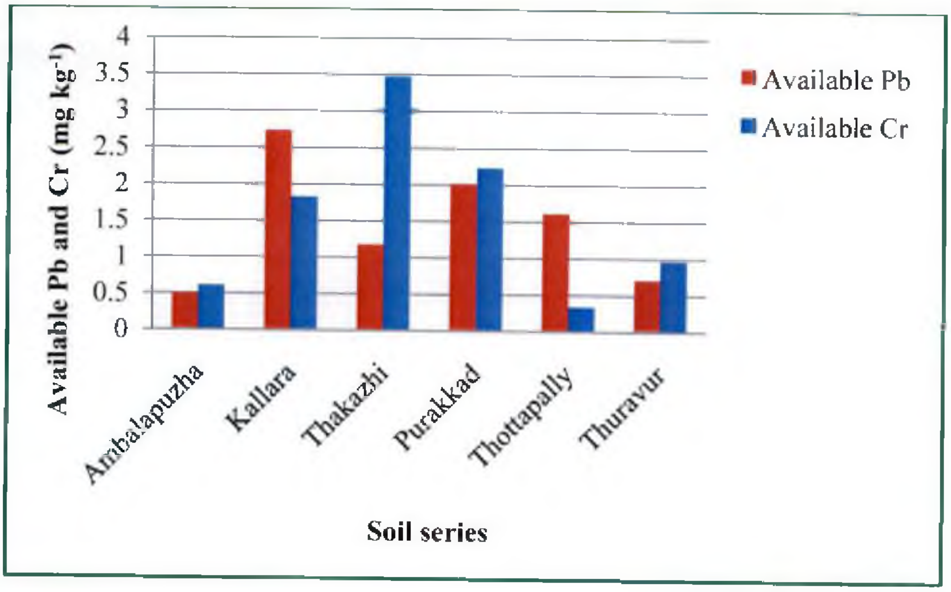

Fig.32 Available Pb and Cr content of sediments collected from six soil series of Kuttanad

5.3 Characterisation of water samples

Quality of irrigation water is very important for long term soil productivity. Poor quality irrigation water will deteriorate soil health by contaminating soil with toxic substances. Most of the water bodies are polluted mainly due to anthropogenic activities. Kuttanad is a location encircled by numerous water bodies. Agricultural activities in Kuttanad may lead to accumulation of some toxic substances like heavy metals in soil and water bodies. The evaluation of physical and chemical properties of water samples in Kuttanad was done to determine the quality of water.

5.3.1 Physical characteristics

Water temperature is an important parameter which affects the growth of living organisms in aquatic environment. There was no significant difference observed in temperature of water from canals/lakes of six acid sulphate soil series. Temperature of 31- 32^{0} C was observed in the water samples. Generally water temperature was high during pre- monsoon season (Sujitha *et al.*, 2012)

All the water samples collected from different canals showed pale yellow colour. There was not much variation in colour of the samples. Change in colour was noticed only during monsoon season due to mixing up of suspended particles, organic and inorganic materials (Kamal, 2011). Sample collection was done during pre- monsoon period and this may be the reason for no variation in colour of water samples taken from different series.

5.3.1.1 Turbidity and suspended solids

Turbidity and suspended solids of water determine the transparency of water to light. It decides the clarity of water. Generally turbidity was mainly due to the presence of suspended solids (suspended solids include fine clay or silt, plankton, microorganism and organic or inorganic compounds in water). Collected canal water samples from six series showed low turbidity. It may be due to the trace amount of suspended solids. Another reason may be the season of sample collection. Since water samples were collected during pre- monsoon season there was no mixing up of water and this may be the reason forwater showing less turbidity.

5.3.2 Electrochemical properties

Water samples collected from nearby water bodies of six acid sulphate soil series were slightly acidic in nature and pH ranged from 5.4 to 6.6 (Fig. 33). pH is a very important parameter, because pH of a water body determines the solubility and toxicity of a metal in water. This low pH may be due to high organic matter content in water. Microorganisms caused breaking down of organic material present in water and produced CO_2 as a byproduct, which dissolved in water forming carbonic acid. So water became slightly acidic and most of the metals were soluble in acidic condition (Sujitha *et al.*, 2012)

Electrical conductivity indicates the ability of water to conduct electric current. Dissolved salts like sodium and potassium chloride determine the electrical conductivity of water. The values of electrical conductivity ranged from 0.02 to 0.74 dS m^{-1}. Electrical conductivity values of all water samples were low to medium. So the quality of water is good for irrigation purpose. Low EC values may be due to the dilution of salt concentration in canals.

5.3.3 Biochemical oxygen demand (BOD)

The BOD is an indication of organic matter present in the system and the amount of oxygen needed for stabilization. The BOD value provides the information about the quality of water. In the present study, BOD values ranged from 6.69 to 12.75 mg L^{-1}. The highest value of BOD was recorded in water samples from Ambalapuzha series (Fig. 34). According to Indian standard, maximum permissible limit of BOD for drinking water is 2 mg L^{-1} and for domestic purpose it is 3 mg L^{-1}. In this regard, all water bodies from six series were polluted. So these water bodies were contaminated with organic load. The maximum BOD value of 9.05 mg L^{-1} was reported in *kayal* land sites of Kuttanad (Thomas *et al.*, 2001). In the present study, highest value of BOD was observed in water samples collected from Ambalapuzha series, may be due to organic waste disposal in water bodies of this area. Rapid decomposition of organic matter present in water and decay of vegetation lead to high BOD value. The BOD values were the lowest during monsoon period and the highest during pre monsoon period (Kamal, 2011). Similar results were reported by Radhika *et al.* (2004).

5.3.4 Chemical oxygen demand (COD)

The COD is an important parameter for evaluating the extent of organic pollution. In the present study, COD of water samples ranged from 85 to 176 mg L^{-1}. The highest value was obtained from water bodies of Thottapally series (Fig. 35). This may be due to the decay of aquatic macrophytes and organic wastes present in the water bodies. Like BOD, COD was also lowest during monsoon and the highest during pre monsoon. Presence of fresh water on receipt of monsoon showers and low temperature during this season may be the reason for low BOD and COD values during this season (Kamal, 2011).

5.3.5 Nutritional characteristics

5.3.5.1 Total nitrogen

Excess accumulation of nitrate leads to eutrophication of water bodies and this will degrade the quality of water. So nitrate content of water samples is an important parameter. Nitrate and ammonia are the two forms of nitrogen. Any form of nitrogen can be toxic to aquatic organisms when its concentration is above maximum permissible limit (Lindau *et al.*, 1988). Ammoniacal nitrogen in the water samples ranged from 0.11 to 0.7 mg L^{-1}. The nitrate nitrogen content ranged from 3.25 to 5.63 mg L^{-1}. Enhanced application of N fertilizers in acid sulphate soils and its subsequent leaching and run off might be responsible for the high nitrate nitrogen in water bodies. The important source of anthropogenically derived nitrate and ammonia in surface water was from agricultural activities and waste disposal in water bodies (Moore, 1991).

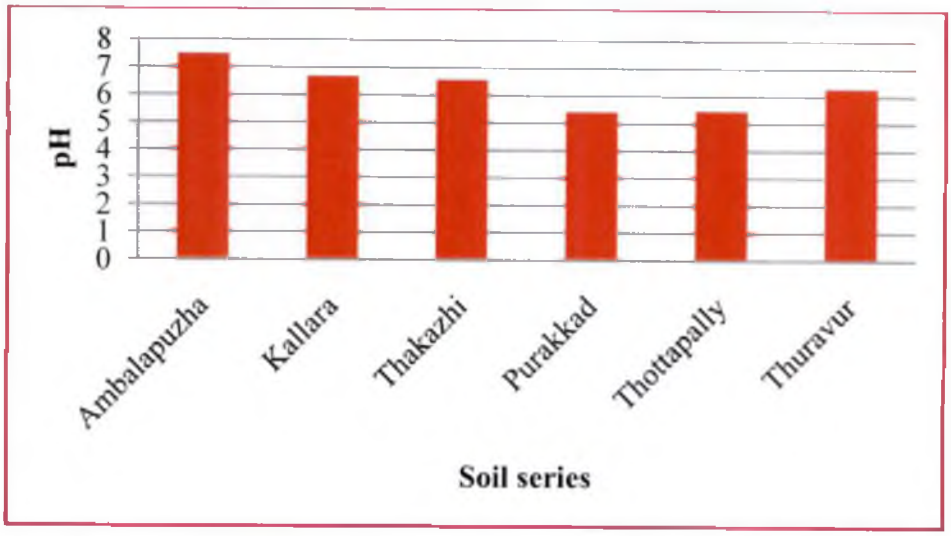

Fig.33 pH of water samples collected from acid sulphate soil series of Kuttanad

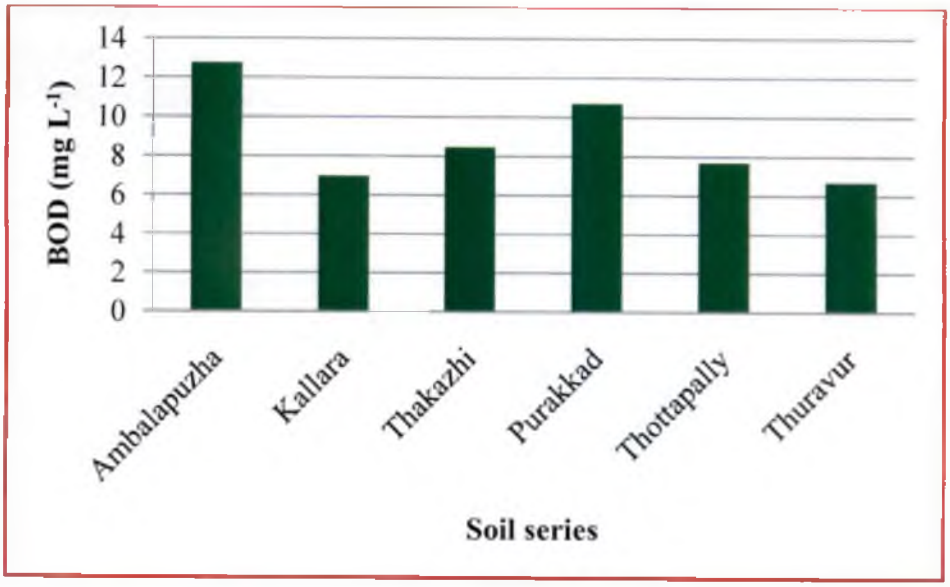

Fig.34 Biochemical oxygen demand (BOD) of water samples collected from acid sulphate soil series of Kuttanad

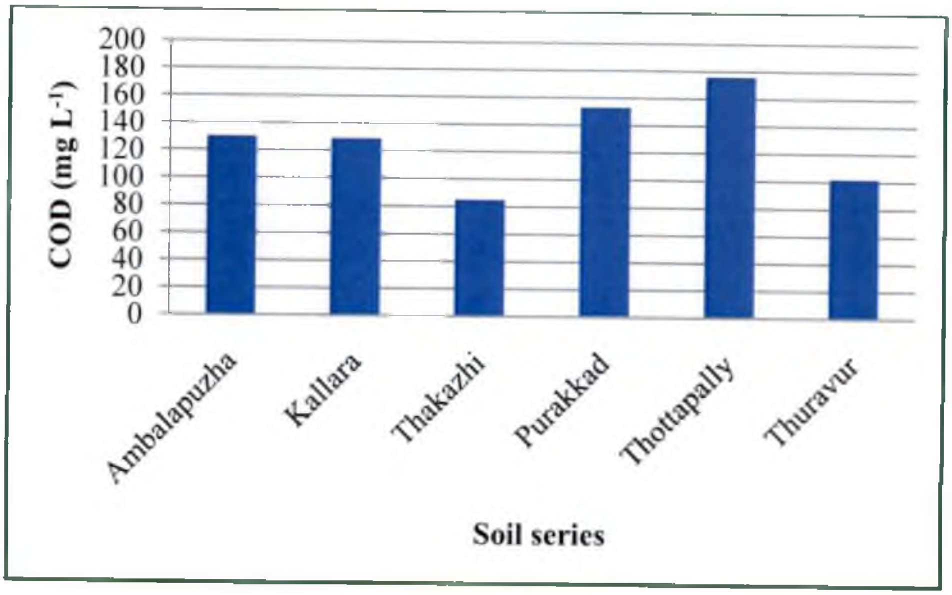

Fig.35 Chemical oxygen demand (COD) of water samples collected from acid sulphate soil series of Kuttanad

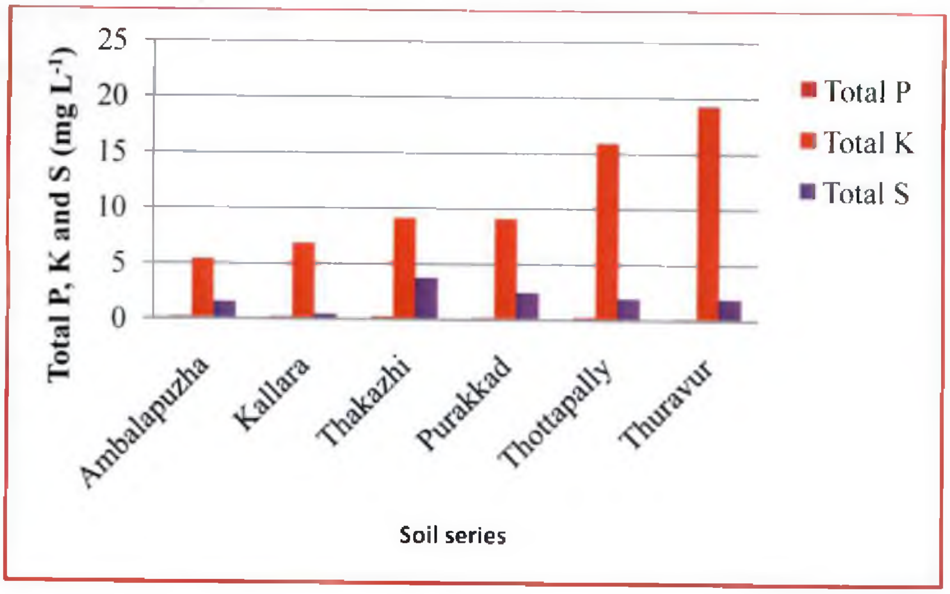

Fig.36 Total P, K and S content of water samples collected from acid sulphate soil series of Kuttanad

5.3.5.2 Total phosphorus and potassium

High content of phosphate in water is responsible for eutrophication. Water samples collected from different series showed very low phosphate content and it ranged from 0.17 to 0.25 mg L^{-1}. There was not any significant variation in P content of water samples among different series (Fig. 36). Low content of P in water bodies may be due to the absorption of phosphorus by macrophytes or may be due to slow release of P from sediments. Kamal (2011) reported that Vellayani lake water samples showed low content of P due to high P fixing capacity of sediments.

The major source of K in fresh water is from weathering of rocks. Water samples collected from canals of different series showed significant variation. The potassium content of the water samples from the six soil series ranged from 5.36 to 19.27 mg L^{-1}. Water samples from canals of Thuravur series recorded the highest value (Fig. 36). This may be due to disposal of domestic wastes in this area.

5.3.5.3 Sulphur

There was no significant difference in sulphate content of canal water among the different series except Thakazhi. Water samples collected from canals of Thakazhi showed highest value (3.76 mg L^{-1}) (Fig. 36). This may be due to leaching of soluble sulphur compounds from nearby lands to water bodies or may be due to decaying of vegetation, organic matter and plankton present in water bodies. As discussed in section 5.1.1, the presence of pyrites in soil might have contributed to the content of sulphates in water bodies.

5.3.6 Micronutrients and heavy metals

Water samples collected from different series showed the presence of micronutrients and heavy metals except Zn, Cu, Cd and Hg. Among the micronutrients, Fe was the dominating element; content ranging from 2.70 to 3.53 mg L^{-1} (Fig. 37).

According to WHO report, the maximum permissible limit of Fe in water is 1.0 mg L^{-1}. All the collected water samples showed Fe content above permissible limit due to the high levels of soluble Fe in the submerged soil and subsequent leaching to water bodies. The highest value was reported in water samples collected from nearby water bodies of Kallara series.

The Mn content ranged from 0.05 to 0.27 mg L^{-1}. Highest value was reported in water samples of Purakkad series (Fig. 38). Kuttanad soils showed rich content of Mn. Continuous submergence leads to its toxicity in soil. Draining out of this water containing toxic quantities of Mn to surrounding canals led to death of aquatic organisms (Nair and Pillai, 1990). Generally the concentration of Zn in surface water was fairly low due to their restricted mobility from its sources or from rock weathering sites. Analysis of water samples revealed that concentration of Zn was below detectable level. The maximum permissible limit for Zn in water set by WHO is 5 mg L^{-1}.

Concentration of Cu and Hg in water samples of six acid sulphate series was also found to be below detectable level. Because of non availability of these two metals in sediments, these elements might be absent in nearby water bodies.

Lead, a soil contaminant is harmful to human body. It transfers to human body *via* biomagnification and accumulates in aorta, bone, kidney and spleen. The maximum permissible limit of lead in drinking water is 0.05 mg L^{-1} as set by WHO. The concentration above this limit can cause harm to living organisms. Representative water samples from nearby canals of acid sulphate series showed lead content ranging from 0.02 to 0.1 mg L^{-1}. Water samples from Purakkad and Thottapally series showed lead content above permissible limit and the water samples from other series showed lead content below permissible limit (Fig. 38). The highest lead content was reported in water samples collected from Thottapally series. Water bodies near Thottapally series were slightly contaminated with Pb. This may be due the water transportation. In the Purakkad area also motorized fishing boats are very common and so there are chances of Pb contamination.

Chromium content in water samples from the six soil series ranged from 0.11 to 0.25 mg L^{-1} (Fig. 38). The maximum permissible limit of Cr in drinking water is 0.1 mg L^{-1} set by WHO. The present study reported that concentration of Cr in water samples collected from all series were above the maximum permissible limit set by WHO. All water bodies in six series were highly contaminated with chromium, since the soils under study were found to be rich in Cr. Mercury was below detectable level in all water bodies of six series. Aluminium content in the water samples ranged from 0.19 to 0.63 mg L^{-1}. As per WHO standard, maximum permissible limit for Al in drinking water is 0.2 mg L^{-1}. Water samples from Thottapally series showed Al content below permissible limit while those from all the other series showed Al content above permissible limit (Fig. 38). So most of the water bodies are contaminated with Al. Kuttanad soils showed more soluble Al due to continuous submergence. Draining the water from submerged area into canals led to increased concentration of Al in water (Nair and Pillai, 1990).

Concentration of Fe, Al and Cr in water samples were above the maximum permissible limit (MPL) as suggested by WHO, hence they are not suitable for drinking water purpose. Water samples from Purakkad and Thottapally series were contaminated with Pb. According to FAO, for irrigation water quality, all heavy metals were within the MPL in the water samples and were safe for irrigation. Along with Cd and Hg, Zn and Cu were also below detectable levels in all water samples.

Heavy metal accumulation was more in sediments as compared to soil and water (Fig. 39). Toxicity of Fe and Al was recorded in soil and sediment samples of all series (Fig. 40). Concentration of Zn and Mn was high in all soil samples of acid sulphate soil series. Even though accumulation of Pb and Cr were reported in soil and sediment samples, their availability were more in sediment samples than in soil samples.

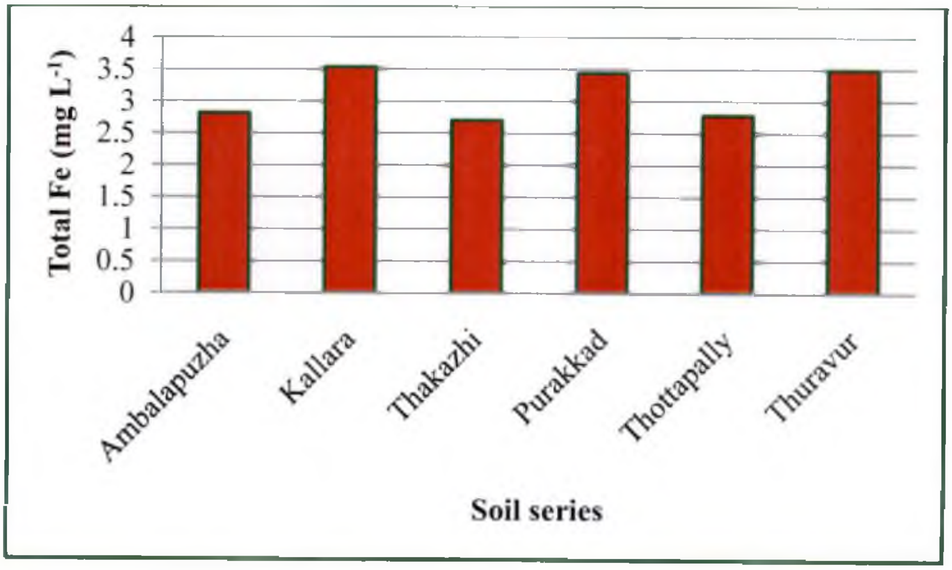

Fig.37 Total Fe content of water samples collected from acid sulphate soil series of Kuttanad

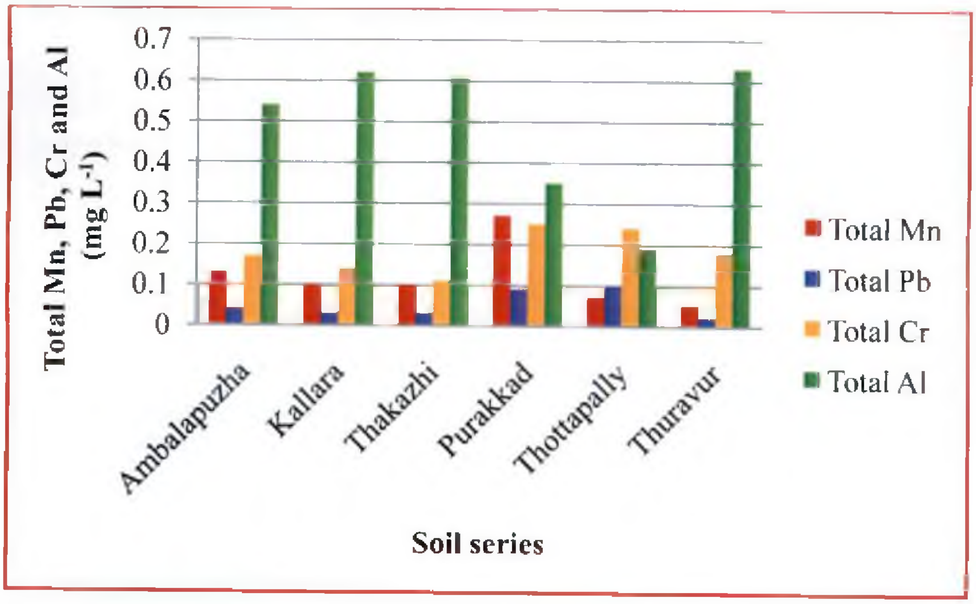

Fig. 38 Total Mn, Pb, Cr and Al content of water samples collected from acid sulphate soil series of Kuttanad

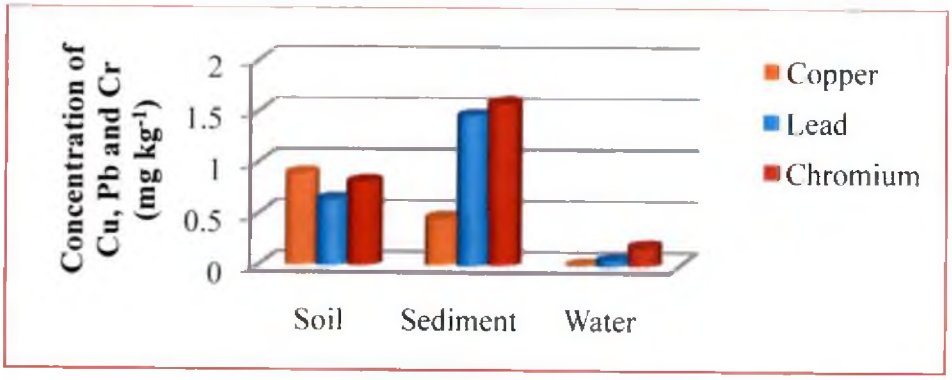

Fig. 39 Heavy metal content in soil, sediment and water samples of acid sulphate soil series of Kuttanad

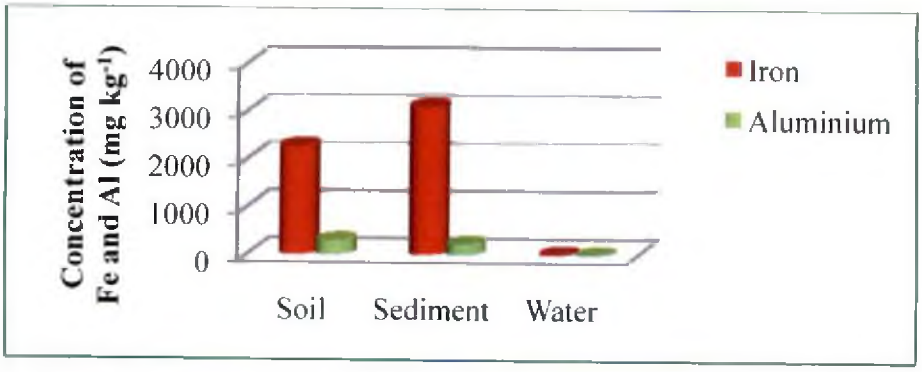

Fig. 40 Iron and aluminium content in soil, sediment and water samples of acid sulphate soil series of Kuttanad

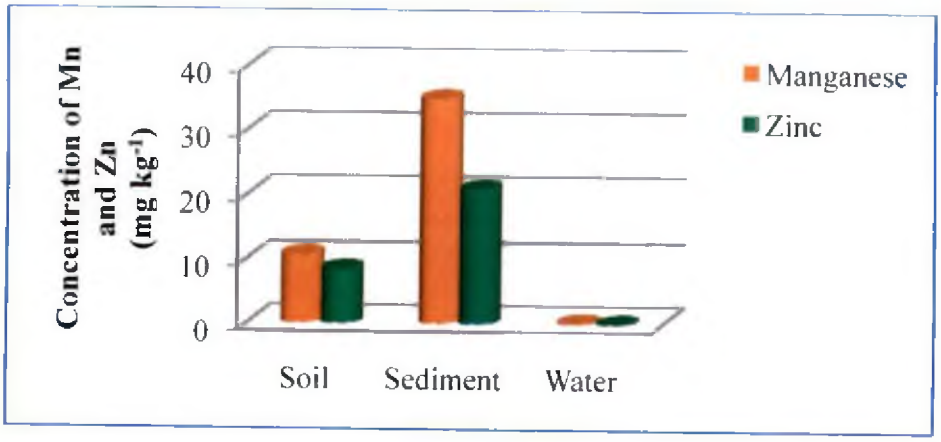

Fig. 41 Manganese and zinc content in soil, sediment and water samples of acid sulphate soil series of Kuttanad

5.4 Suitability of mangroves for phytoremediation

Mangroves play a major role in biogeochemical cycling of carbon, major, minor and trace elements including heavy metals. Mangroves are different from other plants due to their unique features. They have specialized characters that make them adaptive to adverse conditions, they can thrive well in estuarine brackish water environment. The features which are unique to mangrove species are pneumatophores, salt excreting leaves, prop roots and viviparous mode of germination (Duke, 1992). They play a major role in providing goods and services to humans including aquaculture, forestry, and protection against shoreline erosion, firewood and building material (Hogarth, 1999; Walters *et al.*, 2008). Due to rapid urban development mangrove ecosystem is exposed to contamination with pollutants including heavy metals (MacFarlane, 2002).

Heavy metals are included under most serious pollutant because of their toxicity, persistence and bioaccumulation behavior (Jamila and Fernandez, 1995; MacFarlane and Burchett, 1999). In the present study, all the three species had higher content of Fe, Pb, Cr and Al in roots followed by bark and leaves while the other elements like Cu and Mn were accumulated in aerial parts such as bark and leaves.

In *Avicennia officinalis,* different metals showed different mobility to above ground parts. Higher per cent of Fe, Pb, Cr and Al were found in roots and Cu and Mn were highest in leaves (Fig. 42). Zinc, Cd and Hg content were below detectable level. So *Avicennia officinalis* showed restricted mobility of non-essential metals. *Avicennia officinalis* showed greater mobility to essential metals like Mn and Cu. *Avicennia officinalis* translocated essential elements to aerial parts inorder to meet their metabolic requirements, while it restricted the uptake of non- essential metals to avoid toxicity (Chakraborty *et al.,* 2013). Since it restricts the mobility of this metal to above ground part it can be considered as a suitable phytostabilizer. Phytostabilization process reduces the migration of heavy metals in soil.

In *Rhizophora mucronata*, except Mn, all other metals such as Fe, Cu, Pb, Cr and Al were more accumulated in roots (Fig. 44). Similar results were found in *Bruguiera gymnorrhiza* also (Fig. 43). In both *Rhizophora mucronata* and *Bruguiera gymnorrhiza,* Mn was the only element having greater accumulation in aerial parts whereas all other metals accumulated more in roots.This indicated the potential of the plant for well balanced metal accumulation and translocation (Haque *et al*., 2008). Mangroves such as *Avicennia marina*, *Rhizophora* sp. and *Kandelia* sp. showed the mechanism which allowed root to accumulate high levels of heavy metals (Peters *et al*., 1997). Mangrove mud effectively sequestered metals due to fine clays, organic matter and low pH and it immobilized as sulfides in anaerobic sediments (Peters *et al*., 1997). Among three mangrove species, *Bruguiera gymnorrhiza* showed higher accumulation of all metals (Fig. 45).

It can be concluded from the present study that with respect to phytoremediation, these three mangroves, *Avicennia officinalis*, *Bruguiera gymnorrhiza* and *Rhizophora mucronata* having extensive root system can be effectively used for phytostabilization of metals in mangrove ecosystem. The root system of mangrove species reduces soil erosion and stabilizes metals within the sediments. Phytoremediation is environment friendly because they do not produce secondary waste that requires further treatment (Cunningham *et al*., 1995; Prasad, 2003).

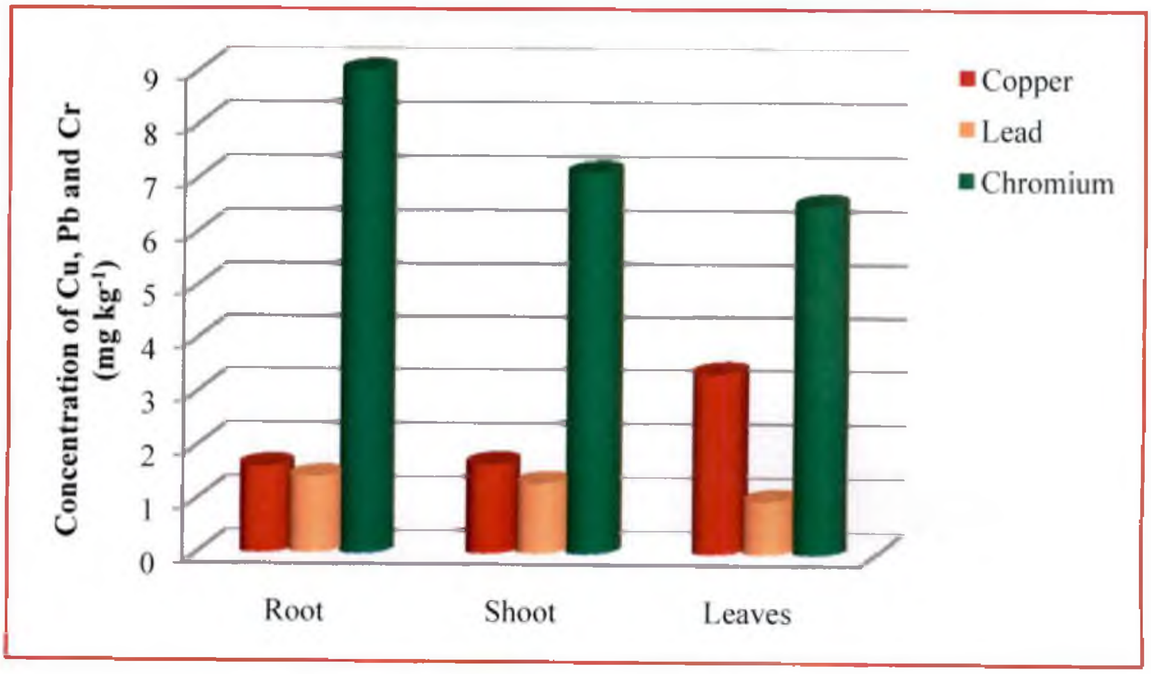

Fig.42 Content of heavy metals in root, shoot and leaves of *Avicennia officinalis*

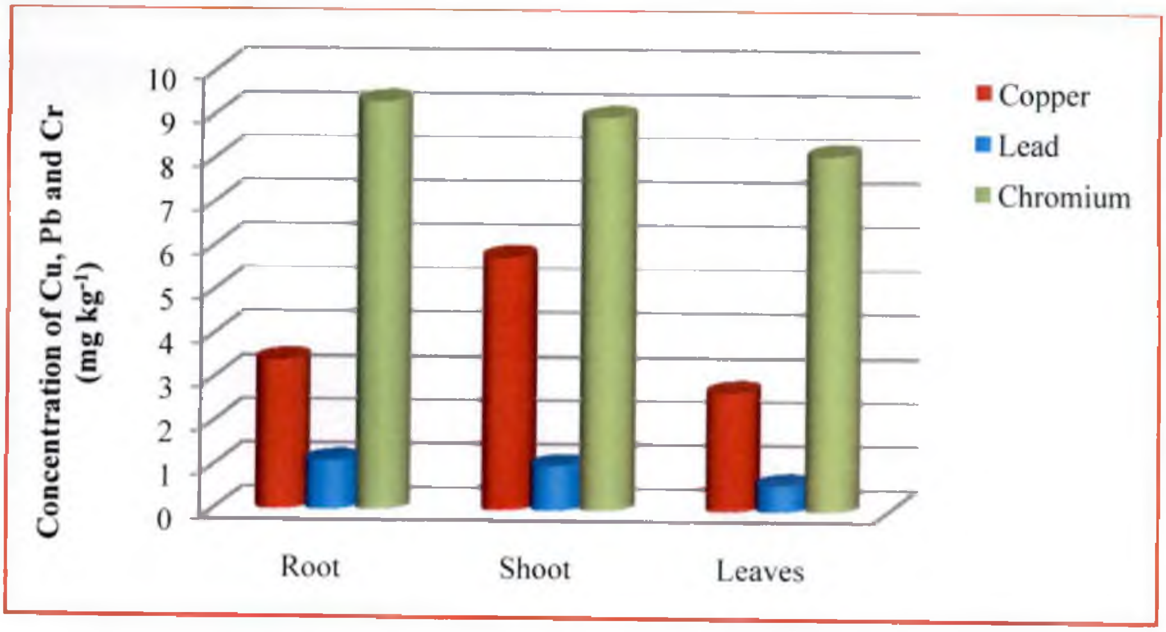

Fig.43 Content of heavy metals in root, shoot and leaves of *Bruguiera gymnorrhiza*

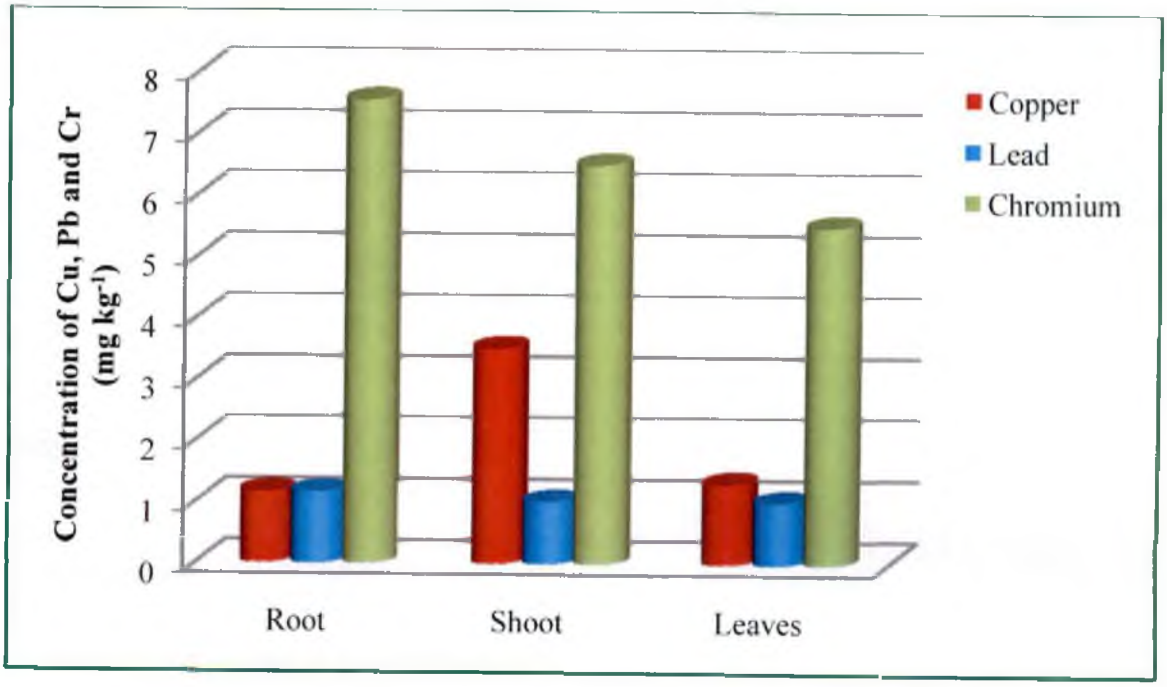

Fig.44 Content of heavy metals in root, shoot and leaves of *Rhizophora mucronata*

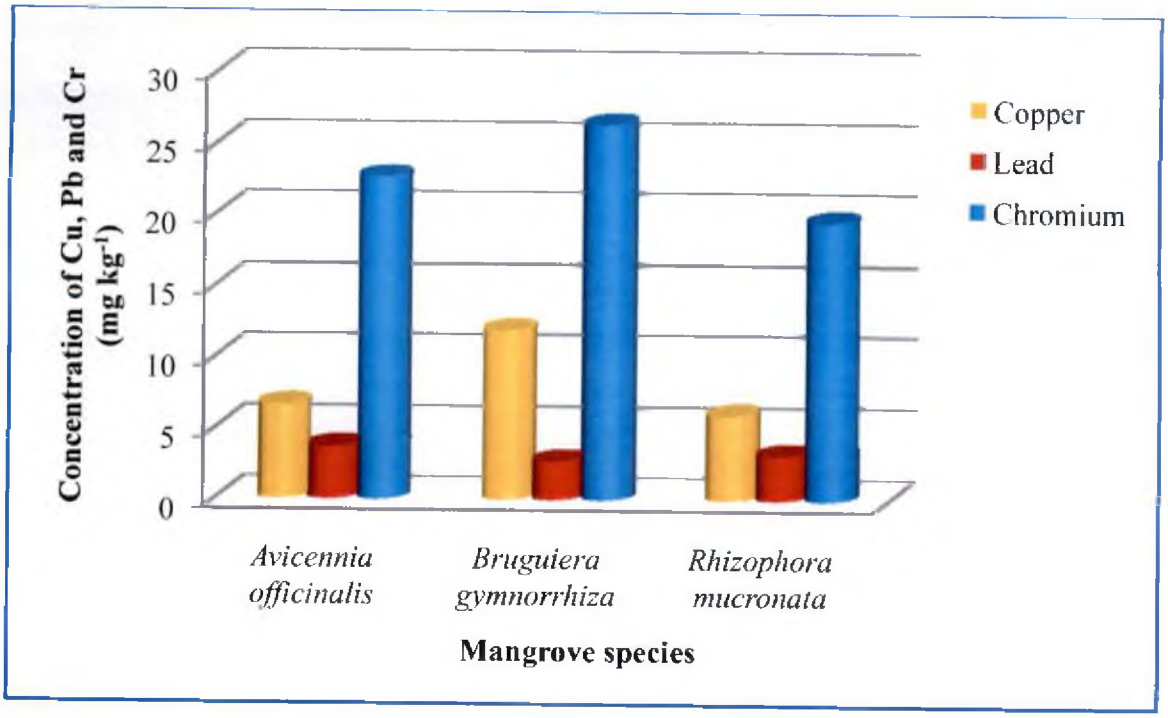

Fig.45 Heavy metal content in different mangrove species

5.5 Potential of dominant macrophytes in the removal of nutrients and heavy metals

Soil, groundwater, sediment, surface water and air contamination with trace metals is one of the major environmental problems. Aquatic system is the final point of all the contaminants. Clean up of metal contaminated aquatic system using aquatic macrophytes is an effective method. Aquatic macrophytes act as a purifier; they take up heavy metals through roots from the sediment and directly from water through shoots. Nutrient and heavy metal removal by dominant native macroflora present in the aquatic system of acid sulphate series is discussed below.

Nutrients like P was highest in *Salvinia molesta* in Ambalapuzha, Kallara and Thuravur series. But plants such as *Monochoria vaginalis* showed high content of P in some series. Content of Ca and Mg varied among different mangrove species. An excellent example of plant facilitated bioremediation process is phytoremediation. Dominant aquatic macrophytes present in these series were *Eichhornia crassipes* and *Salvinia molesta.* These two are free floating macrophytes. Prolific growth of *Eichhornia crassipes* was seen in Kuttanad area due to pollution of aquatic system by nitrites, nitrates and phosphates. The other macrophytes dominant in these series were *Echinochloa crusgalli, Monochoria vaginalis, Leptochloa chinensis, Oryza sativa* f. *spontanea* and *Eleocharis dulcis.*

Plant species collected from different series showed slight variation in nutrient content. The content of Mn, Zn and Pb were highest in *Eichhornia crassipes* collected from Kallara, Thakazhi, Purakkad and Thottapally series. In some series, Ca and Mg were also high in *Eichhornia crassipes.* The order of accumulation of heavy metals in *Eichhornia crassipes* was Fe >Mn >Al >Zn >Cr >Cu >Pb. The higher content of Fe may be due to its high content in sediments. Among the heavy metals, Cd and Cu were below permissible limit and Pb, Cr and Zn were above permissible limit. This indicated the potential of plant to absorb high content of heavy metals. The low content of Cu in *Eichhornia crassipes* may be due to absence of Cu in sediments. Chromium content in *Eichhornia crassipes* was higher among different series due to its higher concentration in lake water. Similar findings were reported by Sasidharan *et al.* (2013). Hence *Eichhornia crassipes* could be used as a phytoremedial agent capable of cleansing the water bodies. *Salvinia molesta* absorb high amount of Fe, Mn, Zn, Cr and Al compared to other plant species. Aquatic weeds such as *Eichhornia crassipes* and *Salvinia molesta* accumulate more amount of heavy metals than the other weed species and hence these can be used as phytoremediators.

Summary

6. SUMMARY

Representative soil, sediment, water, weed and mangrove samples from six acid sulphate soil series namely Ambalapuzha, Kallara, Thakazhi, Purakkad, Thottapally and Thuravur have been collected and characterized for the study entitled "Accumulation of heavy metals in Typic Sulfaquents of Kuttanad ecosystem". The samples were collected from twenty locations of each series. Sediment and water samples were collected from the nearby canals/lakes of each series. Soil and sediment samples were collected and analysed texture, pH, EC, OC, available N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Pb, Cr, Hg and Al. Water samples were characterized for colour, temperature, turbidity, suspended solids, pH, EC, BOD, COD, total N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Pb, Cr, Hg and Al. The dominant weeds and mangrove species present in the study area were also collected and analysed for N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Pb, Cr, Hg and Al. Based on the analytical data, maps were prepared by using GIS software ArcGIS ArcMap version 10 of ESRI. The salient results of the study are summarized and listed below.

Soil

- Sandy clay loam was found to be the predominant texture in Thakazhi and Purakkad series. Soils from Ambalapuzha series showed silty loam texture. Clay loam texture was dominant in Kallara series. Thottapally and Thuravur series showed sandy loam and clayey texture respectively.
- Acid sulphate soils were extremely acidic, and the pH ranged between 2.88 to 3.89. Significantly higher pH was recorded in Ambalapuzha series (3.89). Electrical conductivity showed significant variation in different series, which ranged from 0.42 to 1.02 dS m^{-1}. Purakkad series showed highest value for EC (1.02 dS m^{-1}).
- Organic carbon content varied significantly among different series. It ranged from 1.72 to 6.2 per cent with the highest value in Kallara series. Significant variation was observed in available nitrogen content of different series, which

ranged from 61.15 to 310.01 kg ha^{-1}. Available N was also highest in Kallara series.Available P was found to be in the range of 9.25 to 13.67 kg ha^{-1} with significantly higher value in Thakazhi series. All series showed lowest available P content due to high P fixation. Nutrients such as K, Ca, Mg and S ranged from 116.99 to 388.36 kg ha^{-1}, 204.04 to 584.05 mg kg^{-1}, 92.79 to 141.06 mg kg^{-1} and 228.95 to 550.48 mg kg^{-1} respectively. All these available nutrients were highest in Thuravur series. Acid sulphate soils exhibited medium to high fertility status with respect to K.

- Available Fe content showed significant variation among different series with the highest value in Thuravur series. The highest value of available Al, Mn and Cr was observed in Kallara series. Al, Mn and Cr content ranged from 147.79 to 549.90, 6.25 to 15.58 and 0.28 to 1.41 mg kg^{-1} respectively. Among the six soil series, Thakazhi series showed highest content of Zn, Cu and Pb (13.57, 2.62 and 1.03 mg kg^{-1} respecively).

ss

Sediments

- Sandy clay loam was the dominant texture of sediments collected from waterbodies of different series. Sand was dominant in Ambalapuzha series (84.25 %), the highest silt content was noticed in Kallara series (25.20 %) and sediments from Thakazhi series showed high content of clay (27.06 %).
- The pH and EC ranged from 4.4 to 5.5 and 0.32 to 0.68 dS m^{-1} respectively. Sediments from Thottapally series showed lowest pH.
- Organic carbon and available N content recorded highest value in sediments of Kallara series. Sediments from Thuravur series exhibited the highest content of both P and K. Sediments collected from Purakkad series showed high content of Ca and Mg. The highest content of S was noticed in sediments fromThottapally series.

- Fe and Zn content in sediments registered the highest value in Ambalapuzha series. The sediments collected from all series were deficient in Cu. Among the different series, Thakazhi series showed high content of Mn, Pb and Al content. The Cr content was the highest in sediments from Kallara series. Available Cd and Hg were below detectable level in sediments from all the six series.

Water

- Significant variation was not observed in the physical properties of water samples collected from the waterbodies of six soil series. The water temperature was almost constant among the different series. Light yellow colour was noticed in all the water samples. Significant variation in biochemical oxygen demand (BOD) was noticed in water samples collected from different series. Water samples from Ambalapuzha series showed significantly higher BOD (12.75 mg L^{-1}) compared to other series. The chemical oxygen demand (COD) of water samples ranged from 85 to 176 mg L^{-1}.
- The pH of water samples was non significant among different series. EC ranged from 0.02 to 0.74 dS m^{-1}; the highest value of EC was recorded in water samples taken from Purakkad series.
- Water samples contained less ammoniacal nitrogen compared to nitrate nitrogen. Water samples from Thakazhi series showed the highest nitrate nitrogen (5.63 mg L^{-1}). There was no significant difference in the P content among different water samples. The K and S content of water samples ranged from 5.36 to 19.27 mg L^{-1} and 0.44 to 3.76 mg L^{-1} respectively. There was no significant difference in sulphate content of water among the different series.
- There was no significant variation in Fe and Mn contents of water samples collected from different series. Water samples collected from Kallara series showed high content of Fe compared to other series. Water samples collected from Purakkad series showed high Mn and Cr contents than other series.

Content of Pb in the water samples from Thottapally series were the highest, whereas Al concentration was highest in Thuravur series.

- Concentration of Fe, Al and Cr in water samples were above the maximum permissible limit (MPL) as suggested by WHO, hence they are not suitable for drinking purpose. Water samples collected from Purakkad and Thottapally series were contaminated with Pb. According to FAO, for irrigation water quality, all heavy metals were within the MPL in the water samples collected from study area and were safe for irrigation. Along with Cd and Hg, Zn and Cu were also below detectable levels in all water samples.
- Distribution of different parameters like pH, organic carbon, micronutrients and heavy metals in soil, sediment and water samples of six series were depicted in different maps.
- Maps were prepared by using GIS software ArcGIS ArcMap version 10 of ESRI

Mangroves

- Samples were taken from three species of mangroves *viz., Avicennia officinalis, Bruguiera gymnorrhiza* and *Rhizophora mucronata* found in acid sulphate soils of Kuttanad.
- The highest content of Fe, Pb, Cr and Al were found in the roots followed by shoots and leaves, while the other elements like Cu and Mn were accumulated in aerial parts such as shoot and leaves of all the three species. The concentration of Zn, Cd and Hg were found to be below detectable level.
- *Avicennia officinalis, Bruguiera gymnorrhiza* and *Rhizophora mucronata* translocated essential elements to aerial parts inorder to meet their metabolic requirements, while it restricted the uptake of non- essential metals to avoid toxicity. These mangrove species have extensive root system; hence it can be effectively used for phytostabilization of metals.

Macrophytes

- Dominant macrophytes present in the study area are *Eichhornia crassipes, Salvinia molesta, Echinochloa crusgalli, Alternanthera philoxeroides, Eleocharis dulcis, Monochoria vaginalis, Leptochloa chinensis* and *Oryza sativa* f. *spontanea.*
- *Eichhornia crassipes* was the good phytoremediator among all the dominant macrophytes. The heavy metal content in *Eichhornia crassipes* were in the order of Fe> Mn> Al> Zn> Cr> Cu> Pb. The trend of accumulation was similar for other macrophytes also.
- Among the heavy metals, Cd and Cu were below permissible limit whereas Pb, Cr and Zn were above permissible limit in *Eichhornia crassipes.* Accumulation of Cr and Al was more in *Salvinia molesta* and Pb was more accumulated in *Eichhornia crassipes.* Hence these two aquatic weeds can be effectively used for phytoremediation.

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Appendices

Appendix I Climatic data during study period

Standard week	Temp (Max) ^{0}C	Temp (Min) ^{0}C	RH% (AM)	RH % (PM)	RH % (Avg.)	Rainfall (mm)	Evaporation (mm)	Sunshine (h)	Wind speed (km h^{-1})
01-01-15 to 07-01-15	31.7	23.6	93.9	62.4	78.0	0.00	27.70	9.04	2.3
08-01-15 to 14-01-15	31.8	22.6	86.0	55.9	70.9	5.00	26.80	7.6	2.4
15-01-15 to 21-01-15	32.2	21.1	84.9	67.9	76.4	0.00	32.70	8.4	2.6
22-01-15 to 28-01-15	32.6	21.4	88.9	53.3	71.3	0.00	28.20	9.1	2.5
29-01-15 to 04-02-15	33.2	22.7	89.6	52.1	70.9	0.00	28.90	8.1	2.5
05-02-15 to 11-02-15	32.8	23.5	90.1	54.6	72.4	0.00	28.8	7.2	2.4
12-02-15 to 18-02-15	32.8	23.2	93.7	65.4	80.0	0.00	29.5	7.4	2.7
19-02-15 to 25-02-15	33.1	22.9	89.3	57.0	73.1	0.00	31.7	9.2	2.8
26-02-15 to 04-03-15	33.1	21.5	89.4	62.4	75.9	0.70	28.2	7.4	3.3
05-03-15 to 11-03-15	33.1	21.7	88.3	63.7	76.0	0.60	26.6	6.7	3.1
12-03-15 to 18-03-15	34.1	23.1	94.9	62.3	78.6	68.00	26.1	6.0	2.8
19-03-15 to 25-03-15	34.0	23.9	91.0	61.7	75.8	0.00	29.9	4.4	2.3
26-03-15 to 01-04-15	34.4	25.4	85.7	65.9	75.8	5.00	30.2	5.5	3.3
02-04-15 to 08-04-15	34.1	24.6	93.7	59.4	76.6	51.0	26.7	5.6	3.2
09-04-15 to 15-04-15	33.0	24.5	94.1	64.3	79.2	57.4	24.9	6.8	3.4
16-04-15to 22-04-15	33.0	24.1	93.0	62.1	77.6	145.0	23.8	7.3	3.2
23-04-15 to 29-04-15	32.9	25.4	89.4	64.4	76.9	2.4	28.9	8.1	3.0
30-04-15 to 06-05-15	33.5	26.2	87.4	64.6	76.4	0	29.0	8.0	3.0
07-05-15 to 13-05-15	31.9	25.7	90.3	77.9	84.1	35.9	14.2	1.4	3.0
14-05-15 to 20-05-15	30.7	25.7	92.0	75.7	83.8	84.5	18.5	3.4	3.9
21-05-15 to27-05-15	33.1	26.5	88.9	67.4	78.1	64.2	23.5	5.3	3.3
28-05-15 to 03-06-15	33.1	25.4	85.9	70.1	78.0	49.0	25.6	5.0	3.3

Appendix II Maximum permissible limit of heavy metals in plants and water (WHO, 1971)

Heavy metal	Plants (mg kg^{-1})	Drinking water (mg L^{-1})
Iron	20	1
Zinc	50	5
Copper	10	2
Lead	2	0.05
Chromium	1.30	0.1
Cadmium	0.02	0.01
Nickel	10	0.02

ACCUMULATION OF HEAVY METALS IN TYPIC SULFAQUENTS OF KUTTANAD ECOSYSTEM

By

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ABSTRACT OF THE THESIS

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ABSTRACT

An investigation entitled "Accumulation of heavy metals in Typic Sulfaquents of Kuttanad ecosystem" was conducted in the Department of Soil Science and Agricultural Chemistry, College of Horticulture, Kerala Agricultural University during 2014-2016. Sample collection was done from six acid sulphate soil series of Kuttanad *viz.*, Ambalapuzha, Kallara, Thakazhi, Purakkad, Thottapally and Thuravur series. Twenty soil, sediment and water samples were collected from each series. Dominant aquatic macrophytes were also collected from each series. Mainly three mangrove species (*Avicennia officinalis*, *Bruguiera gymnorrhiza* and *Rhizophora mucronata*) were present in the area, and were collected for analysis. Soil and sediment samples were characterized for texture, pH, EC, organic carbon, macronutrients, micronutrients (Fe, Mn, Zn and Cu) and heavy metals (Pb, Cr, Hg and Al). Water samples were analysed for its irrigation quality parameters such as colour, temperature, turbidity, suspended solids, pH, EC, biological oxygen demand (BOD) and chemical oxygen demand (COD). Also the plant and water samples were analysed for its macronutrients, micronutrients (Fe, Mn, Zn and Cu) and heavy metals (Pb, Cr, Hg and Al). Based on the analytical data, maps were prepared by using specialized software ArcGIS ArcMap version 10 of ESRI.

The soil samples from acid sulphate soil series of Kuttanad were extremely acidic whereas the sediment and water samples were slightly acidic. Highest EC values were recorded for soil, sediment and water samples collected from Purakkad series. Significantly higher OC and available N content were observed in soil and sediment samples collected from Kallara series, while the water samples taken from this series showed high ammoniacal N content. The available P content was low in all the series. Soil and sediment samples collected from Thuravur series exhibited highest content of N, P, K, Ca and Mg. In all the series, Cd and Hg were found to be below detectable levels in soil, sediment and water samples.

The heavy metal accumulation was more in sediments when compared to soil and water. Toxicity of Fe and Al was recorded in soil and sediment samples of all series. Concentration of Zn and Mn was high in all soil samples of acid sulphate soil series. Even though accumulation of Pb and Cr were reported in soil and sediment samples, their availability were more in sediment samples than in soil samples. Soil pH and OC had significant influence on availability of heavy metals in soil and sediments. Concentration of Fe, Al and Cr in water samples were above the maximum permissible limit (MPL) as suggested by WHO, hence they are not suitable for drinking water purpose. The concentration of Pb was below maximum permissible limit in water samples of all series except Purakkad and Thottapally series. According to FAO, for irrigation water quality, all heavy metals were within the MPL in the water samples collected from study area and were safe for irrigation. Along with Cd and Hg, Zn and Cu were also below detectable levels in all water samples.

The heavy metal content in *Eichhornia crassipes* were in the order of Fe >Mn > Al> Zn> Cr> Cu >Pb. Among the dominant macrophytes, *Eichhornia crassipes* accumulated high content of Pb. Hence it can be effectively used as a phytoremediator. *Salvinia molesta* contained high amount of heavy metals, especially Cr and Al. The content of Cd and Hg were below detectable level in all weed species.

The content of Zn, Cd and Hg were found to be below detectable levels in all the three mangrove species. But these contained high concentration of Fe, Pb, Cr and Al in roots, while Cu and Mn were accumulated in aerial parts such as shoot and leaves. Hence the three mangrove species *viz.*, *Avicennia officinalis*, *Bruguiera gymnorrhiza* and *Rhizophora mucronata* restricted the mobility of heavy metals to aerial parts but showed greater mobility of essential elements like Cu and Mn. Since they are having extensive root system, they can stabilise heavy metals within the roots. These plants can be effectively used for phytoremediation, especially for phytostabilisation of metals in mangrove ecosystem.