METHANE EMISSION AND OTHER BIOGEOCHEMICAL PARAMETERS IN VEMBANAD LAKE, KERALA

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Master of Philosophy

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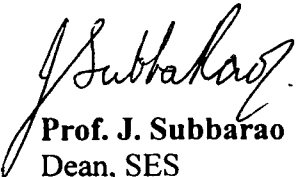Jawaharlal Nehru University
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CERTIFICATE

This is to certify that the work embodied in this dissertation entitled "**Methane Emission And Other Biogeochemical Parameters In Vembanad Lake, Kerala**" has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The Work is original and has not been submitted in part or full for any other degree or diploma of any university.

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Dedicated

To

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Chapter 1

INTRODUCTION AND LITERATURE REVIEW

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

The coastal zone is an important component of the human environment. It comprises of variety of wetlands. The Ramsar Convention (Article 1.1) defines wetlands as:

"areas of marsh, fen, peatland or water, whether natural or artificial,

permanent or temporary, with water that is static or flowing, fresh,

brackish or salt, including areas of marine water the depth of which

at low tide does not exceed six metres".

In addition, the Convention (Article 2.1) provides that wetlands:

"may incorporate riparian and coastal zones adjacent to the wetlands,

and islands or bodies of marine water deeper than six metres at low

tide lying within the wetlands".

As a result of these provisions, the coverage of the Convention extends to a wide variety of habitat types, including rivers and lakes, coastal lagoons, mangroves, peatlands, and even coral reefs. In addition there are human-made wetlands such as fish and shrimp ponds, farm ponds, irrigated agricultural land, salt pans, reservoirs, gravel pits, sewage farms, and canals. The estuaries and coastal lagoons are unique components of coastal wetlands. They are similar in many aspects and thus it is difficult to draw separate definition for these two environments. Since my study area is a coastal wetland the literature review deals with only Coastal Wetlands only.

The Vembanad Lake, Kerala is also a coastal wetland. The nature of the wetland is similar to an estuary as a number of rivers fall into it. Vembanad Lake is characterized

by impounded water, with water currents and circulations as found in lakes. It can be classified as a coastal lagoon because Vembanad Lake is a brackish water lake separated from the Arabian Sea by a narrow strip of sand barrier and has a restricted connection with the sea. This satisfies the required characteristics for being called a 'coastal lagoon'.

1.2 COASTAL LAGOON

Pritchard (1952) has given the definition of estuaries based on the geomorphological structure of coastal systems. He divided estuaries into:

a) Coastal plain/ drowned river valley estuary

b) Fjord estuary

c) Bar-build estuary

d) Tectonically formed estuary.

Pritchard (1952) defined estuary as *a semi enclosed coastal body of water having a free connection with the open sea and containing a measurable quantity of sea salt.* Thus, Kjerfve (1996) classified the inland coastal ocean-connected waters into six categories:

1) *Estuary*: an inland river valley or section of the coastal plain, drowned as the sea invaded the lower course of the river during the Holocene sea-level rise. E.g. Chesapeake Bay and Charleston Harbor-Cooper River system in USA, Ganges-Bhramaputra Estuary etc.

2) *Coastal Lagoon*: an inland water body, usually oriented parallel to the coast, separated from the ocean by a barrier, connected to the ocean by one or more restricted inlets, and having depths which seldom exceed a couple of meters. A lagoon may or may not be subject to tidal mixing, and salinity can vary from fresh-water to hypersaline waters. Lagoons have been formed due to rising sea level during Holocene or Pleistocene and building of coastal barriers due to marine processes. E.g. Laguna de Terminos, Mexico, Lagoa dos Patos, Brazil, Coorong, Australia and The Vembanad Lake, Kerela can also be put into this category.

3) *Fjord*: a glacially scoured inland marine area with sea water measurably diluted by land drainage in the surface layer, consisting of high salinity waters in deep basins, affected by tides, and usually several meters deep. E.g. Oslofjorden, Norway.

4) *Bay*: a coastal indentation, usually the result of faulting or other tectonic processes, strongly affected by tides, exhibiting a range of salinity from oceanic to brackish. E.g. San Francisco Bay, USA, Tokyo Bay, Japan, Baia de Guanabara, Brazil.

5) *Tidal River*: an inland river valley, drowned as the sea invaded the lower reaches of the river during the Holocene sea level rise, containing only fresh water but subject to tidal variations and tidal currents in the downstream section. E.g. Lower Amazon River, Brazil.

6) *Strait*: an inland marine waterway, connecting two sea or oceans. Characteristics of sea straits with respect to circulation, salinity distribution, tidal processes and water depth vary widely between the straits. E.g. Strait of Magellan, Chile

Thus, the definition for a *coastal lagoon is a shallow coastal water body separated from the ocean by barrier, connected at least intermittently to the ocean by one or more restricted inlets, and usually oriented shore-parallel.* Coastal lagoons occupy 13% of coastal areas world-wide and are effected by natural and anthropogenic influences (Mee, 1978; Sikora and Kjerfve, 1985).

Barrier coasts are backed by lagoons and measure 32,068 km. of world's coastline (Fig. 1.1).
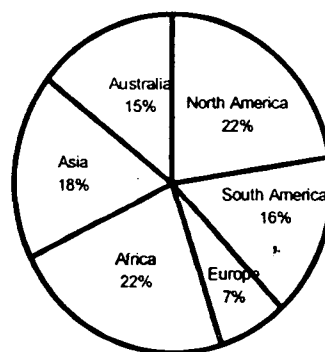
Figure: 1.1: Contribution of lagoons to the Coastline.

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Along the Indian Coast there are numerous water bodies that can be called as coastal lagoons (Tab- 1.1). Some of the well known along the west coast are the Cochin Backwaters, Vembanad Lake, Asthamudi Lake, Veli Lake, Kadinakulam Lake, Paravoor Lake, Cambarjua canal and lagoon system associated with Mandovi and Zuari rivers estuaries, Goa. The lagoonal sysems along the East coast are Mandapam, Killei backwaters, Pichavaram mangroves, Pulicut lake and Chilka Lake (Wetlands Of India, 1990).

The size of the coastal lagoon varies substantially with surface area ranging upto 10,200 km^2 as in case of Lagoa dos Patos, Brazil. The water depth is typically 1-3 m and always less than 5-m exception to inlet and isolated holes. Coastal Lagoons acct as material sinks or material filters as they trap inorganic sediments and organic matter in them. They are short-lived landscape features with their existence on basis of filtering efficiency and rate of relative sea-level changes in response to human activities, global climate change and local tectonics(Knoppers, 1994).

Coastal lagoons experience of force from river input, wind stress, tides, precipitation to evaporation balance, and surface heat balance and respond to these factors variably. Water and salt balance, water quality and eutrophication of the lagoon depend on lagoon circulation. Salt and water exchange with ocean, and turn-over, residence or flushing time.

Kjerfve (1986) sub-divided coastal lagoons into three geomorphic types according to water exchange with the coastal ocean. These are:

1) *Choked Lagoons*: These usually consist of a series of connected elliptical cells, connected by a single long narrow entrance channel, along coasts with high energy waves and significant littoral drift. The tides in the lagoon co-oscillates with tides in the ocean but the entrance channel serves as a dynamic filter which often reduces the tidal oscillations in the choked lagoons to 5% or less compared to the adjacent coastal tides. Long flushing times, dominant wind forcing, and intermittent stratification events due to solar radiation or runoff events also characterize these lagoons. In arid and semi-arid regions the coastal choked lagoons are permanently or temporarily

Table 1.1: Comparative Data of Coastal Lagoons.

Lagoon	Type	Mean Depth (m)	Area (Km.^{2})	Entrance to Sea	Primary Production (gCm^{-2}yr^{-1})
Tropical and Sub-Tropical					
Vembanad Lake, India	Leaky	3.5	500	2	124
Chilka Lake, India	Choked	1.5	896	1	-
Lake Songkla, Thiland	Choked	2	1,040	1	-
Terminos, Mexico	Restricted	3.5	2,500	2	228
Patos, Brazil	Choked	2.5	10,360	1	50
Cianaga Grande, Colombia	Choked	1.6	423	1	1555
Langebaana, S.Africa	Restricted	3.0	35	2	653
Mukwe, Ghana	Restricted	0.5	0.4	-	416
Apalichola Bay, USA	Leaky	-	688	-	370
Asthamudi Lake, India	Restricted	-	32	1	-
Kovalam Lake, India	Restricted	-	2.4	-	-
Pulicut Lake, India	Chocked	1.0	4,403	1	-
Sunderbans, India	Resticted	-	4,200	-	-
Kolleru Lake, India	-	0.5	350	-	125
Temperate					
Beaufort, USA	Leaky	-	4.1	-	115
Alewife Cove, USA	Choked	1	0.2	1	348
Hemstead Bay, USA	Restricted	1.5	46.5	2	281
Wadden Sea, Netherlands	Leaky	3.6	770	2	150
Ems-Dollard, Netherlands	Leaky	3.0	480	-	130-400
Mediterranean					
Biguglia, France	Choked	1.5	14.5	1	289
Diana, France	Choked	6.0	5.7	1	183
Edku, Egypt	Choked	1	-	1	475
Mariut, Egypt	Choked	1	-	-	1847

From: Knoppers, B (1994)

      WWF, 1992

      Weltlands of India, 1990

hypersaline (Moore and Slinn, 1984). Choked lagoons are oriented shore parallel but are sometimes found associated with river deltas. E.g. Lagoa dos Patos, Brazil; Lake St. Lucia, South Africa; Coorong, Australia; Lake Songkla, Thailand.

2) *Restricted Lagoons*: These consist of large and wide water body, oriented shore-parallel, and exhibiting two or more entrance channel or inlets. Thus, restricted lagoons have well-defined tidal circulation, are influenced by winds, vertical mixing, and salinities from brackish to oceanic. Flushing times are shorter than choked lagoons. E.g. Laguna de Terminos, Mexico; Lake Pontchartrain, USA.

3) *Leaky Lagoons*: These are elongated shore-parallel water bodies with many ocean entrance channels along coasts where tidal currents are strong enough to overcome the tendencies by wave action and littoral drift to close the channel entrances. These have salinities close to that of coastal sea, as the water exchange is unimpaired through the numerous channels. .E.g. Mississippi Sound, USA; Wadden Zee, Denmark.
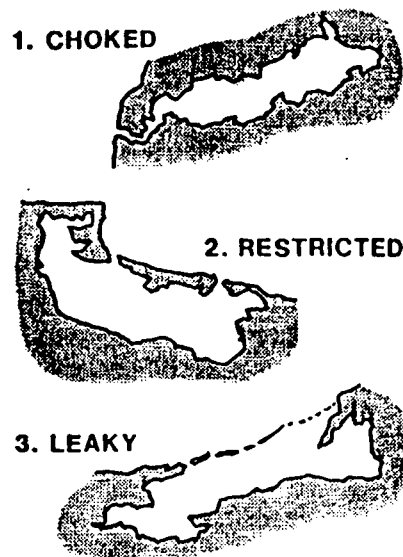
Figure 1.2: Types of coastal Lagoons.

1.2.1 GEOMORPHOLOGY

The geomorphology of a coastal lagoon system depends on a range of hydrological, geological, climatic and ecological factors. The shape of inlet, embayment and shape of the barrier that develops across its mouth determine the configuration of the lagoon.

If the barrier is complete or entrances small, so that marine influences are reduced than the lagoon develops in the manner of a freshwater lake. Sediments carried in are deposited along the shore, there is a reduction in the depth. The shape of the contracting lagoon is related to wave conditions and winds.

More brackish but relative tide less lagoons have little or no shoreline vegetation and are bordered by beaches, splits and cuspate features built and shaped by the action of lagoon waves. Salt marsh or mangroves borders lagoons having permanent entrance from the sea. Their floors have shoals. Such lagoons have features similar to river estuaries and are regarded as estuarine lagoons. Many lagoons are estuarine in vicinity to tidal entrance, brackish and less tidal in central zone and fresh, dominated by inflowing rivers, away from the tidal entrance.

1.3 METHANE

One of the major concern for the global environment is the rapid increase in the concentration of long lived trace gases such as CO_2, CH_4 and N_2O (Tab- 1.2). The total annual global methane emissions are estimated to be 420-620Tg y^{-1} (Khalil and Rasmussen, 1990) of which 70-80% is of biogenic origin.

Atmospheric CH_4 concentrations has doubled in past 200 yrs., raising over past 15 yrs. By an average of 1% per year (Tab- 1.3). This increase began in historic times but has been accelerated in recent years. Ice core samples show that methane has more than doubled overall in last few hundred years after being relatively stable at a value of about 0.7 ppmv since the last ice age up through about 300 years before present (Craig and Chou, 1982: Rusmussen and Khalil, 1984: Pearman et al., 1986). Recent analysis of air bubbles in the older ice cores extend the records back to 100,000 years before present

(Stauffer et al., 1988) and 160,000 years before present (Raynaud et al., 1988). During the glacial maxima the methane concentration fell to about 0.35 ppmv while interglacial value of about 0.65 ppmv, a close estimate of pre-industrial value. Explanations for the recent increase include increase in some methane sources, decrease in methane sinks or a combination of both (Khalil and Rasmussen, 1985; Cicerone and Oremland, 1988; Prinn, 1994).

Trace gases in the atmosphere determine the current state by directly or indirectly affecting the climate of the Earth. Gases are radiatively active, such as CO_2, H_2O (g), O_3, CH_4 and CFC's contribute directly to the green house effect of the atmosphere. Their chemical life times are long except for O_3. All the chemical constituents undergo complex cycles that are biologically mediated and can be perturbed by human activities. The Earth's atmosphere is influenced by the emissions of trace gases from the terrestrial and marine biosphere and by uptake of same by biota over continent and ocean.

1.3.1 METHANOGENIC ECOSYSTEMS

Methanogenesis is the process by which organic matter is degraded to methane under anoxic conditions. Following are the environment in which methanogenesis can take place:

Nonsaline Environments

Acetate is the major substrate for methanogenesis in most nonsaline environment Acetic acid is formed by many fermentative bacteria and then consumed by methanogens so the acetate concentration remains low in the environment. Interaction between methanogens and nonmethanogens in nonsaline environment is seen.

Saline Environments

Most saline environment contain sulfate, so sulfate reducers outcompete methanogens for substrates. When sulfate is abundant. the sulfate-reducing bacteria grow by oxidizing acetate, formate and H_2 and reducing sulfate to sulfide. These activities lower the concentration of acetate, formate and H_2 to lower than can be utilized by the methanogens. However, sulfate reducers do not catabolize some methyl compounds as

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Table 1.2 : Sources and sinks of methane in the environment.

METHANE SOURCES	METHANE (Tg/year)
Natural methane sources	*160 (110-210)*
Wetlands	**115 (55-150)**
Termites	**20 (10- 50)**
Oceans	**10 (5- 50)**
Other	15 (10- 40)
Anthropogenic sources, fossil fuel related	*100 (70-120)*
Natural gas	**40 (25- 50)**
Coal mines	**30 (15- 45)**
Petroleum industry	15 (5- 30)
Coal combustion	? (1- 30)
Anthropogenic sources, biospheric carbon	*275 (200-350)*
Enteric fermentation [*]	**85 (65-100)**
Rice paddies	**60 (20-100)**
Biomass burning	**40 (20- 80)**
Landfills	**40 (20- 70)**
Animal waste	25 (20- 30)
Domestic sewage	**25 (15- 80)**
METHANE SINKS	**METHANE (Tg/year)**
Methane sinks	*560 (460-660)*
Troposphere, oxid. by OH	490 (405-575)
Stratosphere	40 (32- 48)
Removal by soil microbes	30 (15- 45)
Increase of atmospheric methane	*37 (35- 40)*
Total identified methane sources	535 (410-660)
Natural	160 (110-210)
Anthropogenic	375 (300-450)
Total methane sinks + atmospheric increase	597 (495-700)

[*] mostly belching cattle

Sources in bold letters are major sources

Source: IPCC 95

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Table 1.3: Comparative Methane emissions rates from various sources from 1990 to 1994. (Methane / year in Tg)

SOURCE OF METHANE	IPCC 90	IPCC 92	IPCC 94
Wetlands	115 (100-200)	115 (100-200)	115 (55-150)
Termites	40 (10-100)	20 (10- 50)	20 (10- 50)
Oceans	10 (5- 20)	10 (5- 20)	10 (5- 50)
Natural gas	45 (25- 50)	- -	40 (25- 50)
Coal mining	35 (19- 50)	- -	30 (15- 45)
Enteric ferment.	80 (65-100)	80 (65-100)	85 (65-100)
Rice paddies	110 (25-170)	60 (20-150)	60 (20-100)
Biomass burning	40 (20- 80)	40 (20- 80)	40 (20- 80)
Landfills	40 (20- 70)	30 (20- 70)	40 (20- 70)
Domestic sewage	- -	25 (?)	25 (15- 80)

trimethylamine, dimethylsulfide and methanol, so methanogens convert these substrates into methane.

Gastrointestinal Tracts

The rapid turnover of organic matter in gastrointestinal tracts prevents complete anaerobic decomposition because some methanogens and fatty acid-degrading bacteria cannot grow rapidly enough to maintain large populations. However, H_2- and formate-using methanogens are found in many gastrointestinal tracts such as those of the rumens of ungulates (cattle, sheep, deer, etc.) and the lower digestive tracts of herbivores, some insects, and some humans which causes methane production.

1.3.2 PRODUCTION OF METHANE

Methane is produced microbiologicaly in anaerobic environment where O_2 and SO_4 are scarce: swamps, peat bogs, wetlands, paddies and intestinal tracts of animals and termites. Microorganisms can remove CH_4 from the environment through aerobic and

anaerobic (Alperin and Reebugh, 1984) oxidation. In lakes the aerobic methane oxidation occurs in the water column and anaerobic oxidation occurs in the sediments. Soil is also an aerobic sink of atmosphere methane.

In anaerobic conditions, organic carbon is converted to methane and CO_2 by microbial food chain that includes fermentative, acetogenic and methanogenic bacteria. The methanogens are the terminal bacteria in this food chain. The metabolic activity of these organisms is through the process "interspecies hydrogen transfer". Fermentative organisms can convert large organic molecules to low-molecular weight acids and CO_2 and molecular H_2, which acts as the feed-back inhibitor. Methanogens enhance the activity of the fermentation process by removing the hydrogen and hence reducing the feed-back inhibition. Interspecies hydrogen transfer increases carbon turnover, production of more oxidized end- products , greater energy conservation for the fermentative organisms, increased growth of al organisms and displacement of unfavorable reaction equilibra. This results in complete transformation of organic carbon to methane in anaerobic environment

Low porosity, water saturation and high organic content results in anaerobicity and slow diffusion of CH_4 to the atmosphere Due to slow diffusion, a significant fraction is lost through the aerobic and anaerobic oxidation before methane can leave the sediment. Anaerobic oxidation of methane is well documented in sulfate-containing sediments and aerobic waters (Cicerone and Oremland, 1988), little is known about the organisms involved. The gas that diffuses into the aerobic zone is metabolized by methanotropic bacteria present in large numbers in or at the periphery of anaerobic zones. Methanotropes (esp. family *Methylococcaceae*) can obtain all of their carbon and energy from methane under aerobic conditions (Whittenbury and Kreig, 1984).

Diffusion is not the only process for release of methane from the sediments to the atmosphere Methane has low solubility in water; hence it forms bubbles which can escape into the overlying water and then into the atmosphere. Aquatic plants can also provide a path-way for transfer of gases to the atmosphere (Dacey and Klug, 1979).

1.3.3 BIOCHEMISTRY OF METHANE FORMATION

The biochemical pathways for microbial formation of methane have been documented (Vogels et al., 1988; Whitman, 1985; Jones et al., 1987). The major reactions of methanogenisis from carbon dioxide, acetate, and methylated substrates are summarized below in Figure 1.3.

Methanogens live in environment where their catabolic reactions yield very small amount energy. Some methanogens grow by splitting acetate to methane and carbon dioxide, which yields -35.8 kJ/mol under standard conditions. However, concentration of acetate in methanogenic environment are much lower; the threshold above which the acetate is degraded is about $70 \mu M$ (Westermann et al., 1989). At the level of carbon dioxide (30 kPa) and methane (2.5 kPa), the free-energy change for methanogenesis from acetate is -21.8 kJ/mol. (Boorne and Xun, 1987). Thus, the mechanism for coupling ATP formation to methanogenesis must allow production of less than 1 mol of ATP per mol of methane formed.

1.3.4 ENVIRONMENTAL FACTORS EFFECTING PRODUCTION OF METHANE

The rate of input of biogenic methane to the atmosphere depends on two biological processes, methanogenesis and methane oxidation. Following conditions are required for methane production.

Anoxia

Methanogens are the most sensitive to oxygen. The presence of O_2 inhibits methanogenesis by its toxic effects on methanogens and the toxic effects of by-products of O_2, such as superoxide or singlet oxygen. In addition, O_2 stimulates the activity of bacteria, which can outcomptete the methanogens for reduced catabolic substrates. Other electron acceptors such as nitrate, ferric, and sulfate ions can also stimulate activity of organisms, which compete with methanogens. When these electron acceptors are present, concentrations of acetate, formate, and H_2 are maintained at levels so low that methanogens are unable to use them as catabolic substrates (Conrad et al., 1989; Neue and Roger, 1993).

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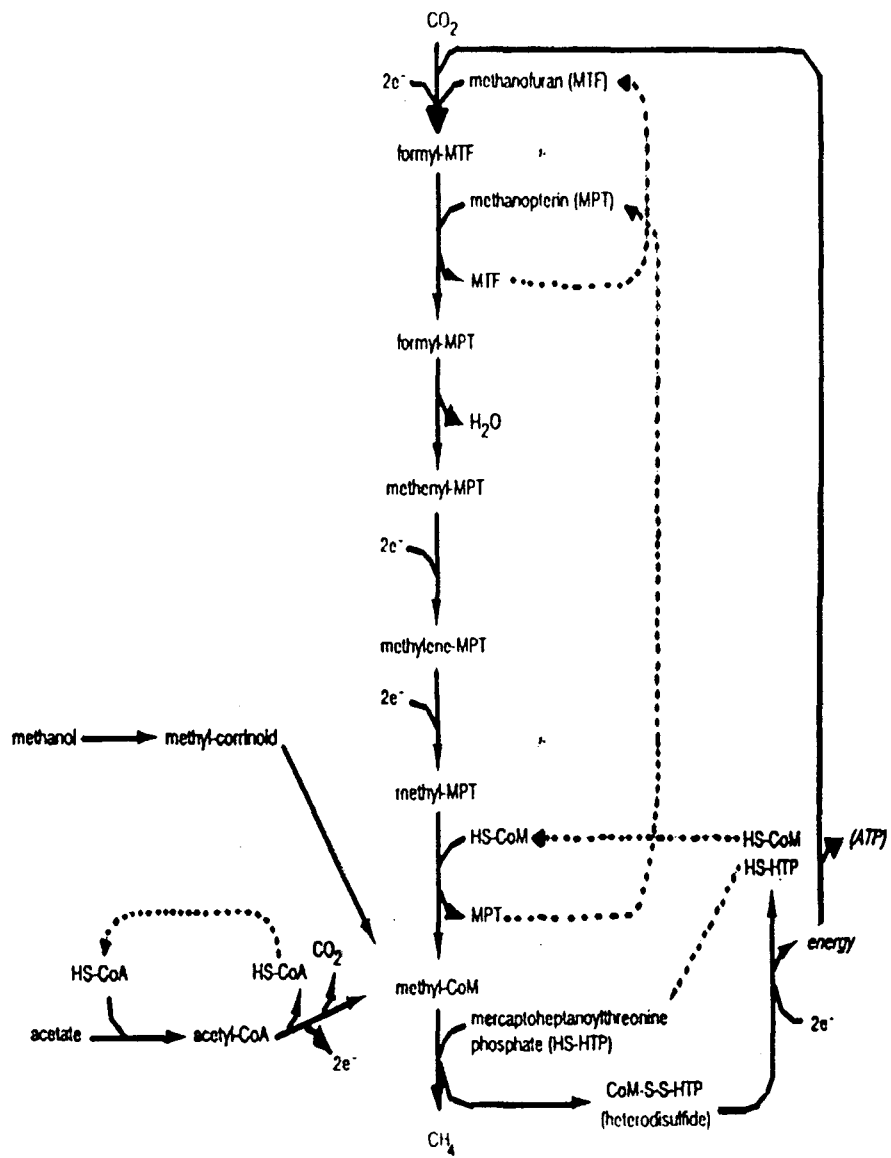
Figure 1.3: Pathway of methane formation

Organic Matter

Yagi and Minami (1990), Parasharet al. (1991), and Singh et al. (1998) have shown that organic matter supply and substrate quality are important for methane production and emissions from wetlands and paddy fields. Very high additions of organic matter in wetland paddies may suppress methane emissions due to formation of toxic metabolic end-products. Neue et al. (1990) insisted that soil and flood water regimes interact with climate through temperature effects, heat capacity and thermal conductivity and water flow.

Temperature

Temperature of sediments and water effects the methane production. A temperature of 30-32 ° C seems to be optimum for methane production (Inubushi et al. 1990). Temperature has effect on methanogens and methane diffusion, which incerases with temperature (Parashar et al. 1991; Verma et al. 1999). In Elbe river marshland, methane production shows temperature optima at 20°C (Wagner et al. 1997).

pH

Methane production is favoured by a pH of 6.0 to 7.7 (DeLaune et al. 1986), the optimum is influenced by the soil type, soil temperature and strain of methanogens (Kimura et al., 1992). Wang et al.. (1993) found the optimum pH for CH_4 production is near neutral and is also supported by studies of Singh et al. (1995). The effect of the hydrological regime on soil pH and redox potential is thus important (Ponnemperuma, 1984). Neue et al. (1992) indicated that a redox potential below -150 to -190 mV, corrected to pH of 7, is required for methanogenesis. Low pH inhibits methane production even through substantial methane fluxes have been observed from acidic bogs. Higher methane concentration and fluxes have been observed in more alkaline bogs or edge areas (pH 4.6 to 5.0) than in the more acidic central regions (pH 3.7 to 4.5) of the same bogs in Minnesota (Crill et al.. 1988).

Electron Acceptors Other than O_2

Electron acceptors other than O_2 may also inhibit methanogenesis by stimulating the activity of bacteria, which outcompete methanogens for the reduced substrates. These acceptors include nitrate, nitrite, trimethylamine oxide, Fe (III), Mn(IV), and sulfate.

These substances tend to disappear with depth in sediment, because as they diffuse downward they are reduced by the catabolic activities of resident bacteria. The order in which these compounds disappear is approximately the order listed and is generally consistent with the redox potential at which the substances function as electron acceptors.

Soil Texture and Mineralogy

Soil texture and mineralogy has effect on puddling, effect percolation rates and thus effect net methane emissions in waterlogged paddy soils (Neue et al. 1990; Parashar et al. 1991). Heavy clay soil may crack upon drying, facilitating the rapid release of entrapped methane, while in slowly cracking soils, there is more time for methane to be oxidised in the soil (Neue et al. 1990). Bender and Conrad (1994) showed that bulk of the methane oxidizing activity is attached with the small mineral fractions (clay, silt and fine sand). Within the mineral fraction greater particles have higher specific activities of methane oxidition than smaller particles.

1.3.5 METHANE CHEMISTRY

Methane is actively involved in atmosphere chemistry. Its chemistry is initiated by reaction with OH radicals to form methyl radicals and water as:

$$CH_4 + OH \Rightarrow CH_3 + H_2O \tag{1}$$

This reaction is slow (methane atmospheric lifetime is 8 to 10 years), the relatively high concentration makes this reaction an important in regulating OH concentration in the atmosphere (Logan et al., 1981). Increasing concentration of methane can reduce the oxidizing power of atmosphere thus increasing the lifetime for other atmosphere pollutants.

The complete oxidation of methane leads to formation of carbon dioxide and water. The intermediate products formed during methane oxidation depends upon the nitrogen oxide (NOx) concentration in the atmosphere (Levine et al., 1985; Thompson and Cicerone, 1986). In high NOx environment, methane oxidation produces ozone and hydrogen oxides. (M represents the third molecule that acts as an energy-absorbing collision partner to help stabilize the reaction product).

$$CH_3 + O_2 + M \Rightarrow CH_3O_2 + M \tag{2}$$

$$CH_3O_2 + NO \Rightarrow CH_3O + NO_2 \qquad (3)$$
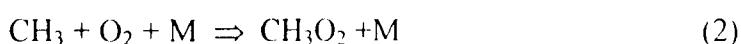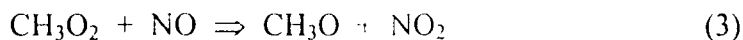
NO_2 is then photolysed, and subsequently produces O_3. An important intermediate product is formaldehyde (CH_2O), which is formed as:

$$CH_3O + O_2 \Rightarrow CH_2O + HO_2 \qquad (4)$$
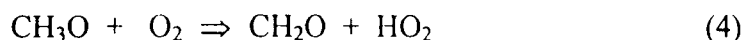
This reaction returns HO_2 to the atmosphere to balance the HOx lost in reaction 1. Formaldehyde is then oxidized to CO and may lead to increase in OH radicals. In low NOx environment, methane oxidation consumes O_3 and HOx in producing carbon dioxide, H_2O and H_2 (Crutzen, 1987). The sequence of reaction is:

$$CH_3O_2 + HO_2 \Rightarrow CH_3OOH + O_2 \qquad (5)$$

The methane that reaches the stratosphere is almost entirely consumed by OH, Cl atoms and other oxidants. In the stratosphere, methane oxidation may increase H_2O vapor concentration by about 50% over the stratosphere had there been no methane (Ramanathan et al., 1987). The resulting water vapor is involved in heterogeneous chemistry as one responsible for Antarctic Ozone Hole. Methane reaction with Cl atoms forms HCl, is one of the way which takes Cl out of the Cl-catalytic chain which destroys ozone. The reaction involved is:

$$CH_4 + Cl \Rightarrow CH_3 + HCl \qquad (6)$$
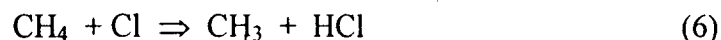
1.3.6 METHANE OXIDATION

Only a small percentage of the gross methane production escapes from the methanogenic habitats into the atmosphere.. A large fraction of the methane formed is consumed by methane-oxidizing bacteria before it can leave the system (Neue and Roger, 1993; Singh, 1995). Methane oxidation occurs both aerobically and anaerobically.

Aerobic Oxidation

Methanotropic bacteria have the ability to utilize methane as source of energy and carbon source during growth. In natural systems, aerobic methane oxidation activity is at or near the interface of oxic and anoxic conditions (Rudd and Taylor, 1980). This is a zone where methane diffuses from the anoxic environment to the oxygenated zone. Oxygen and nitrogen concentration are important factors controlling the oxidation of

methane. Since the substrate supplies no nitrogen, methane oxiders require an external source of combined nitrogen. Most methane oxidisers are capable of fixing dinitrogen (DeBontet al., 1976), only when the oxygen concentration is relatively lower.

In wetland habitats, soil interface is overlain by only a thin film of water, light may become a major controlling factor of methane oxidation and methane release to the atmosphere..

Anaerobic Oxidation

Anaerobic methane oxidation accounts for removal of a large fraction of methane in saline environment. In most cases, any methane passing the anaerobic oxidation zone also passes through the aerobic oxidation zone before reaching the atmosphere. Further, anaerobic methane removal also influences its transport via processes other than diffusion.

Reeburgh and Heggie (1977), Martens and Berner (1977), and Alperin and Reeburgh (1984) have argued from geochemical evidence (methane profile and δ 13 CO2 distribution) that significant methane oxidation takes place in marine sediments but not in fresh- water sediments. This difference is due to sulfate as an oxidant of methane in saline systems. In some marine sediments , anaerobic oxidation removes virtually all methane before it reaches the aerobic zone. However, in certain environment there is no anaerobic methane oxidation or the process not significant. The microbial process involved in anaerobic methane oxidation by methanotrops has been studied by Mancinelli et al. (1991).

1.3.7 METHANE FLUXES FROM WETLANDS

Latitudinal Variability

Wetlands are not equally disturbed across latitudinal zones, and so wetlands will have a different impact on the CH₄ budget latitudes. The variability of the measured fluxes within a climatic zone is greater than the variability between zones. We know that particular wetland types tend to dominate certain latitudes (Matthews and Fung, 1987; Aselmann and Crutzen, 1989) mainly because large-scale patterns of temperature and

rainfall occur over broad latitudinal bands. The result is that latitudinal differences in the wetlands, their aerial extent, and the length of their active season. (Table: 1.4).

High-latitude wetlands

Tundra wetlands are arielly very extensive (8.8 X 10 12 m 2 [Postma et al., 1982]) and continuous. Their most common feature is that they are underlain by permafrost. In these regions methane emission is strongly seasonal. When surface organic soil becomes saturated with water at spring thaw, methane production begins and rises rapidly to maximum rate and continues untill the freeze-up in fall. The production can continue to fall if there is an insulating layer of moss or snow.

Between the permafrost regions and 45°N there many wetlands. These all northern wetlands are marked by large amounts of 'dead" organic matter as peat soils. There is also strong seasonal variation in methane flux due to cold conditions in winters.

Low-latitude wetlands

These wetlands show bimodal distribution with a minimum in the temperate zones (Matthews and Fung, 1987: Aselmann and Crutzen, 1989). There is less seasonal temperature variation in lower latitudes. The seasonal cycle of methane flux is associated with the seasonal cycle of inundation and plant growth and soil saturation. Plants are also important in the physical transport of methane from the anaerobic soils to atmosphere. (Dacey and Klug, 1979; Sebacher et al., 1985). Ebullition is also important mechanism of release for methane in lower latitudes (Bartlett et al., 1988).

Low methane fluxes are observed in highly saline wetlands such as salt marshes or coastal mangroves. Lower concentration of methane flux in fresh-water wetlands is a result of lower organic substrate concentration.

1.3.8 METHANE AND GREENHOUSE EFFECT

Methane's role in global warming is both direct and indirect. CH_4 is a strong absorber of the infra-red portion of the electromagnetic spectrum. Its strong absorption is at about 7.7 µm, a wavelength at which no other atmospheric gas strongly absorbs. Thus, methane is a larger contributor to the total greenhouse effect (Figure: 1.4). The ratio of the infrared absorption and mean residence time terms show that methane to be about 25

Table 1.4: Methane Emission rates from Natural Wetlands.

Source	Methane Flux Rate $(mg\ m^{-2}\ d^{-1})$	Referance
Freshwater Environments		
Water logged, Michigan, USA	110	Baker-Blocker, 1977
Cypress, Waterlogged. S.Carolina, USA	10	Harriss and Sebacher, 1981
Cypress, Fertilized, Florida, USA	970	-do-
Dismal swamp, Virginia, USA	-5	Harriss et al. 1982
Panicum Marsh, Louisiana, USA	440	Delaune et al. 1983
Boreal Marsh, Alaska, USA	106	Sebacher et al. 1986
Tropical Flooting grassmats, Amazon, Brazil	590	Devol et al. 1988
Bog, Minnesota, USA	159	Harriss et al. 1985
Fens, Minnesota, USA	3	-do-
Shoreline Fens, Minnesota, USA	664	-do-
Alpine fens, Alaska, USA	289	Sebacher et al. 1986
Coasstal Tundra, Alaska, USA	119	Sebacher et al. 1986
Moss, Alaska, USA	0.4	Reeburgh, 1989
Manaus Lake, Brazil	27	Bartlett et al. 1988
Lake Miramar, California, USA	2.39	Cicerone et al. 1981
Lake Hodges, California, USA	786	-do-
Lake Guajome, California, USA	36.5	-do-
Adyar River, India	320	Ramesh et al. 1997
Mississippi River Delta, USA	251	Alford et al. 1997
Salt water Environment		
Salt Marsh, Georgia, USA	1.2	King and Wiebe, 1978
Adyar River Estuary, India	38	Verma&Subramanian, 1999
Salt Meadow, Virginia, USA	1	Bartlett et al. 1985
Brackish Spart, Virginia, USA	79	Bartlett et al. 1987
Penasquitos Marsh, California, USA	0.25	Cicerone et al. 1981
Batiquitos Lagoon, California, USA	2.32	-do-
Ennore Estuary, India	0.12	Ramesh et al. 1997
Buckingham Canal, India	3.45	-do-
Vellar-Coleroon Estuary, India	1.6	-do-
Bay of Bengal, India	1.97	-do-
Arabian Sea	3.15	Lal et al. 1996

to 30 times more effective as a greenhouse gas than carbon dioxide on a per-molecular basis (IPCC, 1992).
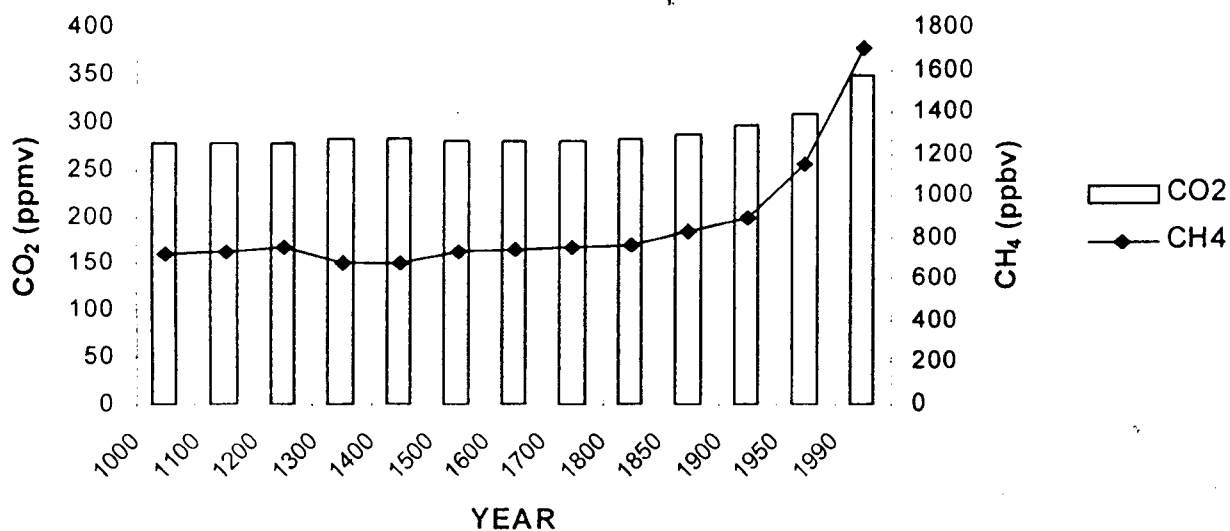
Figure 1.4: Variation in CO2 and CH4 concentration in the atmosphere from 1000 to 1990.

There are many indirect ways that increasing CH_4 can effect global warming. Oxidation of CH_4 produces CO, which gets converted to CO_2. Cicerone and Oremland (1988) calculated the production of CO_2 from atmosphere CH_4 is about 6% as the direct release of CO_2 from anthropogenic sources. Another indirect effect is the chemical production of tropospheric O_3, another strong greenhouse gas, in presence of NOx.

When a comparison of relative greenhouse warming effect of CH_4 verses that of CO_2 takes into account the longer residence time of CO_2, the CH_4 is about 2.1 to 4.9 more effective as a greenhouse gas than CO_2 (Lassey et al., 1990).

1.4 AMINO ACIDS

Organic matter is transported from rivers to ocean and is an important link in biogeochemical cycling of carbon between land and ocean. Total organic matter

transported by rivers annually in low (~ 0.5 x 10^{15} g C a^{-1}) as compared to amount of carbon within soils of earth ~1515 x 10^{15} g C (Schlisinger, 1984) and in ocean 40 600 x 10^{15} g C (JGOFS, 1992).

Coastal lagoons viz. estuaries receive organic matter derived from terrestrial source through runoff and rivers (allochthonous) or from organic matter within the lake (autochthonous). The zone of vigorous biological activity is confined to upper few decimeter of sediments depending on the availability of oxygen and other factors (Degens, 1976).

There is loss of organic carbon during sedimentation and there is decrease in concentration of specific organic substances particularly amino acids, carbohydrates and fatty acids. Concentration of these substances is highest at sediment surface. After burial they show marked loss relative to organic carbon. For amino acids the concentration decreases to zero or almost zero within first few meters (Degens, 1976).

Many of the post-depositional changes which occur in recent marine sediments are either directly or indirectly related to the microbially mediated degradation of organic matter (Berner, 1980). In coastal environments this process is significant in regenerating nutrient elements such as nitrogen and phosphorous (Nixon et al., 1982). The quality and quantity of organic matter plays an important role in organic matter remineralization in sediments.

Amino acids are building blocks of protein and are the largest component of organic nitrogen in most organisms. In marine sediments, amino acids are found as protenious material and incorporated in abiotic "geopolymers" as humic substances (Burdige and Martens, 1988).

Most of the amino acids found in particulate matter originate from marine planktons in sinking particles in ocean (Lee and Cronin, 1984). For every 10-fold increase in productivity the flux of amino acids increased by 250-fold. Amino acids account for about 75-90% of nitrogen present in planktons. The most common amino acids are gly, ala, glu and asp.

Amino acids (AA) and hexosamine (HA) are the most easily degradable constituent of organic matter. The decrease in bulk protein AA's relative to bulk non-

protein AA's in samples may result from the preferential decomposition of protein AA's, that are easily digestible. Non-protein AA's β–ala (β-ala) and γ- aminobutyric acid (γ-aba) in sediments are enzymatically-decomposed products of aspartic acid and glutamic acid (Lee and Cronin, 1982). Ratios of Asp/β-ala and Glu/γ-aba, have been used as indicators of degree of microbial degradation (Degens and Mopper, 1976; Ittekkot et al., 1984).

The ratio between Total Hydrolysable Amino Acid (THAA) and Total Hydrolysable Hexamine (THHA) indicates the nature of organic matter in terms of their relative degree of microbial reworking and their phyto- and zooplankton sources. The low THAA/THHA ratio, with HA mainly Glucoseamine (Gluam), is an indication of of large amounts of chitinous materials (Degens and Ittekkot, 1984).gluan is a major component of chitin whereas Galam (Galactoseamine) is present in trace amount in zooplankton (Muller et al., 1986).

Thus, amino acids have been used as an indicator for the nature of organic matter, its source and kind of depositional environment. A number of studies have been carried out in this area.

Kemp and Mudrochova (1973) Stated that the concentration of soluble combined AA is much greater than that of free AA's and are low in Lake Ontario. Ala, gly, val and leu are prominent free amino acids in the Lake. The study indicates a relation between the source of organic matter with soil nature. The nature organic matter is constant over the lake surface sediments. Amino acids comprise from 15 to 30% by weight of humic substances from carbonate and non-carbonate sediments (Carter and Mitterer, 1978). Nature and amount of particulate and dissolved amino acids in major world rivers and oceans have been studied by Ittekkot et al., 1986 and Haake et al., 1992. In India, Gupta et al. (1996) has studied the organic matter nature for Godavari River.

1.5 NUTRIENTS

Coastal lagoons are coupled with adjacent land and ocean system by exchange of water and particulate and dissolved materials. Materials enter the lagoons via stream runoff or ground water flow, accumulate in the sediments and are removed to the ocean

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without reaction. The lagoon-ocean system is complex. Tidal flow through the lagoons causes bi-directional exchange and mixing.

If a material moves through the lagoonal system in direct proportion to its relative abundance relative to some non-reactive material as salinity then this material is said to be "conservative' with respect to salinity, this means that the passage has no control on the fate of the material. If the material moves disproportional relative to a conservative tracer, it is said to be "non-conservative' with respect to the tracer. Materials, which are non-conservative, are of biogeochemical and ecological interest.

Nutrients as phosphorus, nitrogen, and carbon are non-conservative and hence of interest. They are also essential for biological productivity of the system. Nitrogen and phosphorus are present in low concentrations in unpolluted waters and are limiting for the growth of organisms in the system. Nutrient chemistry of coastal lagoon-lake have been dealt in a number of papers by Nixon (1982); Boutière et al. (1982); Vaulot and Frisoni (1986); Cossu et al. (1987) and Yáñez-Arancibia and Day (1988).

Net mass balance for lagoons has not been worked out in detail. If lagoons are considered to be net producers of organic matter, then they will be expected to take up dissolved nutrients from terrestrial and/or ocean exchange. If they are considered to be net consumers of organic matter, then net oxidation should release dissolved nutrients into the water and transported to the ocean. The 'net ecosystem stoichiometry' can be understood on the basis of 'Redfield Ratio'. General Redfield Ratio is used to describe the C:N:P ratio in organic matter or a locally appropriate modification thereof and is used to construct net chemical reactions for partition of carbon, nitrogen and phosphorus flux among organic matter(Richards, 1965).

Biogeochemical cycling refers to the biologically driven chemical transformations that underlie exchanges of water and nutrients between the biosphere and atmosphere, biosphere and geosphere, or biosphere and hydrosphere. Microorganisms are crucial to this recycling. An imbalance in a biogeochemical cycle will have dramatic consequences on a global scale. Microorganisms are intimately involved in the biogeochemical cycling of biological matter. Reservoirs are sources of elements. Not all

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reservoirs can be tapped by biological organisms. For instance, although the largest carbon reservoir is within rocks in the Earth's crust, this source is biologically useless since organisms do not perform reactions capable of utilizing it.

1.5.1 CARBON

Carbon in environment is present in atmosphere as CO_2 ("oxidized" carbon) in earth's atmosphere escaped from molten rock when it erupted and cooled on the earth surface. Photosynthesis in plants and algae converts atmospheric carbon dioxide and water into living tissue (biomass is a form of "reduced" carbon) releasing oxygen. Microbes and other organisms decompose biomass, thereby producing humus (another "reduced" form of carbon). Soil humus accounts for three times more "reduced" carbon than biomass. Many researcherss have tried to calculate global carbon cycle like Garrels and Mackemzic (1972), Meybeck (1982)., Kemp (1984), Meybeck (1993), Subramanian and Ittekkot (1997), Meybeck et al., (1999) and Subranmanian (1999).

Each year, photosynthetic organisms convert 14% of the total atmospheric carbon dioxide into biomass totaling about 100 billion metric tons. Half of this, 50 billion metric tons, is immediately respired by the plants and algae that fixed it. The remaining 50 billion metric tons is respired by organisms in the soil that comprise the decomposition food chain.

Respiration, which releases the energy stored in biomass and humus by combining it with atmospheric oxygen to release carbon dioxide and water, is very sensitive to changes in temperature while the photosynthetic rate does not change much with temperature. A global rise in temperature triggered by elevated carbon dioxide levels will create a positive feedback, which will further accelerate the rise in carbon dioxide levels and temperatures.

Anaerobic respiration of organic matter in wetlands and waterlogged soils is the primary source of methane. Methane is 20 times as effective as carbon dioxide trapping long-wavelength radiation from the earth. Global temperature increases could also stimulate the release of methane from wetlands. Anaerobic respiration uses the oxygen in

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biomass, residue and humus for respiration and produces the oxygen-free product methane (CH4).

There are five principle global carbon pools. These are fiven below in figure 1.5.

Rivers play an important role in terrestrial water cycle, mobilization and transport of constituents from land to coastal oceans. Riveraine carbon flux is a minor component in global carbon circulation (Meybeck, 1999). The riverine carbon transfer is given in table 1.5.

1.5.2 PHOSPHOROUS

Phosphorous is an important nutrient, which is necessary in small quantities for all plant and animal growth. The availability of phosphorous can influence both the growth of individual organisms and the productivity of entire ecosystems. Phosphorous is normally the limiting nutrient in aquatic systems. Many papers have illustrated the vital biogeochemical role of phosphorous in the environment. Eg. Meybeck, 1982; Winteringham, 1992; Meybeck 1993, Subramanian, 1999.

In freshwater systems, iron oxides are formed by the chemical reaction of iron with dissolved oxygen in the water column. These iron oxides adsorb phosphorous, trapping it in the sediment. This immobilization restricts the availability of phosphorous to organisms in the water column, resulting in a phosphorous limitation. Adsorbed phosphorous is recycled to the water column when iron oxides are chemically and biologically reduced to Fe+2 under anoxic conditions.

In saltwater systems, high sulfate concentrations in the water column cause more sulfate reduction in these sediments than in freshwater sediments, where sulfate concentrations are approximately 150 times lower. Sulfides produced as a byproduct of sulfate reduction react with iron to precipitate iron sulfides (FeS) and pyrite (FeS2, commonly known as "fool's gold") which are then stored in the sediments. Therefore, saltwater sediments contain a larger percentage of iron-sulfur compounds and a smaller percentage of iron oxides than freshwater sediments. The absence of large amounts of iron oxides in saltwater systems allows the phosphorous released during decomposition

Table 1.5: Riverine Carbon Transfer

Sources	Age (y)	Flux $(10^{12}gCy^{-1})$	Sensitivity to Global change					
			A	B	C	D	E	F
PIC								
Geologic	$10^4 - 10^8$	170	✓					✓
DIC								
Geologic	$10^4 - 10^8$	140		✓	✓			✓
Atmospheric	$0 - 10^2$	245		✓	✓			✓
DOC								
Soil	$10^0 - 10^3$	200			✓			✓
Pollution	$10^{-2} - 10^{-1}$	(15) ?					✓	
CO_2								
Atmospheric	0	(20 to 80)		✓	✓	✓		
POC								
Soil	$10^0 - 10^3$	(100)	✓					✓
Algal	10^{-2}	(< 10)				✓		✓
Pollution	$10^{-2} - 10^0$	(15)					✓	
Geologic	$10^4 - 10^8$	(80)	✓					✓

Where: A= Land Erosion, B= Chemical Weathering. C= Global warming and UV changes, D= Eutrophication, E= organic pollution, F= basin management.

From : Meybeck, 1999.

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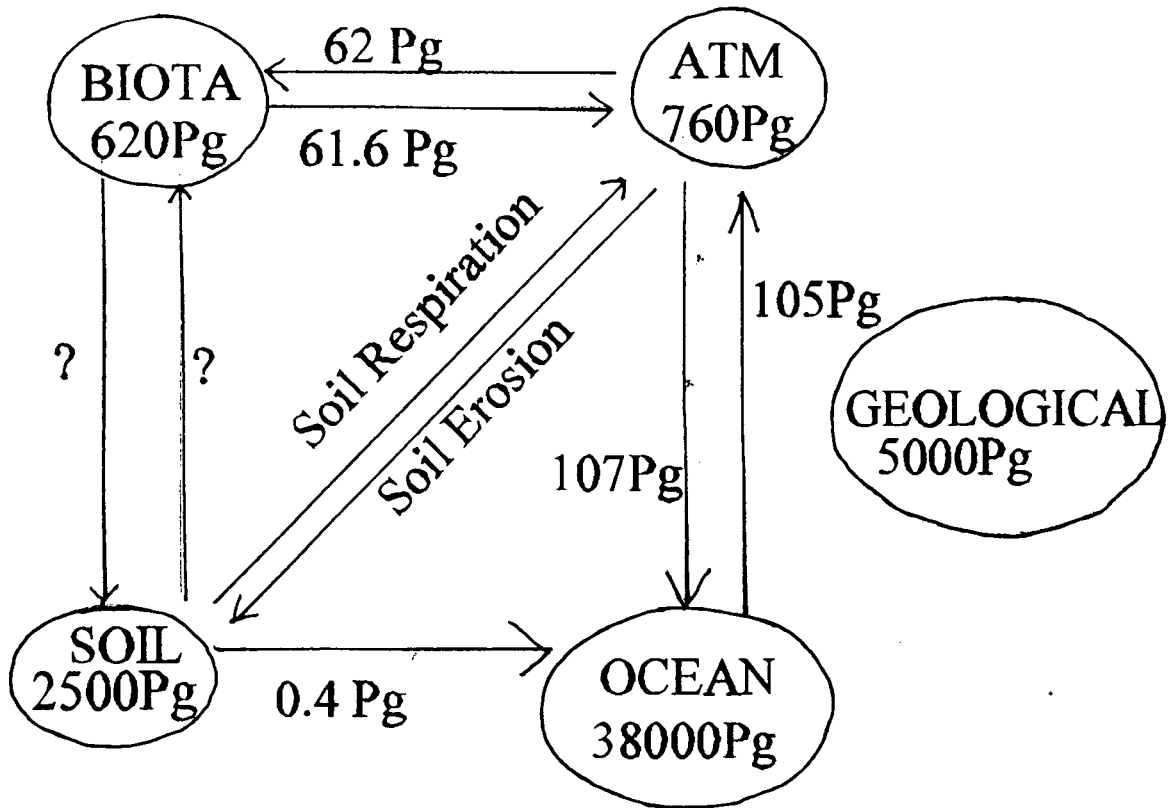
Figure 1.5: Various carbon pools in the environment (From Lal, 1999); 1 Pg = 10^{12} g.

to diffuse into the water column. Phosphorous limitations are consequently not as prevalent in saltwater systems as in freshwater systems.

Differences in phosphorous availability among salt and freshwater environments are caused by differences in water column sulfate concentrations, sediment iron content, and water column oxygen conditions. Projected Global phosphorous flow for year 2000 is given in table 1.6.

1.5.3 NITROGEN

Nitrogen is always present and most abundantly as a gas, however small quantities of nitrogen occurs as NH_4, NO_3^-, NO_2^-, urea, and dissolved organic compounds of nitrogen. Nitrate is most important in aquatic systems. Concentration and rate of supply of nitrate is related to land use practices in watershed since nitrate moves easily through soils and is rapidly lost from land even in natural drainage systems. Denitrification, bacterial reduction of nitrate to nitrogen gas occurs at low DO levels in sediments and hypolimnion of some lakes. Major forms of N available to bacteria, fungi, and plants are NO_3^- and NH_4^+. N fixation and denitrification are ultimate sources and sinks of combined N. Nitrogen fixation is restricted to certain blue-green algae (Aphanizomenon, Anabaena, Gleotrichia, Nodularia, and Nostoc) and is the transformation of N_2 gas to ammonia by enzyme reaction.

Runoff and precipitation are major sources of NO_3 in water. Nitrate can only be metabolized after transformation by nitrate reductase. Nitrate levels are not usually toxic in water, about 1 mg/L; NO_2 is only present briefly in small quantities. Concentrations follow regular seasonal pattern - biological uptake lowers concentration in spring, and summer in photic zone. During fall and winter, releases from sediments, tributary inflows, precipitation and replenishment from hypolimnion increase nitrate and sometimes ammonium.

Table 1.6 :Projected Global Phosphorous Flow for the year 2000.

Source	Mt year^{-1}
HUMAN	
Rural Population	< 1.8
Sewage	>0.7
Coastal/Estuary Discharge	< 0.1
As PH_3 from sewage	0.2
CHEMICALS	
Fertilizer- Phosphorous	28
All non-agricultural Wastes	15
Total Mining, etc.	43
NATURAL	
Volcanic	Unknown
Uptake by plants	250
Leaching	< 20
All Human Food	< 3
Erosion	Unknown
Natural Decay of Biota	> 100
River Discharge, etc.	20
Sedimentation	> 10

From Wintheringham, 1992.

1.6 STUDIES ON NUTRIENTS IN THE INDIAN SUBCONTINENT

India has a number of large and small rivers and drains into the ocean through estuaries and coastal waters. Thus, physical, biological and chemical aspects of estuaries are essential. In India, estuarine studies started about four decades ago. Significant amount of work has been carried out in charactersing sediments of Tapti and Narmada estuary (Bhaskaran et al. 1984; Barole et al. 1982), Hooghly estuary (Subramanian et al., 1988), Mahanadi estuary (Ray et al. 1984; Chakarapani et al., 1995), Ganges-Bhramaputra estuary (Dutta and Subramanian, 1997), Godavari estuary (Vadhyanathan et al.1989; Gupta et al., 1997), Cavery estuary (Ramanathan et al., 1994).

Most of the early studies involved the studies on mineralogical and sedimentological aspects of estuarine sediments. More recent studies involves the nature of water and sediments of the estuary.

Measurements of nutrients as carbon, nitrogen and phosphorous in suspended and bulk sediments have been carried out by many reaserchers. These studies have helped in assessing the nature of organic matter (Subramanian and Ittekkot, 1991; Ittekkot etal. 1985). Gupta et al, 1997, reported that most of the organic matter in Godavari river and estuary is from terrestrial source and showed that estuaries play an important role in trapping most of the riverine material transport.

Heavy metals as Fe, Mn, Pb, Zn, Cu, Ni, Cr, Cd and Hg have been studied in various estuaries in India by Subramanian et al., 1988 (Ganga Estuary), Ramesh and Subramanian, 1988 (Krishna Estuary), Biksham and Subramanian, 1988 (Godavari Estuary), Subramanian et al. 1989 (Cauvary Estuary). Fe (3.4%) and Mn (1310 ppm) levels are lower in Cauvery estuary sediments than other tropical estuary as Krishna Estuary, Fe = 4.2% and Mn = 732 ppm (Ramesh and Subramanian, 1988), Godavari Estuary, Fe = 10.0% and Mn = 6978 ppm (Biksham and Subramanian, 1988). Organic carbon have relation with heavy metal concentration as they adsorb metals or form

organic-metal complexes in estuarine waters. In Godaveri, Krishna and Cauvery estuaries, most trace metals show an enrichment by a factor of 1-5 times due to anthropogenic activities (Subramanian et al. 1989).

1.7 VEMBANAD LAKE IN LITERATURE

Studies have been carried out in Vembanad Lake, Kerala since late 1970's. Most of the early studies were on the sedimentological aspects of the Vembanad Lake.

Mallik and Suchindan (1984) defined that the average depth is around 3 mts. for Vembanad Lake. Quartz is the main constituent of the sediments. Sediment is a mixture of clay, sand, silt and shell fragments.

Murty and Veerayya (1972) studied sediments of Vembanad Lake for organic matter, phosphorus and trace metals. The organic matter content was found to vary from 0.1 to 6.0% and showed dependence on the grain size. The average phosphate content was found to be 416 µg/g and fine grained sediments showed higher concentration of phosphate. Trace metals as Fe, Mn, Ti, Ni, Co and Cu were studied in the sediments of Vembanad Lake and adjoining rivers- Muvattipuzha, Ittupuzha and Pamba. Metal concentration were found to be associated with the texture of the sediments. Estuarine regions were found to be impoverished in Mn (402-828) and Co (52-59) contents and enriched in Ni(46-11) and Cu (98-48) contents. All metals showed relationship with organic matter (Murty and Veerayya, 1981).

Sankaranarayanan and Panamunnayil (1979), studied the distribution and seasonal changes in ratios of C,N,P in Cochin backwaters. They found that most of the organic matter in sediments is from the plant and animal matter derived from land brought into the Lake through runoff. The Average C/N ratio was found to be 6.4 for Cochin backwater sediments and 7.6 for the detritus. C/P ratio was found to average at 10.67:1 and N/P ratio of 1.51 for Cochin backwaters.

Nutrients in water of Vembanad Lake was studied by Lakshmanan et al.(1987). The emphasised the effect of salinity on the distribution of nutrients in waters of the Vembanad Lake. Nitrite in surface water varied from 1.9 to 7.2 ppm anfd varied from 10-45 ppm in bottom layers. Nitrate was found to be between 0-20.3 ppm and 0-22.7 ppm at bottom waters. Phosphate concentration at surface and bottom waters is around <40 ppm.

Sankaranarayanan et al. (1984) and Anirudhan and Nambisan (1990) studied distribution of dissolved silica and salinity in Vembanad Lake. Silicate concentration varies from 0.31 to 6.70 ppm in the Vembanad Lake. The salinity varied from 0 to 34.32 ppt in the Vembanad Lake. A negative correlation exists between salinity and silica in the Vembanad Lake (estuary) indicating conservative behavior of silica in the estuary.

Jayashree and Nair (1995) studied trace metals Fe, Mn, Cu, Cr, Pb, Sr, Zn, Co, Cd and Ni in surface sediments of Vembanad Lake. The order of abundance was found to be Fe>Mn>Sr>Zn>Pb>Ni>Co>Cr>Cd>Cu. Most metals were found to be enriched in middle estuarine sediments. Higher concentration of most elements are attributed to anthropogenic contribution if industrial and municipal effulents.

1.8 OBJECTIVES

1. Estimation of methane emissions from the Brackish water lake, Vembanad Lake, Kerala.

2. To determine the diurnal and seasonal variation in methane efflux from Vembanad Lake.

3. To measure the spatial and seasonal variation of various inorganic nutrients in water and their accumulation in the bed sediments of Vembanad Lake.

4. To assess the level of eutrophication in the lake and the major limiting factor for primary production.

5. To determine the nature of organic matter in the bed sediments on basis of amino acid analysis.

6. To determine the source of the organic matter on basis of basic biogeochemical ratios.

7. To understand the nutrient recycling dynamics in the Vembanad Lake- brackish water ecosystem.

Chapter 2

STUDY AREA

STUDY AREA

2.1 INTRODUCTION

Kerala, one of the smallest states in the Republic of India, was formed in 1956. It has an area of 15,005 sq. miles. 38,863 sq. km.], which is about one percent of the total land area of India. It extends between 8°17'30"N to 12°27'40"N and 74°51'57"E to 77°24'47"E.

The state stretches for about 360 miles (560 km) along the Malabar Coast on the western side of the Indian peninsula; its width varies from 11 to 124 km. It is bordered by the states of Karnataka on the north, Tamil Nadu to the east and the Arabian Sea to the west. The state has 14 districts and the capital is in Trivandrum [now Thiruvananthapuram].

The state can be classified into five physiographic zones:

The *mountain peaks* with an altitude above 1800 m. and occupies 0.64% of the total area.

High lands with an altitude between 600-1800 m. and occupies 20.35% of the total area.

Mid lands with an altitude between 300-600 m. and occupies 8.44% of the total area.

Low lands with an altitude between 10-300 m. and occupies 54.17% of the total area.

Coastal Plains and lagoons have an altitude below 10 m. and occupy an area of 16.40%.

2.2 DRAINAGE

Rivers: The Kerala state is drained by 44 rivers of which three are east flowing (Kabani, Bhavani and Pambar). These streams originate in the Western Ghats and are short and shift-flowing, showing varied gradient (1/250 or more in some cases). These rivers are characterized by cascades and water-falls in the upper reaches and absence of delta at the mouth. Most river courses are straight indicating structural control and the general course of rivers concides with the prominent lineament direction (NW-SE and NE-SW). The five major rivers of Kerala are Periyar, Bharathapuzha, Pamba, Chaliyar and Chalakudy. These together drain 40% of geographical area of the state.

Backwaters- Estuaries And Lagoons (Kāyals): A chain of water bodies, locally known as Kayals (backwaters) run parallel to the coastline. They are interconnected by natural or

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man-made canals, facilitating internal navigation and harbors. These Kayals are a body of brackish, marine or hypersaline waters, impounded by a sandy barrier and having an inlet connecting it to the open sea. These kayals of Kerala coast are separated from the sea by elongated sand bars and based on this they can be treated as "coastal lagoons" (Encyclopedia of Geomorphology, 1968). Perennial rivers debauch into the sea through these water bodies, thus these can be considered as lagoonal-estuarine system or partially mixed estuarine systems (Biggs, 1978).

Kerala Public water department has identified 27 estuaries and 7 lagoons in Kerala (Water Resources of Kerala, 1974). Most of the kayals are within the coastal plain formations of Quaternary Period e.g. Vembanad Lake (Fig- 2.1), Asthamudi Lake.

2.3 CLIMATE

Kerala lies in the realm of tropical climate with monsoon as a dominant feature.

2.3.1 Rainfall: Kerala experiences two monsoons: Southwest (June to September) and northeast (October to December). The annual rainfall varies from less than 100 cm. to more than 500 cm. and an annual average of about 300cm. South-west monsoon yields more than 60% of the total precipation. North-east monsoon yields about 24% of the annual rainfall (Fig- 2.2).

2.3.2 Temperature: Temperature data from 1931 to 1979 indicates that the period from March to May is the hottest with an average temperature of more than 32 ° C. Temperature is minimum in July during the rainy season. In the coastal areas, the temperature often goes upto 30-34 ° C. Lowest mean annual temperature is between 17.5 to 19.5 ° C. Maximum temperature rises gradually from July to March. Night temperature rises from January till May and is minimum in July.

2.3.3 Winds: Winds in Kerala are seasonal and undergo change in speed and direction between coast and inland regions. In North Kerala, dominant wind direction is North-West. In Cochin and Alleppey, winds are mainly from the west and north-west direction.

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SCALE

Km 20 10   0   20   40   60   80   100 Km

Western Ghats

11

50'

Cochin

10

TAMILNADU

ARABIAN SEA

Alleppey

10

1	CHALAKUDI
2	PERIYAR
3	MUVATTUPUZHA
4	MEENACHIL
5	MANIMALA
6	PAMBA
7	ACHENCOIL

50'
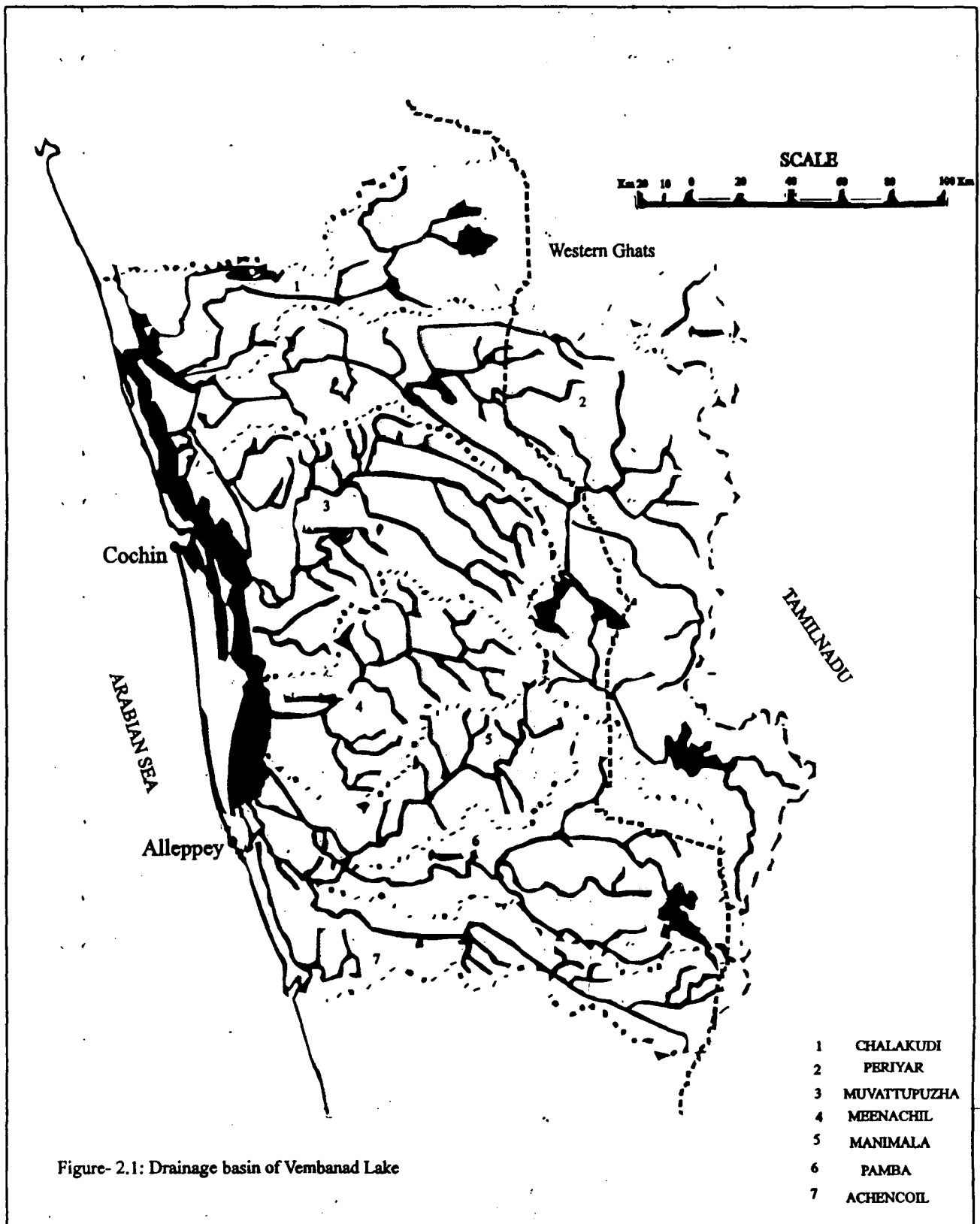
Figure- 2.1: Drainage basin of Vembanad Lake

76 0'

77 0'
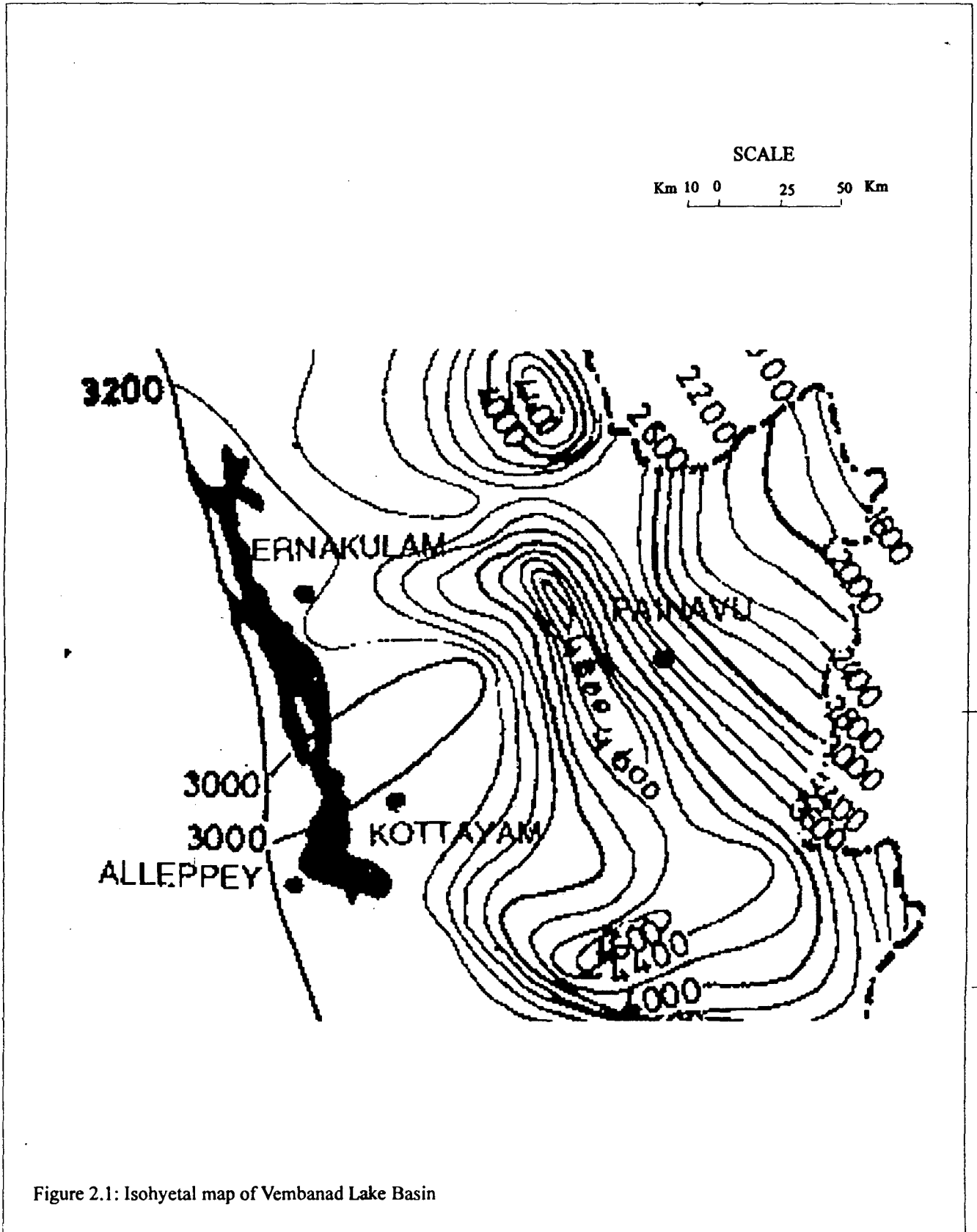
Figure 2.1: Isohyetal map of Vembanad Lake Basin

76 0'   77 0'

Generally there is a North-east and east winds in the morning and west and north-west winds in afternoon.

2.3.4 Humidity : Mean annual humidity is from 79 to 84% in the mornings and 73 to 77% in the evenings in the coastal areas. During January to March, afternoon humidity reduces to 60 to 63% (Kerala State Gazetteer, Vol-1, 1986).

2.4 SOILS

Soils of Kerala are classified into 10 broad groups based on the morphological features and physio-chemical properties (Soil of Kerala, 1978) (Fig- 2.3).

i) *Red Loam* : These are localized in the southern parts of Trivandrum district. Soil is porous, acidic, kaolinitic in nature and poor in organic matter and plant nutrients.

ii) *Lateritic Soil* : Most dominant kind of soil in Kerala. These are reddish brown to yellowish red in colour. Texture ranges from gravelly loam to gravelly clayey loam. These are poor in nitrogen, phosphate, potash and organic matter. The pH is between 5 to 6.2.

iii) *Coastal Alluvial Soil* : It is found along the west coastal tract and has recent marine deposits and is dominated by sand.

iv) *Riverine Alluvial Soil* : It occurs along the riverbanks and has a wide range of physico-chemical properties depending on provenance features.

v) *Geryish- Onattukara Soil* : It is confined to Karunagapally, Karthikapally and Mavelikkara taluks of Quilon and Alleppey districts. It has marine deposits extending into the lateritic belt and has low organic content and high water tables.

vi) *Brown Hydromorphic Soil* : These occur in valley bottoms and exhibit variations in physio-chemical properties and morphological features, resulting from transportation and deposition under varying conditions. They are generally deep brown in colour with clay to sandy loam texture.

Legend:

- Coastal Alluvium
- Riverine Alluvium
- Forest Loam
- Greyish Onattukara
- Acid Saline
- Brown Hydromorphic Soil
- Black Soil
- Lateritic Soil

SCALE
km. 100 50 0 50 100 km

TAMIL NADU

COCHIN

LAKSHADWEEP SEA

ALLEPPEY

11 0'
11 50'
10 0'
10 50'
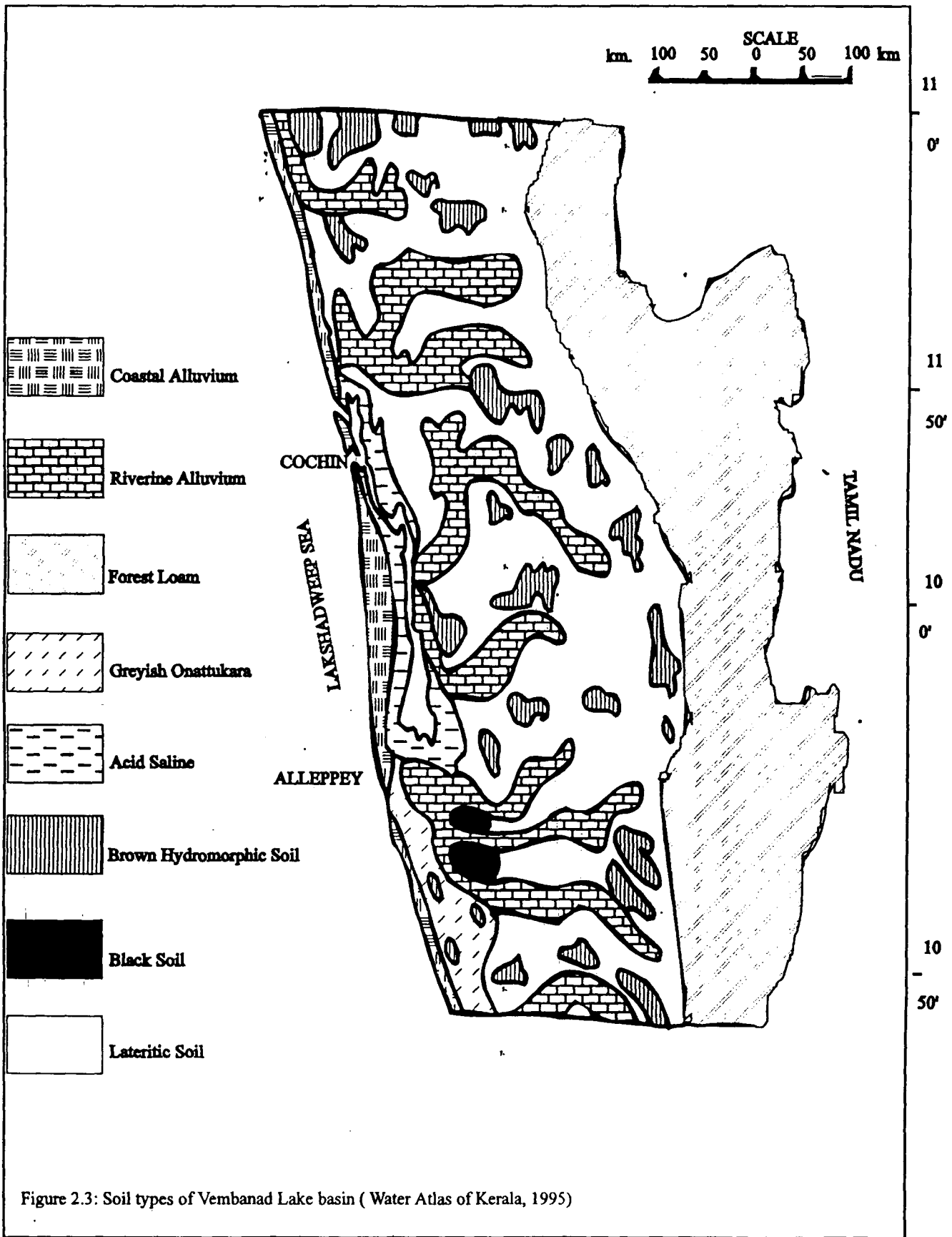
76 0'   77 0'

Figure 2.3: Soil types of Vembanad Lake basin (Water Atlas of Kerala, 1995)

vii) *Hydromorphic Saline Soils* : It is seen in coastal tract of Ernakulam, Alleppy, Trissur and Cannanore districts. It is generally brownish, deep and poorly drained with a wide variation in texture. Salinity is due to tidal influence.

viii) *Acid Saline Soils*: It is confined to Kuttanad region where a substantial portion is below sea level and submerged for most part of the year. Soil is typical water logged type of soil. Three varieties have been identified: Kayal soil, Karapadam Soil and Kari soils.

ix) *Black Soil* : Patches of these occur in parts of Palghat district. These are dark in colour, low in organic matter, calcareous, moderately alkaline, high in clay content and cation exchange capacity.

x) *Forest Loams* : These are restricted to eastern part of state developed over crystalline rocks of Western Ghats. These are shallow, immature soils under the vegetation canopy. These are dark reddish-brown to black in colour with loam to silty loam in texture.

2.5 VEMBANAD LAKE

The Cochin Backwaters, including the Vembanad Lake, occupies an area of roughly 256 sq. km. The area is about 96 km. long and width varies from few hundred meters to 15 Km. It extends from about 9 30` lat. N to 10 20` lat. N and 76 13` E to 76 50` long. E. It is elongated and oriented in NW-SE direction. The backwater occupies an alluvial plain lying parallel to and in between the Arabian Sea to the west and the Western Ghatts to the east in peninsular India. The complex system has two opening to the sea, the northern most at Gangannore and one at Cochin. The one at Thollappally, south of Aleppey, is open only during the SW monsoon. Six major rivers Chalakudi, Periyar, Muvattupuza, Meenachil, Manimala, Achankovil and Pamba discharges into the lake.

Vembanad Lake originally covered an area of 700 km^2 but has reduced to 80 km^2 because of reclamation for agriculture. A dyke* (The Tanneermukkam bund) was

constructed across the lake in attempt to reclaim the wetland for paddy cultivation. The area of the lake from 1912 to 1983 shrank by 43.15% (Nair et al, 1987).

2.6 ORIGIN OF LAKE (on the basis of landsat imagery)

From the landsat imagery, it is clear that the lake is elongated and originated in nearly 315° -135° direction. The western part is also marked by a number of beach ridges nearly parallel to the coast and boundary of the lake margin in some places. The orientation of the beach ridges varies from 10° - 190° to 155°- 335° and the orientation of the beach ridge at various parts A,B,C,D,E,F as shown in fig- 2.4. The beach ridges are due to repeated regression and transgression of the shore and orientation is controlled by waves.

Faulting, uplifting and down wraping are seen in a number of places in the west coast and off shore, geometrical linearity of the coast reflects tectonic role in its formation. Vembanad lake con be considered as an embayment of a large fracture zone in the offshore (Varadharajan et al.,1980). Maximum ecstatic sea level change recorded is about 150 m and several terraces at several depths reflect fluctuating conditions. Rivers formed offshore bars that gradually formed the lagoon and thus the Vembanad Lake. The present shape is to a large extent is controlled by sediments brought by rivers and modified by marine processes like tides, waves and currents.

GENERAL FEATURES

The *bathymetry* of the lake on the basis of available information is that the southern part , south of the Tannermukkam bund, has the maximum depth of 8.5 m. Major part is covered by 2-4 m depth contour. The marginal areas close to the shore are shallow. The average tidal range in northern part (at Cochin) is about 1m and in the southern part (near Tannermukkam bund) is 0.2 to 0.6 m (Mallik, 1984) (Fig- 2.5).

The Cochin backwaters constitute a vast estuary under monsoonal regime, flushed by rains and runoff from land during the SW monsoon, that sets in late May and extends

PART OF LANDSAT FRAME E 1202-04454.

ORIENTATION OF BEACH RIDGES

A 155° - 335°
B 175° - 355°
C 10° - 190°
D 2° - 182°
E 155° - 335°
F 10° - 190°

COCHIN

ARABIAN
SEA

VEMBANAD LAKE

ALLEPPEY
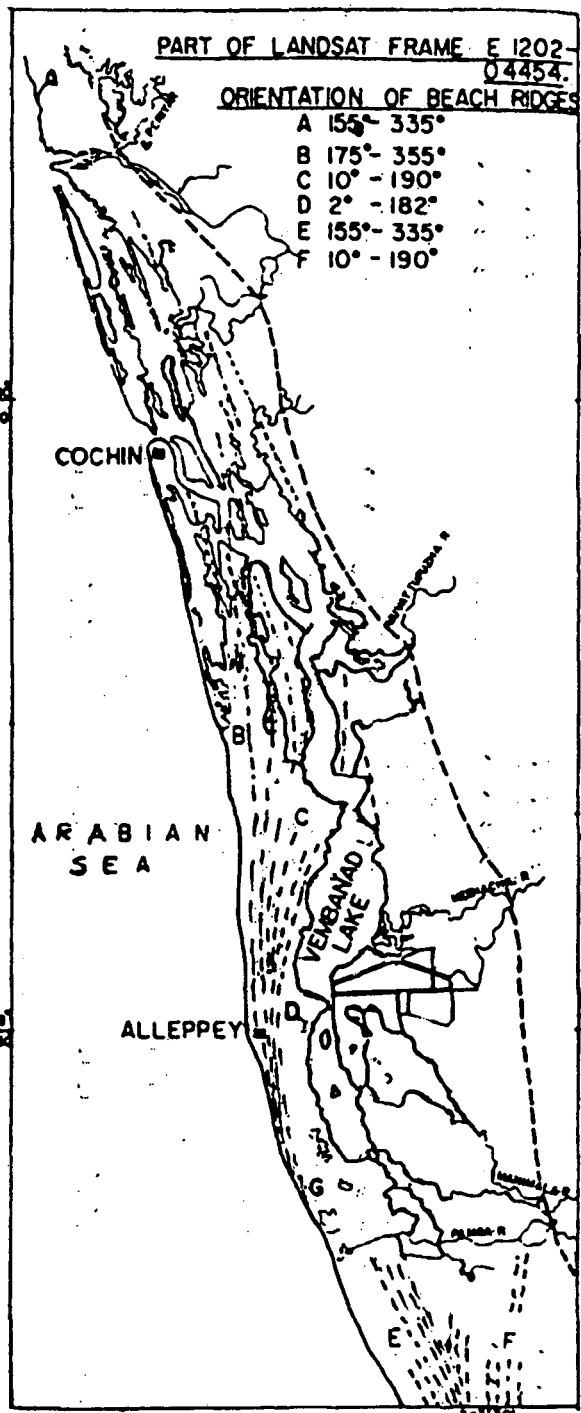
Figure- 2.4: Landsat Imagery of Vembanad Lake basin showing lineaments (Varadharajan et al., 1980).

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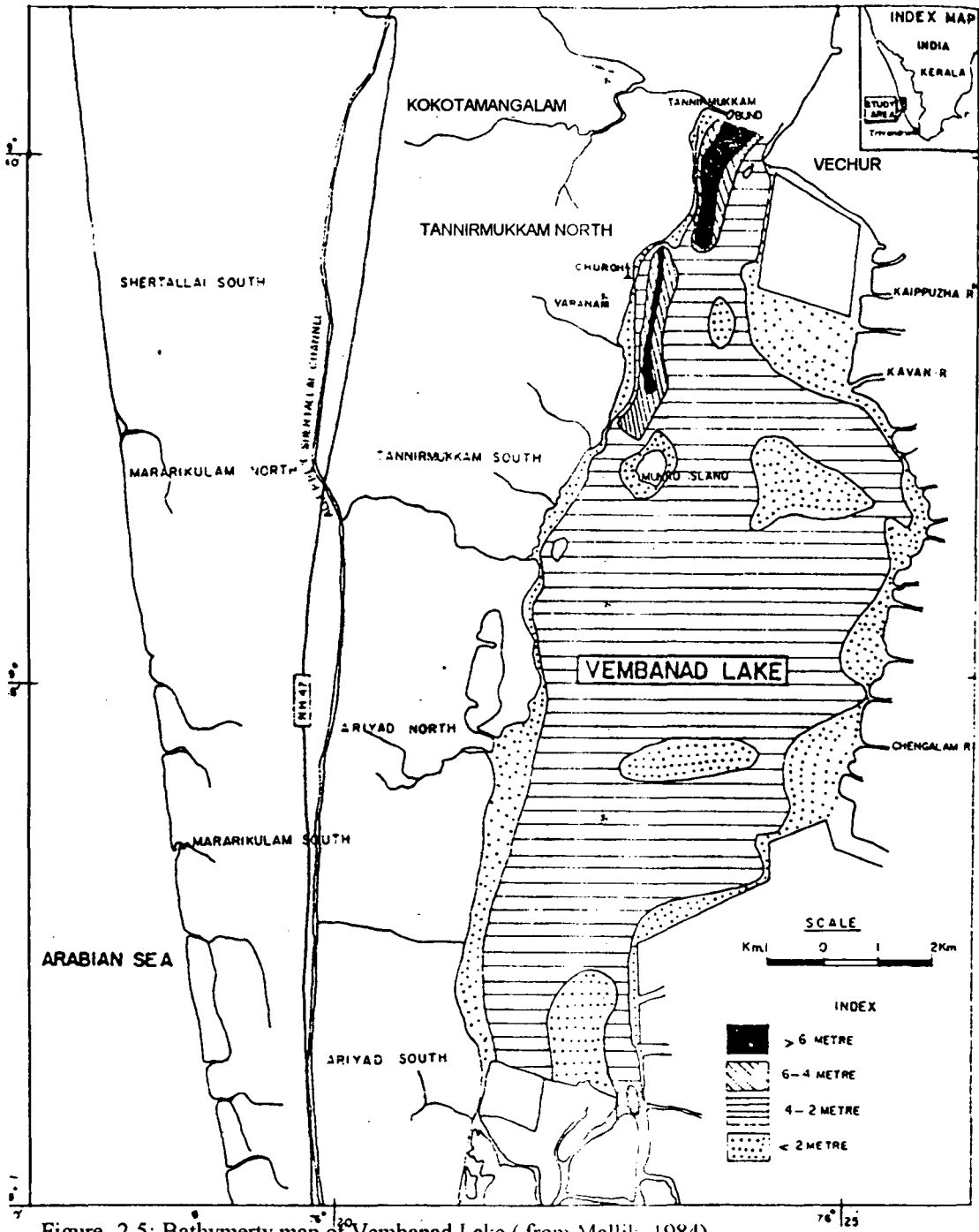
Figure- 2.5: Bathymerty map of Vembanad Lake (from Mallik. 1984).

through September with mean annual rainfall of 120 in. There is practically no NE monsoon in the area. After rainy season, an intrusion of seawater invades the estuary and can be identified upto 15-20 km. upstream during inter monsoonal period. While traveling upstream, the seawater gradually loses its identity by mixing with fresh water from surface runoff. Upwelling Arabian Sea subsurface water normally and almost every year penetrates the estuary to some extent and forms a wedge-shaped bottom layer rich in nutrients, cooler then estuarine waters and poorer in dissolved oxygen content. Anoxic conditions occur in localized pockets mainly in higher reaches of the estuary. The surface water salinity range varies from almost fresh water condition during monsoon to almost full salinity upto 34 ppt at the bar-mouth of Cochin back waters in inter-monsoon.

The *sediment distribution* pattern of the coastal lake depends on the sediment source, texture of transported sediments, bottom topography and hydrographic feature of the lake waters. The sediments of the lake consist of different admixture of clay, silt and sand. Coarsest sediments are confined to south of the Taneermukkam bund and clay in the central portion of the lake. In southern part, higher percentage of coarse fraction is found and fine sand fraction is confined to the western margin of the lake. In northern part, coarse fraction is restricted to opening to the sea and at the mouth of Muvattupuzha River. The trend decreases from river to estuarine region. Central portion of the lake is mainly silt and clay, narrow canals have course sandy sediments (Verrayya and Murthy, 1981; Mallik, 1984).

The *bore hole logs* available from PWD office at Tannermukkam Bund, show a varying mixtures of sand and clay (Fig- 2.6). In 4 boreholes clay with coal (perhaps lignite) and sand are reported. The thickness of sediment varies from 34 to 63 m before hard bottom is reached.

The *minerals* of the lake are grouped into allogenic, endogenic and authigenic. Quartz is the major constituent of the sediments. Heavy mineral quantities vary from 0.5 to 47.9 % in sediments. Maximum quantity was noticed in southern part. The major rock

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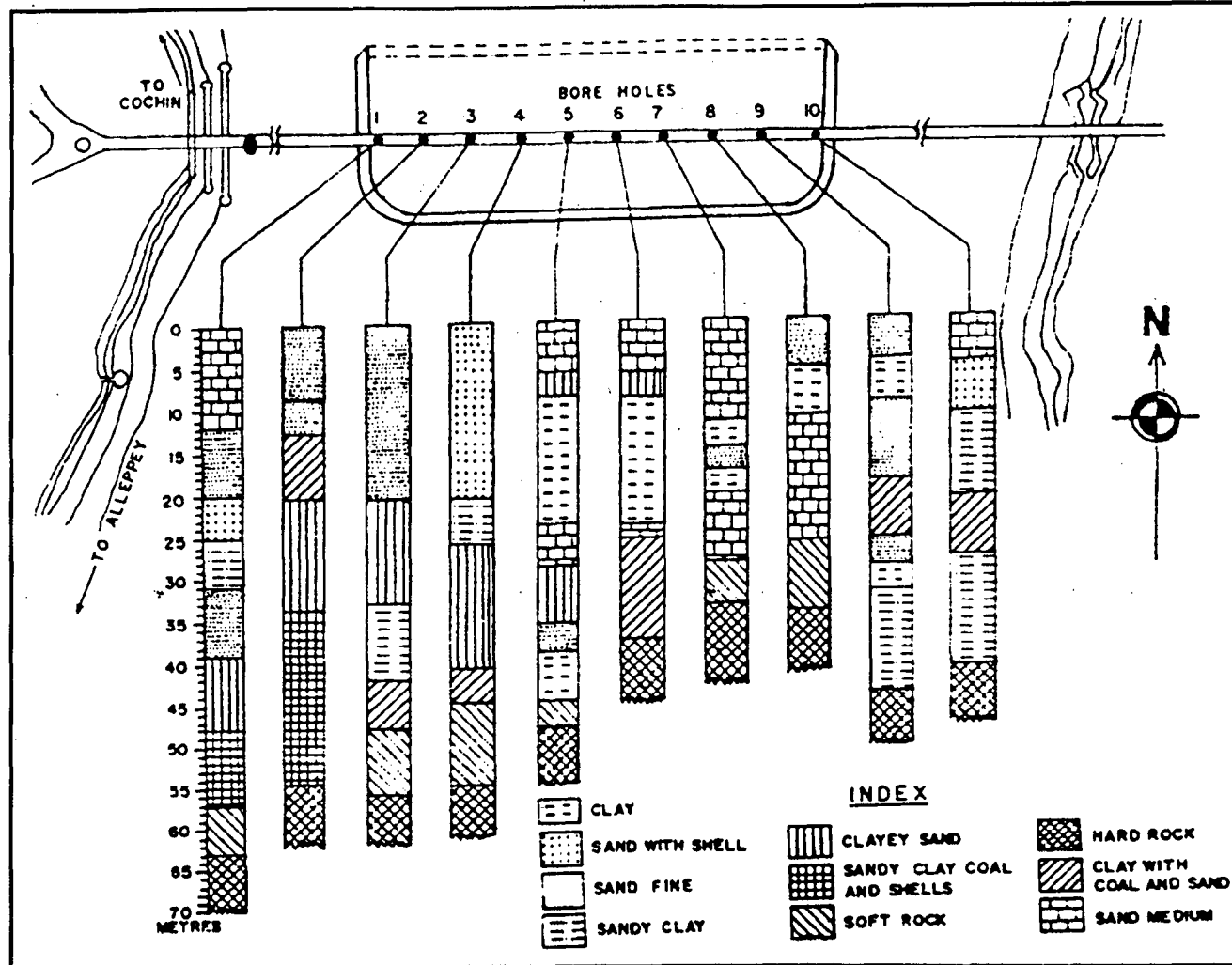
Figure 2.6: Borehole data for Vembanad Lake (Mallik, 1984)

types of the area are Precambrian crystalline, Tertiary and Quaternary sediments (Mathai, 1983). Tertiary sediments occur as sand and clay intercalation and western part is covered by alluvium. These minerals have been derived from charnockites, granite gneissess, khondalites and pegmatites of Western Ghats and adjoining foothills. The framboidal pyrites in the samples is from decay of organic matter under reducing conditions, indicating an early diagenetic origin (Mallik, 1984).

Chapter 3

MATERIAL AND METHODS

MATERIALS AND METHODS

3.1 FIELD METHODS

Lagoons or coastal lakes are rivers - Ocean system having various dynamic physiochemical and biological processes taking place in them. They are the places where fresh-waters from the rivers meet the saline waters form the ocean. The suspended and dissolved materials derived from physical and chemical weathering of rocks in the catchment with anthropogenic pollutants reach the system and undergo a variety of physico-chemical and biological changes. Systematic sampling of gas, water, bed sediments and core sediments were done at ten locations in the Vembanad Lake. The sampling locations were chosen carefully in order to get maximum representation of the diverse environments of the lake. The water samples and gas samples were collected in two seasons namely Pre-monsoon (March-April, 1998), and Post-Monsoon (December 1997-January, 1998). The sampling locations (Table - 3.1) are shown in Figure 3.1. The bed sediment sampling was done only once in Post Monsoon (December, 1997).

3.1.1 GAS SAMPLES

Gas samples from the sediment water interface was collected using the "Closed Chamber" technique (IAEA, 1992). The flux chamber is a simple inverted container made of Perspex Glass. A Perspex base was inserted into the sediment column, and over it the chamber was placed. This trapped the gases emitting from the sediment - water interface and prevented mixing with atmospheric air. The base was imbedded in sediment a few hours in advance to sampling so that the ambient soil environment is maintained. The Perspex Chamber is fitted with rubber tube to which a pump was attached and was used to draw air samples into sampling bottles. The chamber is fitted with a fan that is used to homogenise the gas within the chamber. There is also a hole to hold a thermometer, which is useful in monitoring temperature within the gas chamber. The gas is collected in

Table 3.1: Sampling locations along the Vembanad Lake, Kerala.

L.No.	Location Name	Bed Sediments	Water Samples	Suspended Sediments	Gas Samples
1	Pulloot	✓	✓	✓	✓
2	Azhikode	✓	✓	✓	-
3	Palliport	✓	✓	✓	-
4	Marine Drive	✓	✓	✓	-
5	Vypeen	✓	✓	✓	-
6	Vendurvthy	✓	✓	✓	✓
7	Thaneermukham	✓	✓	✓	✓
8	Kumarakom	✓	✓	✓	✓
9	Punnmada	✓	✓	✓	-
10	Finishing Point	✓	✓	✓	-

Bed Sediments were collected only once during the post- monsoon.

Water, suspended sediments and gas samples were collected during the pre-monsoon and post-monsoon.
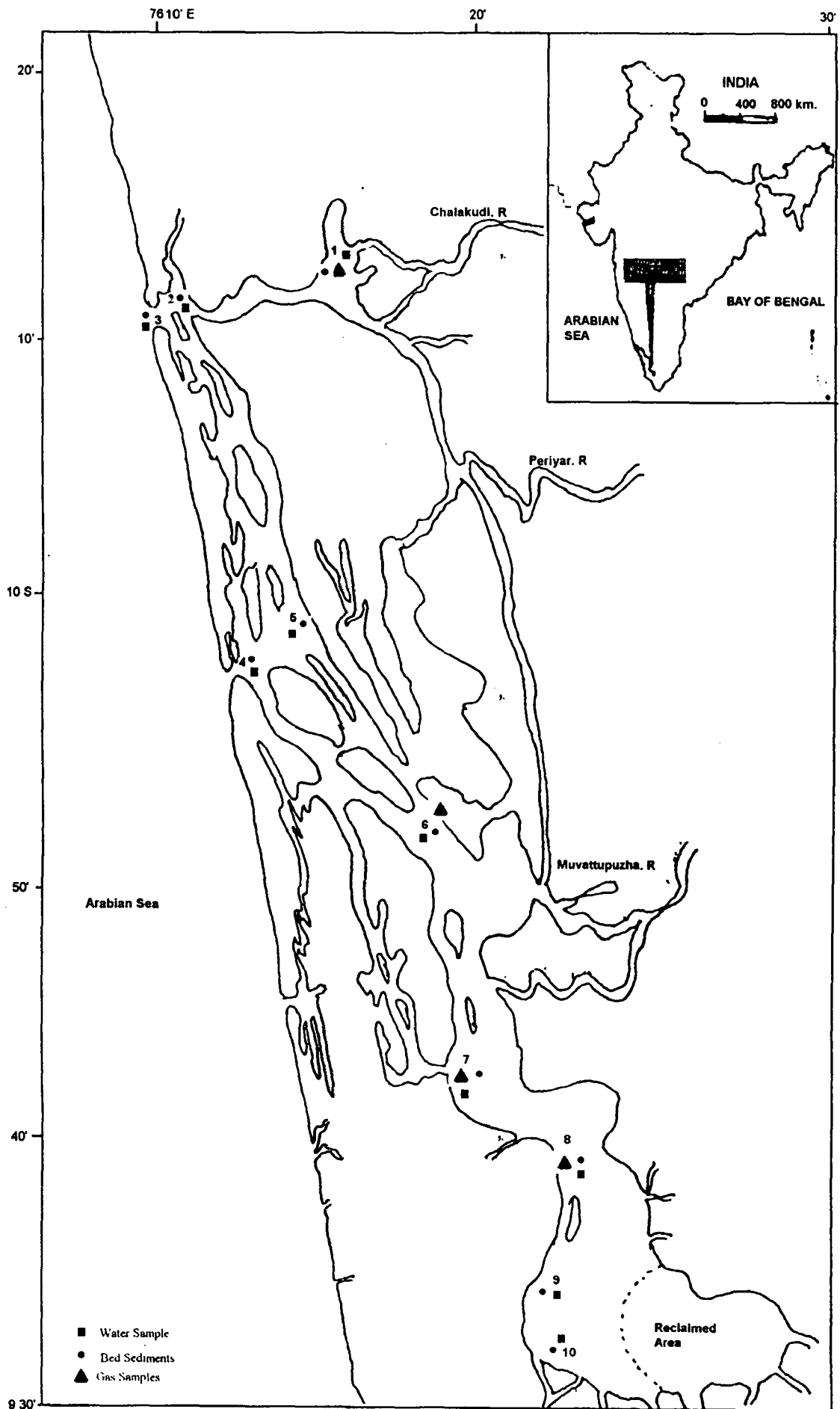
Figure- 3.1: Study area with sampling location in Vembanad Lake

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glass sampling bottles by the 'displacement' method of water by gas from the chamber. This method further ensures that there is no interference from atmospheric air. The gas collected was stored and transported in a number of vials, sealed immediately after collection. Triplicate for each sample was made (Subramanian et al., 1998). The Perspex chamber inserted had a base of 12" x12"x 3" and chamber of 12" x12" x 18" dimensions. The samples were collected at regular intervals of one hour during the course of the day. This will help to assess the time of day variation in methane efflux.

Besides collection of air samples, temperature of air (atmosphere), water (3-4 cm above sediment surface) and sediment (2-3 cm below the sediment surface were also noted. Water column depth within the chamber was noted to make a correction for the box volume at every collection. The gas samples were brought to the laboratory for Gas Chromatographic Analysis.

3.1.2 WATER SAMPLES

Water samples were collected from about 10 cm below the surface in cleaned polyethylene bottles. Bottles were completely filled with water sample and capped air-tight. These water samples were brought to laboratory for various physico-chemical analysis and stored at 4°C.

3.1.3 BED SEDIMENT SAMPLES

Bed sediment samples were collected from the sampling locations by scooping the top 5-10 cm layer using a small plastic scoop along the river bed, at sediment water interface. The bed sediment samples were then transferred to a polyethylene bags, which was sealed to air by fastening the mouth immediately. These samples were brought to the laboratory for studying its physico-chemical properties and mineralogy.

3.2 LABORATORY METHODS

3.2.1 GAS ANALYSIS

The gas samples were analyzed in the laboratory at Anna University, Chennai within 24 hrs of sampling, using a Hewlett Packard Gas Chromatograph (GC, Model: HP 5890). Column, injector and detector temperatures were maintained at 80°C, 100°C and 90°C respectively, with a flow rate of 30 ml min^{-1} high purity Argon was used as the carrier gas. The gas chromatograph was calibrated, before and after each set of measurement, using 1 ppm CH_4 in N_2 obtained from M/s Mathesons, USA, as primary standard and 2.04 ppm, 2.81 ppm and 10.9 ppm CH_4 in N_2 as secondary standards, obtained from the National Physical Laboratory, New Delhi. Under these conditions, the retention time of CH_4 was 0.65 min. and minimum detectable limit was 0.5 ppm. The gas flux was calculated using the formula:

$$F = \frac{\Delta x}{10^6} \times BV_{(STP)} \times \frac{16 \times 10^{-3}}{22400} \times \frac{1}{A} \times \frac{60}{t}$$

Where :

F = Efflux of methane in mg / m^2 / hr.

Δx = Change in concentration of methane in ppmv from time "0" min. to "t" min.

$\Delta x = \dfrac{\text{Standard conc. of methane}}{\text{Area obtained in G C for standard}} \times$ Area obtained in Gas Chromatograph for sample

$BV_{(STP)}$ = Box volume at standard temperature and pressure in cm^3

A = Area of the box.

3.2.2 SUSPENDED MATTER SEPARATION

Water sample bottles were shaken vigorously to make a homogeneous suspension. Known volume of this suspension was transferred immediately to the filtration unit. Sediments were collected on pre-weighed Millipore, 0.45μ filter paper, which was dried

to constant weight at 80°C. Then weight of total suspended matter (TSM) was calculated. The filtered water was used for analyzing cations, anions and silica content.

3.2.3 WATER ANALYSIS

pH and Conductivity

The pH and conductivity were measured in unfiltered water samples. "Rachho" (Model No. 123) pH meter was used to measure the pH. The glass electrode was conditioned and calibrated with buffer solutions of pH 4, 7 and 9. The temperature of the instrument was set according to the temperature of the samples. The samples were stirred continuously to maintain homogeneity before noting the pH. Conductivity was measured in micro mhos/cm using Systronics Conductivity Meter 306. The instrument was calibrated with 0.01 M KCl standard (1413 in mhos/cm at 25°C). The results are reported in mS/m.

Bicarbonate

The bicarbonate content was determined by potentiometric titration method (APHA, 1985). 20 ml of sample and a series of bicarbonate standards ranging from 100 mg/l to 1000 mg/l were titrated against 0.02 N HCl. The end-point was noted at pH 4.5. A graph between bicarbonate standards and volume of HCl consumed was plotted. The readings for the samples were found out from this graph.

Chloride

Chloride content was determined by 'Radelkis' chloride ion selective electrode, in combination with a double junction reference electrode and 'Rachho' pH/mV meter. 25 ml of each sample and a series of standards were mixed with equal volume of Ionic Strength Adjustment Buffer (ISAB). ISAB was prepared by dissolving 15.1 gm. Sodium bromate in 800 ml of distilled water. 75 ml of concentrated nitric acid was added and the solution was stirred well before diluting to 1 litre by distilled water. The electrodes were

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conditioned and dipped into sample to note stable reading in mV. The standard graph was plotted between known concentrations and mV values and the final reading was recorded from the graph.

Fluoride

Constant Ion Meter P-306 was used to determine fluoride concentration. 25 ml of each samples and standard solutions (0.1 to 10 mg/l) was mixed with equal volume of Total Ionic Strength Adjustment Buffer (TISAB) (prepared by mixing 1M Sodium Chloride, 0.23M Acetic Acid, 0.75M Sodium acetate and 0.001M Sodium Citrate). The instrument was calibrated with standards. The concentration of fluoride was recorded from the instrument directly.

Sulphate

The sulphate concentration was determined by turbidimetric method (APHA, 1985). Sulphate standards ranging from 1-25 ppm were prepared from Sodium sulphate. 20 ml of each sample and standard was taken and 4 ml of buffer solution was added to it. One spoon of Barium Chloride crystals was added to it while stirring. The solution was stirred for about 5 mts. and absorbance read immediately at 420 nm using Cecil Spectrometer (Model No. 594).

The buffer was prepared by dissolving 30 gm. magnesium chloride, 5 gm. of Sodium acetate, 1 gm. of potassium nitrate and 20 ml acetic acid in 500 ml distilled water and made upto 1000 ml

A graph was plotted between the concentrations of standards and absorbance. The final values were obtained from this graph.

Phosphate

Phosphate was determined by the Ascorbic Acid method (APHA, 1985). Phosphate standards ranging from 0.1 to 3 mg/l were prepared from KH_2PO_4. 40 ml of each sample and standard solution was pipetted out in 50 ml volumetric flask and 5 ml of

Molybdate Antimony solution (prepared by dissolving 4.8 gm of Ammonium Molybdate and 0.1 gm of Potassium. Antimony tartarate in 400 ml 4N H_2SO_4 and making the total volume to 500 ml with same acid) and 2 ml of Ascorbic Acid solution (2.0% w/v) was added and mixed well. The mixture was diluted to 50 ml and optical density was measured at 650 nm. using Cecil Spectrometer (Model No. 594). A graph was plotted between concentrations of the standards and optical density and sample concentrations were obtained from this graph.

Dissolved Silica

The dissolved silica content was determined by the Molybdate Silicate Method (APHA, 1985). Silica standards were prepared, ranging from 0.1 to 10 mg/l from Sodium metasilicate nanohydrate. 20 ml of each sample and standard was pipetted out in 50 ml volumetric flask and 10 ml of Ammonium molybdate solution (prepared by dissolving 2 gm of Ammonium molybdate in 10 ml distilled water, 6 ml concentrated HCl was added and final volume was made upto 100 ml by distilled water) and 15 ml of Reducing Reagent (prepared by mixing 100 ml Metol sulphite solution, 60 ml 10% oxalic acid and 120 ml 25% Sulphuric acid and making the final volume to 300 ml by adding distilled water) was added and mixed well. Metol sulphite was prepared by dissolving 5 gm metol in 210 ml distilled water and 3 gm Sodium sulphate was added and the volume was made upto 280 ml with distilled water. The samples were stirred properly and kept for 3 hrs. to complete the reaction. The optical density was measured at 650 nm using Cecil Spectrometer - 594. Graph between concentration of the standards and optical density was drawn and concentration of samples were recorded from it.

Calcium, Magnesium, Sodium and Potassium

Calcium and Magnesium were analyzed in absorption mode and Sodium and Potassium in the emission mode by GBC-902 double beam Atomic Absorption Spectrometer (AAS). A range of salt standards was used to calibrate the instrument.

3.2.4 SEDIMENT ANALYSIS

The sediments were analyzed for Total Carbon, Total Nitrogen and Total Phosphorus. Samples were taken out from cold room and were oven dried at 60°C for 24 hrs. (Raaphosst, 1994). Homogenization was done by quartering.

Following analysis were done for the bed sediments:
1. Kjeldahl Nitrogen Analysis
2. Carbon Analysis
3. Analysis for the major and minor elements.

Kjeldahl Nitrogen Analysis

Nitrogen was analysed by Kjeldahl digestion method of Anderson (1993). 0.2 gm sediments was taken in digestion tube and 4.4 ml of digestion mixture was added to each tube. This was digested at $90°C$ till a solution becomes colourless. The solution was allowed to cool down to room temperature. 50 ml of distilled water was added in each tube and stirred. The final volume was made upto 100 ml by adding distilled water. The clear solution was used for analysis.

Digestion mixture was prepared by dissolving 0.42 gm Selenium powder and 14 mg Lithium Sulphate in 350 ml 30% (v/v) H_2O_2 and mixed. In this mixture 420 ml H_2SO_4 was added carefully while cooling in an ice bath. The digestion mixture was kept at 4°C for further use.

Nitrogen was determined by steam distillation. Free ammonia is liberated from the solution by steam distillation in the presence of excess alkali. The distillate is collected in a receiver containing excess Boric Acid indicator and nitrogen is determined by Acid titration.

Distillation process is done by transferring 10 ml of aliquot to reaction chamber and adding 5 ml Alkali mixture and starting distillation immediately. About 25 ml of distillate was collected in 5 ml Boric Acid-indicator solution. The distillate was titrated

against N/140 HCl to a grey end point using microburette.

Present Kjeldahl Nitrogen was calculated using the following equation:

$$\%N = \frac{(a-b) \times N \text{ of HCl} \times 1.4 \times V}{v \times S}$$

a = ml of HCl used against sample

b = ml of HCl used against blank

V = ml of total digest titrated

v = ml of digest distilled

s = Weight of sediment taken

Alkali solution was prepared by dissolving 500 gm NaOH and 25 gm Sodium thiosulphate in water and final volume was made upto 1000 ml with distilled water.

Boric acid-indicator solution was prepared by Okalibo (1993) method. 0.3 gm Bromocerol green and 0.165 gm methyl red were dissolved in 500 ml of 95% ethanol to make the Indicator Mixture. 20 gm Boric acid was dissolved in 700 ml distilled water and cooled and 200 ml of 95% ethanol was added. 20 ml of Mixed Indicator was added to it and mixed well by shaking. 0.05N NaOH was added to it till 1 ml of indicator with 1 ml distilled water changes colour from pink to pale green. The solution was then made upto 100 ml.

The Nitrogen values obtained were compared with those obtained from Nitrogen Analyser Nature-1500 from Carlo-Erba at University of Hamburg, Germany. The values showed a discrepancy of ± 5%.

Carbon Analysis

Carbon was analyzed using ELTRA (CS 1000) Carbon Analyser. Before analysis

sediments were made free of halogens by washing with distilled water. Untreated samples were used for determining Total Carbon.

The measuring method is based on the principle of sample combustion and analysis of gases given off through infrared absorption. The sample is put in a ceramic boat which is made free of any carbon and pushed into the silicon carbide furnace set at a temperature of 1300°C. The combustion occurs in presence of oxygen supplied and the carbon present in the samples is converted to CO_2 and is carried to the infrared absorber by oxygen, which also acts as a carrier gas. The flow of oxygen is maintained to a constant value through an electronic flow regulator. The moisture traps ensure that dry gas mixture reaches the infrared cell. The infrared cell signals are selective and respond to Carbon-di-oxide concentration in the gas mixture. The signals are electronically linearised, integrated and percentage of carbon in the given weight of sample is shown digitally.

Analysis for the major and minor elements

Finely ground homogenized sediments were taken in the beaker and boiled with 30% (v/v) H_2O_2 (Jackson, 1973) for removal of organic matter. The treatment is repeated until the emission of CO_2 stopped.

Analysis of major and minor elements were carried out by the two solution method (Shapiro, 1975). Solution 'A' was used for silica and phosphorus analysis and Solution 'B' was used for metal analysis.

(a)   Solution 'A'

0.025 gm of finely powder sediment was taken in 50 ml Nickel crucible and 3-4 pellets of NaOH were added to it. The crucible was gently heated on a furnace in order to mix sediment and melt pellets, then the crucible was constantly heated to dull redness for 30 mts. Then, the crucible was allowed to cool down to room temperature. 10 ml of distilled water was added in the crucible and kept overnight. The solution was transferred to 250-ml volumetric flask with help of a policeman. 5 ml of (1:1) HCl and 25 ml water

was also added. This solution was boiled till it was clear and the total volume was made upto 250 ml by adding distilled water.

Silica Analysis

0.8 ml of solution 'A', standard solution (Canadian soil standards i.e. SO1, SO2, SO3, SO4) and reagent blank were transferred to 50 ml Teflon beaker. 20 ml of distilled water was added to each beaker. 0.2 ml of ammonium molybdate solution was added and kept for 10 mts.). 4 ml of 10% (w/v) tartaric acid was added by swirling the beaker. 0.1 ml of reducing reagent was added and samples properly stirred and kept for 30 mts. Optical density was measured by Cecil Spectrophotometer- 594 at 650 nm.

Ammonium molybdate solution was prepared by dissolving 1.875 gm. ammonium molybdate in 19 ml distilled water and adding 6 ml 20% (v/v) H_2SO_4 . The reducing reagent was prepared by dissolving 0.07 gm. sodium sulphite in 1.0 ml distilled water and then 0.015 gm. 1-amino-2-naphthol-4-sulphonic acid was added and stirred well until dissolved. 9 ml of 10% (w/v) sodium bisulphite solution was added to it and mixed well.

Alumina Analysis

15 ml of Solution 'A' (sample, standard and blank) were taken in 100 ml volumetric flasks. 2 ml of Calcium chloride solution (prepared by dissolving 7 gm. $CaCO_3$, and adding 100 ml of water and 15 ml of concentrated HCl and diluted to 500 ml) was added. 1 ml of hydroxylamine hydrochloride (prepared by dissolving 5 gm. of hydroxylamine hydrochloride in 50 ml) was added by swilling the flask. 1 ml of potassium ferricyanide (0.75%) was added to each flask and mixed. 2 ml of thioglycolic acid solution (4%) was added and kept for five minutes. 10 ml of buffer solution (prepared by dissolving 100 gm. of sodium acetate in water and adding 30 ml of glacial acetic acid and diluted to 500 ml) was added and kept for 10 minutes. 10 ml of Alizarin Red-S solution (0.05%) was added to each flask and the volume was diluted to 100 ml by adding distilled water. The samples were properly stirred and kept for 50 minutes. The absorbance was measured at 470 nm using Cecil Spectrophotometer- 594.

Phosphorus Analysis

Phosphorus in bed-sediments and suspended sediments were analyzed from solution 'A'. Phosphate was determined by ascorbic acid method as described in water analysis section. The standards used in this case were standard soil samples, which were digested to make solution 'A' 40 ml of each solution 'A', and sediment standard was used for analysis.

(b)   Solution 'B'

0.10 gm. of finely ground sample were transferred to the Teflon crucibles and 2 ml of aqua regia (HNO_3 and HCl ratio 1:3)and 5 ml HF were added to each crucible, these were then sealed in metallic cases. The crucibles were heated for 1 1/2 hrs. at 100°C and allowed to cool down to room temperatures. 5.6 gm. of Boric acid crystal (H_3BO_3) was dissolved in 20 ml distilled water and then added to the bomb contents which was made upto 100 ml. The solution was transferred to polypropylene bottles for storage. The sample was left undisturbed overnight to allow the formation and settling of borosilicate from the solution. This gelatinous precipitate is separated by centrifugation. The solution thus obtained is used for analysis of major and minor elements by GBC - 902 double beam Atomic Absorption Spectrophotometer.

3.2.5 AMINO ACID ANALYSIS

Amino acids were determined with LKB Amino Acid Analyser (4151 Alpha Plus) from Pharmacia Biotech at University of Hamburg, Germany. Details of the methodology have been given by Michaelis and Ittekkot (1982). In brief, acid hydrolysed amino acids elute in accordance with their molecular structure and charge under the influence of sodium citrate buffers with ascending pH. The eluted amino acids form o-Phthaldialdehyde (OPA)/mercaptoethanol complex, which is quantified by a fluorescence detector.

70-150 mg bed and core sediments (5-10 mg suspended matter) were hydrolysed under argon gas atmosphere with 3 ml 6 N HCl (suprapure) for 22 hrs. at 110°C. 2 ml supernatant was pipetted out and evaporated to dryness 3-4 times (each time the residue, was dissolved into ca. 5 ml DDW) with a rotary evaporator until free of acid. The residue was then dissolved into 1-ml dilution buffer. 20-60 Hl of this solution was injected in the sample-loading capsule, which transferred the sample to gas liquid chromatography (GLC) column of the amino acid analyzer. Total amino acids were calculated as the sum of individual amino acid detected and quantified. Hexosamine concentrations were multiplied by 1.4 (Muller et al , 1986) in order to compensate for the partial loss during hydrolysis. The analytical error in this method was less than 10%.

Instrument and operating conditions

GLC column	No. 138, 150x4.6 mm steel column
Ion-exchange	DC4-75, special 7µl (cation exchange, Na form) resin
Detector	Fluorescence detector (FLD-6A from Shimadzu) with 100 µl flow through cell
Standard	AA standard solution AA-S-18 (Sigma®), and a mixture of hexosamines and non-protein amino acids.

Flow rate:

Buffer	19.1 ml/h
Reagent	17.5 ml/h

The amino acids in the present work have been grouped as follows:

Acidic AA	Asp, Glu
Basic AA	His, Orn, Lys, Arg
Neutral AA	Ser, Thr (hydroxy), Gly, Ala (straight)
	Val, Ile, Leu (branched)
Aromatic AA	Phe, Tyr

Non-protein AA   Orn, ß- ala, γ –aba

Sulphur containing AA   Met

Programme

Step	Time (min.)	Buffer	Reagent
1	18	2	x
2	4	4	x
3	6	2	x
4	18	3	x
5	10	4	x
6	15	5	x
7	70	5	x
8	8	6	x
9	5	1	x
10	13	1	
11	5	1	x
12	2.5	1	x
13	0.5	2	x
14	1	1	x
15*	1	2	x

* Capsule loaded

Table 3.2: Reagents and Buffers used for amino acid analysis.

Reagents (2 litres)

Chemicals	Quantity
Potassium Hydroxide	63.0 g
Boric Acid	74.2 g
o-Phthaldialdehyde	1.0 g
Ethanol	10.0 ml
Mercaptoethanol	5.0 ml
Brij Solution (30%)	6.0 ml

Buffers

Buffer (1 litre)	Chemicals	Quantity (gm.)	pH
1	Sodium citrate	14.79	
	Sodium chloride	1.10	2.85
	Isopropanol	84.91 ml	
2	Sodium citrate	9.8	3.46
	Boric acid	50.0 mg	
3	Sodium citrate	9.8	4.65
	Boric Acid	50.0 mg	
4	Sodium citrate	9.8	6.15
5	Sodium citrate	10.45	
	Lithium chloride	8.48	10.30
	Boric Acid	50.0 mg	
6	Sodium hydroxide	16	
Dilution Buffer	Sodium citrate	14.79	
	Sodium chloride	1.10	2.20
	Isopropanol	84.91 ml	

Chapter 4

RESULTS

RESULTS

4.1 METHANE EMISSIONS

Methane was collected from sediment-water interface in pre-monsoon and post-monsoon from four locations in the Vembanad Lake, Kerala. The Lake was divided into four sectors of different environmental conditions that exists within the lake. The different environments are (according to the sampling locations map- Fig- 3.1):

1. Pullot: This location has waters of moderate salinity and extensive coconut husk fermentation is carried out in this area, hence higher sulphate and organic matter.

6. Venupady: It is located near Cochin. This location has high salinity and tidal influence and due to its closeness to the sea. There is influence of city drainage.

7. Thaneermukham: It has low salinity. Dominated by village environment and local fishery industries.

8. Kumaragam: Low salinity, near land reclamation area, plenty of emergent and macrophytes as water hyacinths.

4.1.1 Methane Emissions

Methane concentrations showed a wide variation among the locations and ranged from 2.54 to 175.91 mg $m^{-2}h^{-1}$ in pre-monsoon and from 16.12 to 210.59 mg $m^{-2}h^{-1}$ in post-monsoon (Table- 4.1)(Fig- 4.1). Thus, there is a wide variation in the methane efflux both spatially and temporally. No sampling was done during monsoon as the lake was flooded and there was a steady current in the water.

Dial variation in methane efflux was studied at these locations during the pre-monsoon. Dial variation is considered essential to understand the effect of solar radiation, temperature of water and sediment and currents on methane emissions. There is an appreciable variation in methane efflux during the day and at all locations.

The average *sediment temperature* in the study area at time of sampling during both the seasons ranged from 29.0 to 33.0°C.Sediment temperature highly affects the activity of soil microorganisms. The optimum temperature for methane production is between 30°C to 33°C (Ramesh and Purvaja, 1996; Verma and Subramanian, 1999).

Table- 4.1: Methane and other water and sediment chemistry parameters in Vembanad Lake, West coast, India

Post-Monsoon

L.No.	Name	pH	Methane	Salinity	SO4	PO4	NO3	Sed C%	Sed N%	Diss Mn*	Diss Fe*	Sed Mn	Sed Fe
1	Puloot	7.64	16.12	4.6	1949	0.064	4.1	2.99	0.171	0.036	0.872	198	32180
4	Venupady	7.87	51.43	10.98	3112	0.159	2.6	2.94	0.263	0.014	0.872	593	6931
7	Thameermukham	6.2	138.48	0.04	75	0.219	2.8	0.54	0.02	0.034	1.38	593	47528
8	Kumaragum	6.41	210.59	0.02	72	0.064	1.0	0.11	0.013	0.008	1.12	198	3466

Pre-Monsoon

L.No.	Name	pH	Methane	Salinity	SO4	PO4	NO3	Sed C%	Sed N%	Diss Mn*	Diss Fe*	Sed Mn	Sed Fe
1	Puloot	7.06	2.54	14.24	2133	0.064	37.4	1.58	0.103	0.029	1.13	198	32180
4	Venupady	7.17	4.30	12.69	1745	0.491	5.5	2.75	0.265	0.132	2.15	593	6931
7	Thameermukham	6.14	3.80	3.52	805	0.188	25.9	0.35	0.014	0.038	1.64	593	47528
8	Kumaragum	6.87	175.91	3.19	615	0.197	18.8	0.04	0.006	0.036	0.61	198	3466

Methane is in mg/ m2/ h, Salinity is in ppt, all other parameters in mg/L
Sed C% means Total sedimentary carbon
* These values though measured in water might represent colloidal fraction as at this pH dissolved Mn and Fe cant be measured

Figure 4.1: Spatial and Seasonal variation in Methane emissions from Vembanad Lake.

| | Post-Monsoon | Pre-Monsoon |
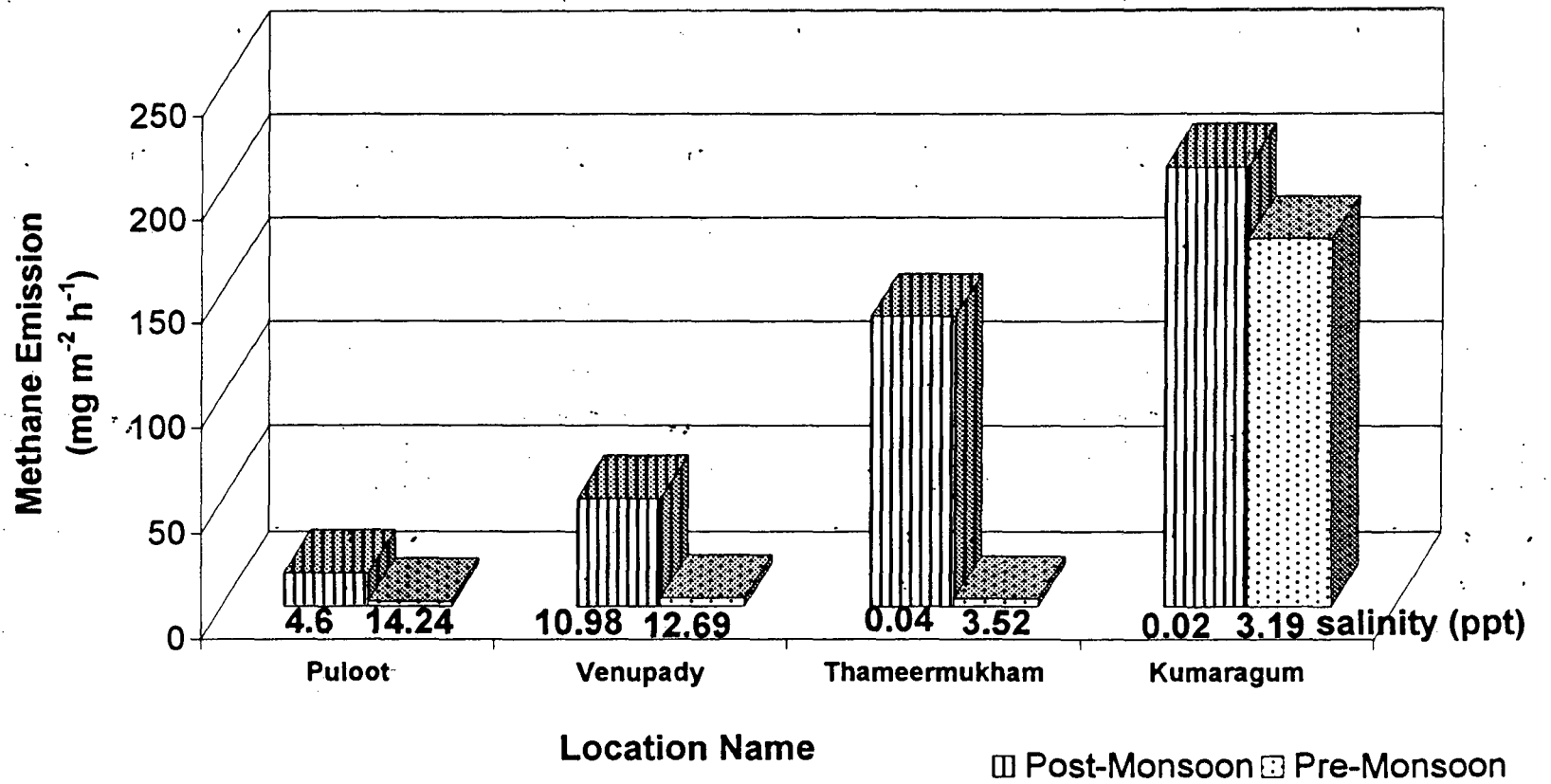
The peak in methane efflux is obtained at noon. This reaffirms that *solar radiation* has effect on methane efflux. Except at Location-6, there is reduction in emissions due to tidal influence. Location-7, shows exceptionally high methane efflux values due to plant mediated effect. There is presence of water hyacinth in the area. It acts as gas conduits for transporting gas from sediment to atmosphere, without getting oxidised in the surface waters.

Methane emissions show strong negative correlation with sulphate (r=-0.83) and salinity (r= -0.72) (Tab- 4.2), which is in confirmation with Schutz and Seiler, 1989 and Ramesh et al. 1996). *Sulphate and salinity* inturn are controlled by natural environmental conditions or by anthropogenic activities as disposal of domestic sewage and industrial effluents.

It has been shown that competitive interactions occur between sulfur-reducing bacteria and methanogens. Generally, sulfur-reducing bacteria out compete methanogens for hydrogen and acetate- two precursors for methane generation in the environment (Sansone and Martens, 1981; Capone and Kiene, 1988). In environments rich in sulphate, methanogenesis occur below the sulphate depletion zone (Martens and Berner, 1974; Lovely and Klug, 1986). Thus, a strong negative correlation exists between methane and salinity and sulphate.

Methane also shows a negative correlation with dissolved *iron* (r= -0.77), dissolved *manganese* (r= -0.98), sediment iron (r= -0.61) and sediment manganese (r= -0.57).

Heavy metals also have effect on methanogens as they can be toxic for microorganisms by inactivating a wide range of enzymes (Shen and Kosaric, 1994). Methanogens are most sensitive of the anaerobic consortia to environmental factors as toxicant concentrations (Kugelman and Chin, 1971).

It is known that neither sulfur-reducers nor methanogens can dominate in anaerobic sediments, untill all reducible Fe (III) oxide are depleted as they compete for organic substrates with methanogens (Lovely, 1991). However, several studies on lakes conclude that Fe (III) reduction is of minor importance for organic carbon decomposition. But, Lovely (1991); Westermann (1993) and Roden (1996) have shown that microbial

Table 4.2: Correlation table between methane and other water and sediment chemistry in Vembanad Lake.

Post-Monsoon

	Methane	Salinity	SO4	PO4	NO3	Sed C%	Sed N%	Diss Mn	Diss Fe	Sed Mn	Sed Fe
Methane	1.00										
Salinity	-0.72	1.00									
SO4	-0.83	0.98	1.00								
PO4	0.02	0.06	-0.05	1.00							
NO3	-0.88	0.33	0.47	0.09	1.00						
Sed C%	-0.96	0.85	0.94	-0.14	0.73	1.00					
Sed N%	-0.84	0.98	1.00	-0.04	0.49	0.94	1.00				
Diss Mn	-0.51	-0.18	-0.05	0.26	0.85	0.26	-0.02	1.00			
Diss Fe	0.69	-0.78	-0.85	0.57	-0.34	-0.84	-0.84	0.18	1.00		
Sed Mn	-0.12	0.36	0.23	0.95	0.07	0.07	0.23	0.08	0.31	1.00	
Sed Fe	-0.22	-0.39	-0.31	0.50	0.62	-0.06	-0.29	0.93	0.52	0.26	1.00

Pre-Monsoon

	Methane	Salinity	SO4	PO4	NO3	Sed C%	Sed N%	Diss Mn	Diss Fe	Sed Mn	Sed Fe
Methane	1.00										
Salinity	-0.60	1.00									
SO4	-0.65	0.99	1.00								
PQ4	-0.13	0.17	0.05	1.00							
NO3	-0.16	0.07	0.20	-0.95	1.00						
Sed C%	-0.61	0.87	0.82	0.62	-0.39	1.00					
Sed N%	-0.50	0.77	0.69	0.75	-0.56	0.98	1.00				
Diss Mn	-0.30	0.42	0.31	0.96	-0.85	0.80	0.90	1.00			
Diss Fe	-0.77	0.39	0.37	0.71	-0.49	0.72	0.74	0.78	1.00		
Sed Mn	-0.57	-0.06	-0.08	0.67	-0.54	0.34	0.41	0.62	0.89	1.00	
Sed Fe	-0.61	-0.09	0.04	-0.53	0.67	-0.25	-0.38	-0.49	0.16	0.26	1.00

Fe(III) reduction could be significant to suppress both methane production and sulfur-reduction in Fe rich fresh-water sediments.

However, in marine sediments sulfur-reduction is much more dominant as sulphate binds with iron under these conditions to form sulfides and hence make iron unavailable for microbial working. Thus, there can be a coexistence of sulfur-reducers and Fe (III)-reducers in the marine and coastal sediments.

4.1.2 Location wise variation in Methane Emissions

Location-1 has a low salinity but lower methane efflux values in both seasons (Tab- 4.3). This is due to high sulphate concentrations at this location. The sulphate is derived from large-scale coconut husk fermentation being carried out there. The husk fermentation creates anoxia and releases hydrogen sulfide, which on passing through the oxic waters oxidises to sulphate. It has been shown that competitive interactions occur between sulfur-reducing bacteria and methanogens (see above). Thus, in these sediments mineralization of organic matter is mainly through sulphate reduction, hence lower methane efflux.

Location-6 has higher salinity but also higher methane emissions. This is due to higher amount of organic matter in the sediments at this location (Tab- 4.3). Higher methane emissions can be explained by the fact that methanogens and sulphate-reducers can coexist in this environment due to abundance of food precursors as reported by Oremland et al. 1982. This has also been found for Adyar Estuary, East Coast, India by Ramesh and Purvaja (1997) and Verma and Subramanian (1999).

Location-7 and 8 are nearly freshwater with sea water intrusion during summers, which accounts for lower values for methane emissions during pre-monsoon as compared to post-monsoon. Location-7 is also rich in organic matter derived from decomposing water hyacinth. The lower sulphate and higher organic content (Tab- 4.3) in sediments facilitates high production of methane from these locations. In fresh-water sediments, concentration of sulphate and nitrate is low, thus methanogenesis is dominant and responsible for mineralization of organic carbon in the sediments (Fig- 4.2).

Table- 4.3: Day time variation in methane emissions from Vembanad Lake during Pre-Monsoon

Location-1 : Pullot (Salinity= 14.24, Organic Carbon= 1.58%)

Time	Methane	Sed Temp	Water Level
9:00	1.86	30	9
10:00	2.58	30	8.5
11:00	2.79	31	9.5
12:00	1.01	31.5	11.5
13:00	2.03	32	11.2
14:00	3.97	32	12
15:00	2.11	31.5	10.5
16:00	1.65	30.7	10.7
Sum	20.30		
Av.	2.54		

Location- 4: Venupady (Salinity= 4.3, Organic Carbon= 2.75%)

Time	Methane	Sed Temp	Water Level
9:00	2.8	30.5	9.0
10:00	1.4	31	8.5
11:00	2.8	31.5	8.2
12:00	17.9	32.5	8.0
13:00	2.5	34	8.5
14:00	2.4	35	8.2
15:00	2.2	35.5	7.7
16:00	-	-	-
Sum	34.4		
Av.	4.3		

Location- 7: Thaneermukham (Salinity= 3.52, Organic Carbon= 0.35%)

Time	Methane	Sed Temp	Water Level
9:00	2.3	30	8.8
10:00	3.88	31	9
11:00	3.09	32	9.5
12:00	2.41	32	14.5
13:00	4.78	32.5	16
14:00	2.59	31.8	12
15:00	2.87	31	11.8
16:00	3.56	30.5	10.5
Sum	30.43		
Av.	3.8		

Location- 8: Kumaragum (Salinity= 3.19, Organic Carbon= 0.04%)

Time	Methane	Sed Temp	Water Level
9:00	70.15	30	11
10:00	89.69	30.5	10.8
11:00	75.5	32	10.2
12:00	191.9	32.8	11
13:00	242.7	33	11.2
14:00	167.3	33	11.5
15:00	272.1	32.5	10.5
16:00	291.2	31.5	10.2
Sum	1407.2		
Av.	175.91		

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Puloot

Venapady

Thaneermukham

Kumaragam
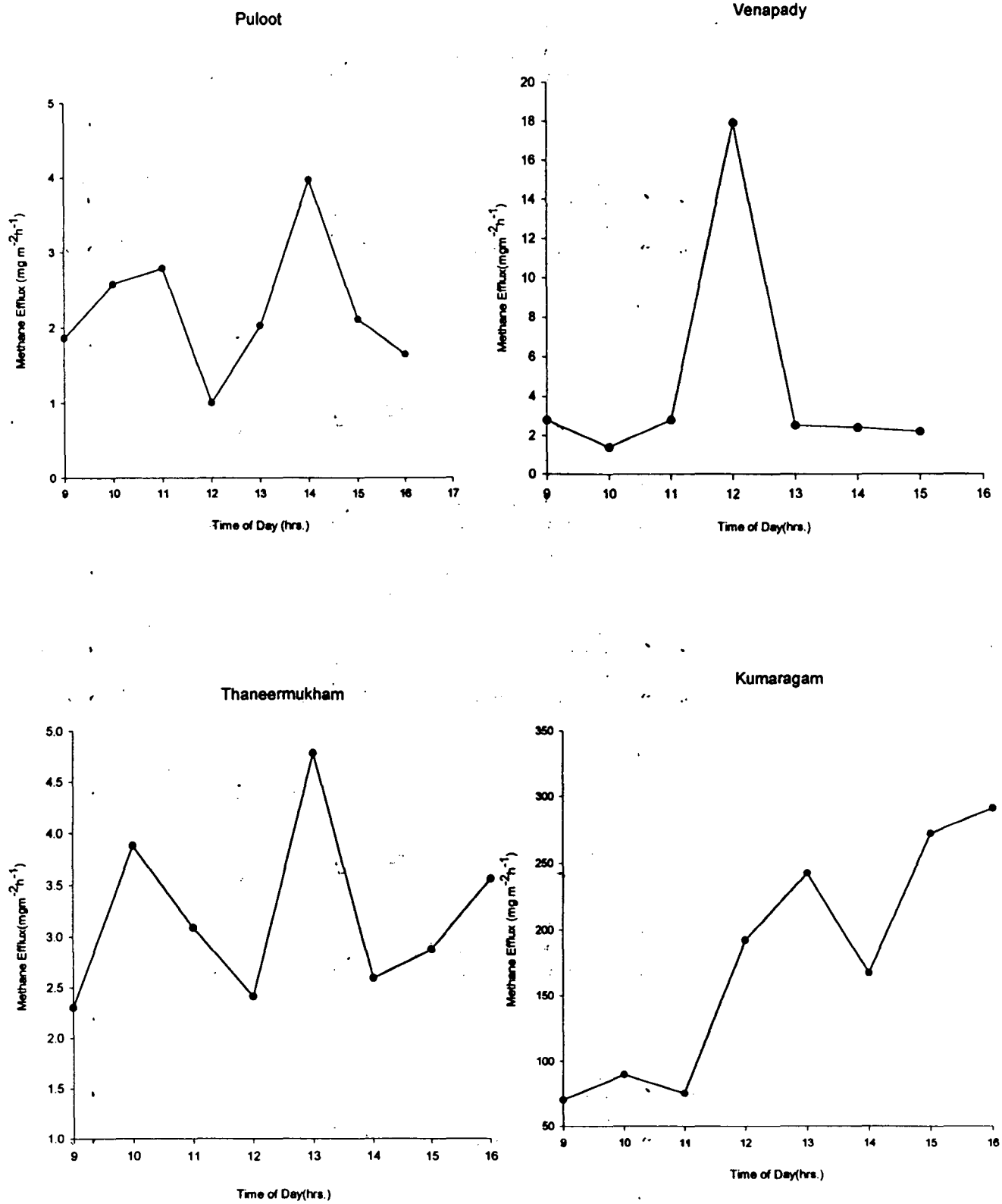
Figure- 4.2: Day-time variation in Methane emission from Vembanad Lake during Pre-Monsoon

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In Location-8, has the highest CH_4 emissions value of all locations. It has salinity close to that of fresh water and there is also presence of vegetation as water hyacinth. These plants transport methane through aerenchyma from sediments to surface or from lower anoxic waters. This prevents oxidation of methane when passing through oxic surface waters. This mechanism dominates to ebullition or diffusion of gas through the water-air interface, hence higher emissions.

4.2 AMINO ACIDS

Spectral distribution of individual amino acids shows uniform relative concentrations for all amino acids except Met and Try. Non Protein amino acids (b- aba, g-ala and Orn), show increase in relative concentrations towards the estuarine region (Tab- 4.4).

THAA content doesn't show a trend in the lake sediments. It ranges from 157.5 to 9847 $\mu g/g$ in the Vembanad Lake bed sediments. THAA consists of mainly protein amino acids (> 95%). Contribution of THAA-C% to organic carbon in bed sediments varies from 2.14 to 85.51 % and THAA-N% to the total nitrogen varies from 6.05 to 66.44% (Table 4.5).

Bed sediments have almost uniform composition of organic matter in terms of molar concentration of individual amino acid spatially across the Vembanad Lake. Except for Met, Try, Arg and non-protein amino acid (b- aba and Orn), amino acids show variation of less 10% or less (Fig – 4.3).

Distribution of amino acid after grouping them into acidic, basic, neutral, aromatic and non-protein amino acids (Fig – 4.4), show a consistency in their molar concentrations except for S-containing amino acids. Neutral amino acids are most abundant followed by acidic, basic and aromatic amino acids.

In general the distribution of amino acids emphasizes that land-derived detritus is the major source of organic matter in the Vembanad Lake, Kerala.

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Table 4.4: Amino acid characterstics of bed sediments of Vembanad Lake

Site	1	2	3	4	5	6	7	8	9	10
ASP	14.7	13.2	10.4	13.0	10.4	13.4	11.2	15.7	12.8	11.9
GLU	11.5	11.7	9.0	10.4	9.0	11.7	8.0	10.6	10.2	11.3
HIS	1.4	1.7	1.1	1.6	1.1	1.3	1.8	4.1	1.7	1.8
ORN	0.3	0.8	0.4	0.1	0.4	0.2	0.5	0.4	0.4	0.3
LYS	4.0	3.8	3.0	3.4	3.0	3.9	4.6	4.2	4.0	4.2
ARG	4.1	4.3	4.1	4.7	4.1	4.0	4.7	4.6	4.1	4.3
THR	6.8	5.7	6.9	6.1	7.0	6.5	7.0	5.9	7.2	6.4
SER	6.8	7.2	7.4	6.7	7.4	6.3	7.4	9.6	7.2	6.7
GLY	15.4	16.2	18.1	17.3	18.2	15.6	15.0	14.3	14.6	14.6
ALA	9.8	11.1	12.1	12.1	12.2	11.1	12.0	10.1	11.9	11.3
VAL	7.3	7.7	8.0	7.1	8.1	7.7	7.9	6.9	7.9	8.1
ILE	4.3	3.8	4.1	3.8	4.2	4.3	5.0	3.3	4.3	4.5
LEU	7.0	6.3	8.1	7.3	8.1	6.9	8.1	5.6	7.3	7.4
TYR	1.3	0.6	0.7	1.6	0.7	1.8	1.6	0.2	1.3	2.1
PHE	3.8	3.8	4.0	4.0	4.0	4.0	4.4	3.0	4.0	4.1
b-ALA	0.7	0.6	0.8	0.3	0.8	0.6	0.5	0.9	0.8	0.5
g-ABA	0.7	0.7	1.2	0.6	1.2	0.6	0.4	0.4	0.3	0.5
ORN	0.3	0.8	0.4	0.1	0.4	0.2	0.5	0.4	0.4	0.3
MET	0.0	0.5	0.4	0.0	0.0	0.0	0.0	0.3	0.0	0.0

All in mole%

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Table 4.5: Biogeochemical characterstics of amino acids of sediments of Vembanad Lake.

Site	1	2	3	4	5	6	7	8	9	10
THAA	3647.18	159.94	157.51	542.40	168.72	6435.27	469.32	202.82	276.18	9847.33
Prot.AA	3596.19	156.80	154.14	537.93	165.09	6355.72	463.76	200.02	272.67	9741.72
Non-prot.	50.99	3.14	3.37	4.47	3.63	79.55	5.55	2.80	3.51	105.61
THHA	343.0	10.4	12.1	26.2	13.1	534.9	33.4	17.6	16.19	848.32
THAA-C%	10.03	3.45	85.51	9.44	60.54	10.24	5.95	9.59	3.90	10.69
THAA-N%	48.8	66.4	8.6	59.0	6.1	33.5	48.9	51.2	22.42	52.64
ASP/b-ALA	21.21	21.57	12.45	38.30	12.45	21.88	24.04	18.43	16.50	24.02
GLU/g-ABA	17.21	16.36	7.60	17.38	7.60	19.09	22.75	27.18	29.27	22.77
AM/GALAM	1.39	1.91	0.52	0.88	0.52	1.48	1.98	1.88	0.38	1.85
THAA/THHA	10.63	15.38	12.99	20.71	12.93	12.03	14.05	11.55	17.05	11.61

All in mole% except THAA-C% and THAA-N%

Figure- 4.3: Distribution of Amino Acids and Aminosugers in Bulk Sediments of Vembanad Lake, Kerala
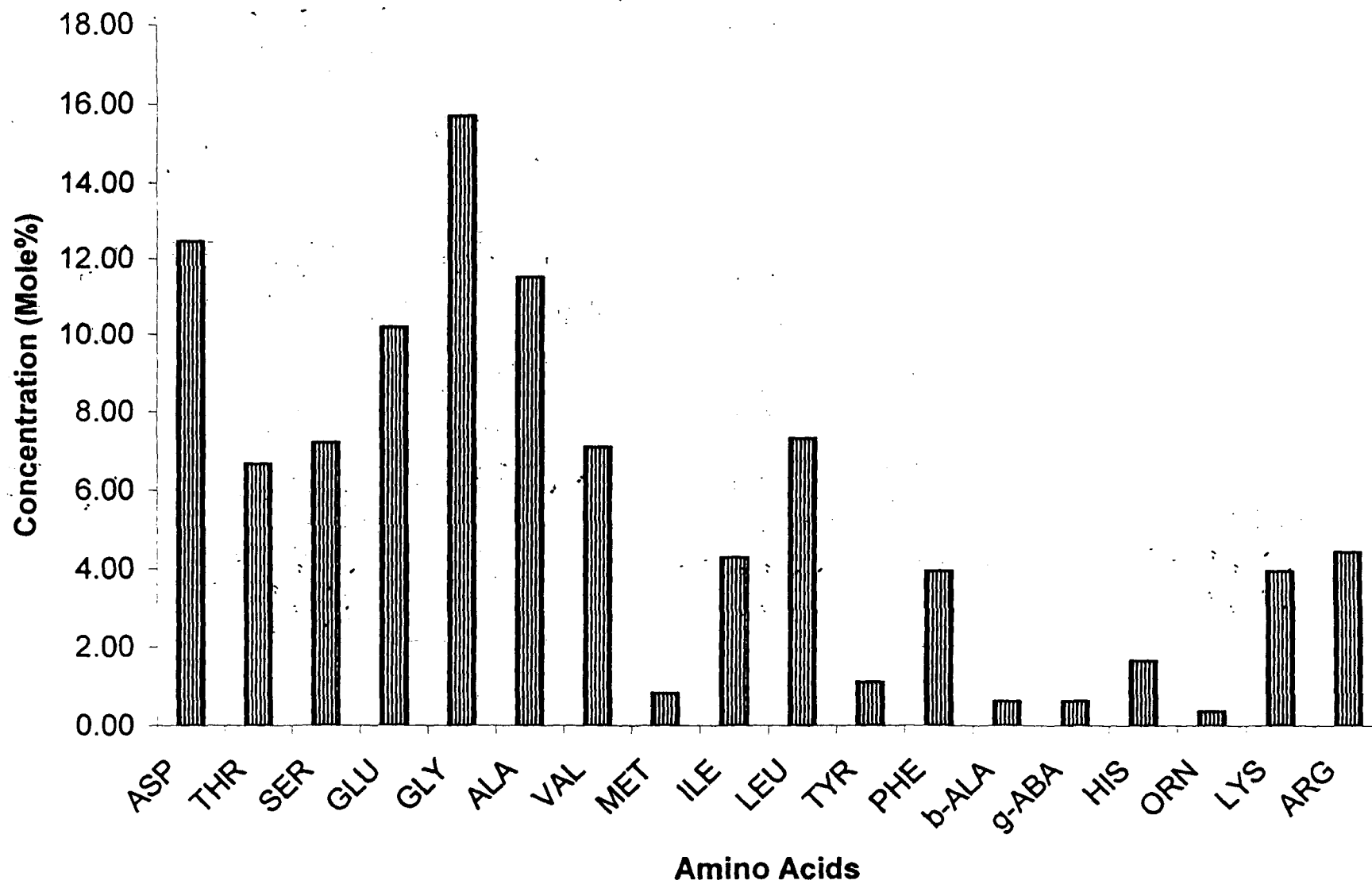
Figure-4.4: Distribution of amino acids in the Bulk Sediments of Vembanad Lake, Kerala
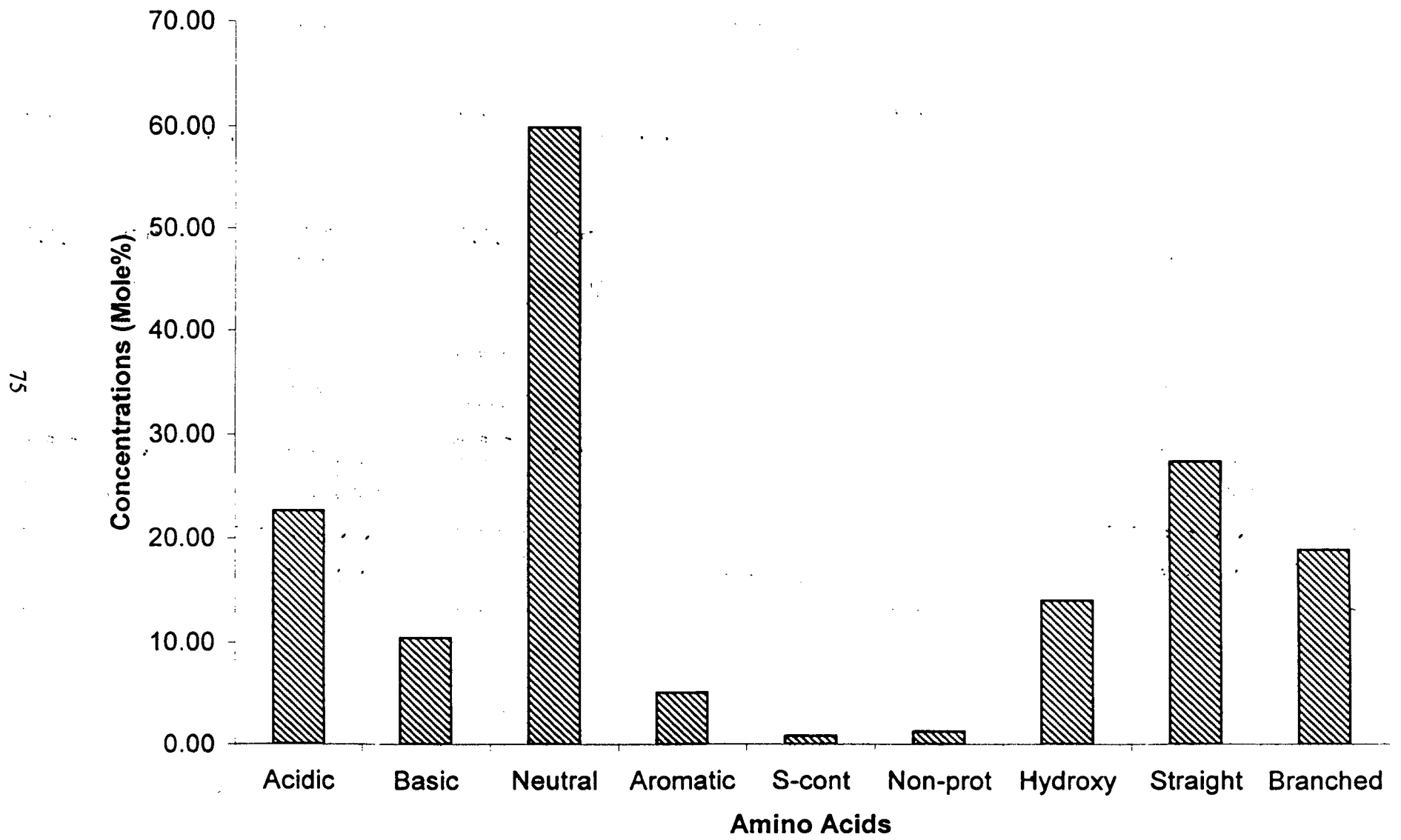
4.3 WATER CHEMISTRY

Water samples were collected from ten locations across the Vembanad Lake during pre-monsoon and post-monsoon. The results for water analysis are presented in the following paragraphs. The accuracy of analysis can be assessed on the basis of discrepancy. It is within the acceptable limits for lake waters i.e. ±10 (Tab- 4.6, Fig- 4.5). Higher discrepancy in certain locations can be due to higher organic matter in the area, which may bind ions and account for the missing charges in the balance.

4.3.1 Electrical Conductivity, pH and TDS

In Vembanad Lake, the pH varies from 6.14 to 7.94 (Table- 4.7). There is no significant variation in pH between the pre-monsoon and post-monsoon samples. The waters show fairly neutral character.

Electrical Conductivity variation within the lake is from 0.16 to 51.8 mS/cm. The large variation is due to gradient in Lake waters from fresh to brackish to marine. There is considerable variation in EC values of pre-monsoon and post-monsoon. This variation is due to concentration of salts during summers when the fresh water input is low and evaporation is large.

TDS shows that same trend as EC and ranges from 140 to 43463 mg/L. TDS is nothing but the sum of all dissolved ions in the water. It can also be calculated by multiplying EC (μS/cm) by 0.7 (for fresh-water).

The correlation table shows that EC has good correlation with Na, K, Ca, Mg, HCO_3, SO_4, Cl and TDS. It shows strong negative correlation with SiO_2. (Table - 4.8).

4.3.2 Sodium, Potassium and Chloride

Chloride concentration varies from 34 to 25120 mg/L in the Vembanad Lake. There is a gradual gradient from fresh-water to marine. Lower concentrations are in the southern part of the lake, which is far from the mouth to the sea, and a number of rivers fall into the lake at this end. There is a buildup of chloride in the lake in pre-monsoon due to concentration by evaporation.

Table 4.6: Chemical characterstics of waters of Vembanad Lake

Postmonsoon

L.No.	HCO3	SO4	PO4	NO3	Cl	Na	K	Ca	Mg	S cation	S anion	Disc.
1	0.56	40.54	0.002	0.067	180.72	150.14	1.74	10.03	109.73	271.65	221.88	10.08
2	0.92	64.72	0.003	0.710	273.39	299.28	5.18	13.39	160.21	478.06	339.75	16.91
3	1.01	32.47	0.006	0.293	372.69	385.78	9.23	15.00	195.33	605.34	406.47	19.66
4	0.98	80.85	0.022	0.289	352.83	329.86	6.56	14.72	186.55	537.68	434.97	10.56
5	0.89	32.47	0.016	0.028	246.92	199.91	3.81	12.65	139.36	355.73	280.33	11.85
6	1.48	64.72	0.005	0.042	432.27	363.41	8.31	15.39	216.17	603.29	498.52	9.51
7	0.05	3.63	0.007	0.045	1.67	1.49	0.12	0.19	1.45	3.25	5.41	-24.97
8	0.11	1.53	0.002	0.017	0.95	1.09	0.08	0.12	1.05	2.34	2.61	-5.50
9	0.22	0.32	0.002	0.027	1.21	1.56	0.08	0.15	0.76	2.55	1.79	17.67
10	0.25	0.41	0.003	0.042	1.28	1.54	0.09	0.20	0.83	2.65	1.98	14.52

Premonsoon

L.No.	HCO3	SO4	PO4	NO3	Cl	Na	K	Ca	Mg	S cation	S anion	Disc.
1	0.95	44.36	0.002	0.60	559.54	389.08	45.51	28.33	165.87	628.79	605.45	1.89
2	1.64	51.36	0.004	0.48	614.90	435.00	46.88	28.69	169.44	680.01	668.37	0.86
3	1.88	53.63	0.006	0.44	708.39	472.06	51.91	29.43	176.57	729.96	764.34	-2.30
4	1.60	44.17	0.004	0.04	614.90	438.22	49.85	29.06	166.76	683.90	660.71	1.72
5	1.32	29.99	0.009	0.05	478.00	383.44	36.59	21.72	138.24	580.00	509.36	6.48
6	1.76	36.23	0.016	0.09	498.36	348.81	39.57	22.82	146.26	557.46	536.46	1.92
7	0.39	16.75	0.006	0.42	138.30	129.29	4.62	9.76	15.30	158.97	155.87	0.98
8	0.23	12.78	0.006	0.30	125.46	88.61	2.51	5.21	17.92	114.24	138.78	-9.70
9	0.47	0.36	0.003	0.83	2.60	2.60	0.47	0.42	0.88	4.37	4.27	1.13
10	0.35	0.28	0.004	0.15	2.68	1.89	0.43	0.39	0.75	3.46	3.47	-0.16

All variables in meq/L except discrepency in percentage

Post-Monsoon

$y = 0.7554x + 3.12$
$R^2 = 0.9835$

Sum Cations

Sum Anions

Pre-Monsoon

$y = 0.9701x + 2.9618$
$R^2 = 0.9913$

Sum Cations

Sum Anions
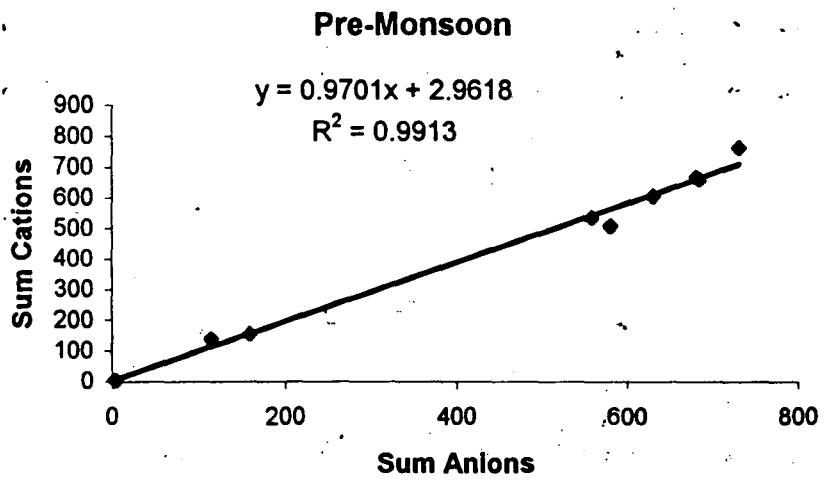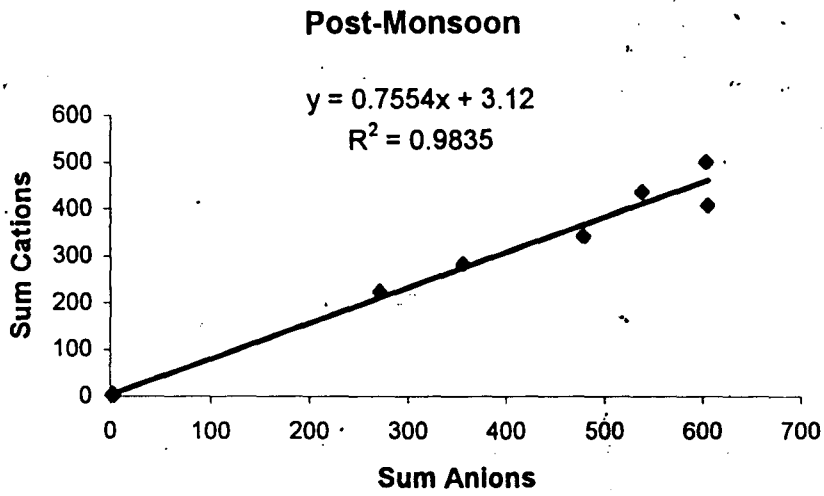
Figure- 4.5: Graph showing accuracy of analysis for anions and cations

Table- 4.7: Water Chemistry parameters of Vembanad Lake, Kerala

Postmonsoon
All values in mg/L except pH, Electrical Conductivity(mS/cm) and Salinity(ppt)

L.No.	pH	EC(mS)	HCO$_3$	SO$_4$	PO$_4$	NO$_3$	Cl	SiO$_2$	Na	K	Ca	Mg	TDS	TSM	Salinity	(Ca+Mg/Na+K)
1	7.64	14.5	34.0	1949	0.06	4.14	6408	4.45	3451	68	201	1333	13476	19	4.59	0.44
2	7.55	22.7	56.2	3112	0.09	44.09	9695	3.79	6880	202	268	1947	22238	364	6.94	0.31
3	7.76	26.3	61.3	1561	0.18	18.22	13216	2.33	8869	361	301	2373	26797	28	9.47	0.29
4	7.87	25.4	59.6	3887	0.71	17.96	12512	2.78	7583	256	295	2267	26914	2151	8.96	0.33
5	6.99	18.2	54.5	1561	0.49	1.74	8756	5.37	4596	149	253	1693	17096	56	6.27	0.41
6	6.76	28.7	90.3	3112	0.16	2.61	15329	4.68	8354	325	308	2627	30188	1300	10.98	0.34
7	6.2	0.21	3.3	175	0.22	2.80	59	6.66	34	4.60	3.90	17.60	314	147	0.04	0.56
8	6.41	0.25	6.7	74	0.06	1.03	34	7.13	25	3.00	2.40	12.80	172	2	0.02	0.54
9	6.45	0.25	13.5	16	0.08	1.70	43	7.91	36	3.20	3.00	9.30	140	13	0.03	0.31
10	6.39	0.16	15.2	19	0.10	2.61	45	8.21	35	3.40	4.00	10.10	150	34	0.03	0.37
Mean	7.00	13.67	39.5	1546	0.22	9.69	6610	5.33	3986	137	164	1229	13749	411	4.73	
Std Dev	0.65	12.25	29.1	1463	0.22	13.76	6156	2.08	3763	141	142	1106	12614	729	4.41	
Std Err	0.20	3.87	9.2	483	0.07	4.35	1947	0.66	1190	45	45	350	3989	231	1.39	

Premonsoon
All variables in mg/L except pH, EC(mS/cm) and Salinity(ppt)

L.No.	pH	EC(mS)	HCO$_3$	SO$_4$	PO$_4$	NO$_3$	Cl	SiO$_2$	Na	K	Ca	Mg	TDS	TSM	Salinity	(Ca+Mg/Na+K)
1	7.06	44	58	2133	0.064	37.4	19842	3.6	8944	1778	568	2023	35383	140.0	14.21	0.24
2	7.94	45.3	100	2469	0.112	29.5	21805	1.9	10000	1831	575	2066	38877	13.2	15.62	0.22
3	7.77	51.8	115	2578	0.178	27.6	25120	1.2	10852	2028	590	2153	43464	15.1	17.99	0.21
4	7.17	46.8	97	2124	0.121	2.4	21805	1.4	10074	1947	582	2034	38667	33.3	15.62	0.22
5	7.02	37.8	80	1442	0.273	2.9	16950	2.9	8815	1429	435	1686	30841	26.7	12.14	0.21
6	6.93	39.3	107	1742	0.491	5.5	17672	3.9	8019	1546	457	1784	31333	115.0	12.66	0.23
7	6.14	10.7	24	805	0.188	25.9	4904	3.1	2972	180	196	187	9295	23.3	3.51	0.12
8	6.87	13.6	14	615	0.197	18.8	4449	4.2	2037	98	104	218	7555	3.8	3.19	0.15
9	6.53	0.59	29	17	0.102	51.8	92	4.5	60	18	8	11	288	5.7	0.07	0.24
10	6.90	0.32	21	14	0.121	9.4	95	7.6	43	17	8	9	217	2.0	0.07	0.28
Mean	7.03	29.02	65	1394	0.185	21.1	13274	3.4	6182	1087	352	1217	23592	37.8	9.51	
Std Dev	0.53	20.31	40	973	0.123	16.4	9760	1.9	4373	886	246	968	17186	48.7	6.99	
Std Err	0.17	6.42	13	308	0.039	5.2	3086	0.6	1383	280	78	306	5435	15.4	2.21	

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Table- 4.8 : Correlation Table for various Water Chemistry Parameters in Vembanad Lake, Kerala
Post-Monsoon

	pH	EC(mS)	HCO₃	SO₄	PO₄	NO₃	Cl	SiO₂	Na	K	Ca	Mg	TDS	TSM	Salinity
pH	1.00														
EC(mS)	0.78	1.00													
HCO₃	0.62	0.96	1.00												
SO₄	0.77	0.90	0.85	1.00											
PO₄	0.38	0.42	0.36	0.50	1.00										
NO₃	0.63	0.51	0.39	0.58	0.06	1.00									
Cl	0.74	0.99	0.97	0.88	0.43	0.44	1.00								
SiO₂	-0.91	-0.90	-0.76	-0.82	-0.43	-0.61	-0.88	1.00							
Na	0.78	0.99	0.94	0.87	0.39	0.56	0.99	-0.92	1.00						
K	0.68	0.95	0.93	0.77	0.37	0.47	0.97	-0.86	0.98	1.00					
Ca	0.82	0.99	0.94	0.89	0.45	0.50	0.98	-0.91	0.97	0.91	1.00				
Mg	0.78	1.00	0.97	0.89	0.42	0.48	1.00	-0.90	0.99	0.95	0.99	1.00			
TDS	0.77	1.00	0.96	0.90	0.43	0.50	1.00	-0.90	0.99	0.96	0.98	1.00	1.00		
TSM	0.39	0.57	0.58	0.77	0.67	0.21	0.60	-0.49	0.56	0.54	0.52	0.57	0.61	1.00	
Salinity	0.74	0.99	0.97	0.88	0.43	0.44	1.00	-0.88	0.99	0.97	0.98	1.00	1.00	0.60	1.00

Pre-Monsoon

	pH	EC(mS)	HCO₃	SO₄	PO₄	NO₃	Cl	SiO₂	Na	K	Ca	Mg	TDS	TSM	Salinity
pH	1.00														
EC(mS)	0.73	1.00													
HCO₃	0.73	0.90	1.00												
SO₄	0.75	0.98	0.87	1.00											
PO₄	-0.12	0.16	0.34	0.07	1.00										
NO₃	-0.07	-0.24	-0.29	-0.13	-0.53	1.00									
Cl	0.75	1.00	0.92	0.98	0.13	-0.22	1.00								
SiO₂	-0.48	-0.78	-0.70	-0.81	-0.01	-0.01	-0.79	1.00							
Na	0.71	0.99	0.91	0.97	0.15	-0.25	0.99	-0.80	1.00						
K	0.74	0.99	0.92	0.96	0.12	-0.22	0.99	-0.73	0.98	1.00					
Ca	0.69	0.99	0.88	0.98	0.10	-0.20	0.99	-0.78	0.99	0.99	1.00				
Mg	0.74	0.99	0.92	0.96	0.15	-0.22	0.99	-0.72	0.99	1.00	0.98	1.00			
TDS	0.74	1.00	0.91	0.98	0.13	-0.22	1.00	-0.79	1.00	0.99	0.99	0.99	1.00		
TSM	-0.02	0.44	0.30	0.41	0.32	-0.02	0.41	-0.06	0.41	0.46	0.48	0.49	0.42	1.00	
Salinity	0.75	1.00	0.92	0.98	0.13	-0.22	1.00	-0.79	0.99	0.99	0.99	0.99	1.00	0.41	1.00

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Sodium is also a major ion in the system. Its concentration ranges from 25 to 10852 mg/L (Tab- 4.7). This also follows the salinity gradient of the Lake. There is a large variation in pre-monsoon and post-monsoon concentrations. Na and Cl together make up a major percentage of TDS. This indicates strong marine influence on the water chemistry of Vembanad Lake.

Potassium ion concentration in Vembanad Lake ranges from 3 to 2027 mg/L. There is a significant difference in the pre and post-monsoon values. It shows a strong positive correlation with HCO3, SO4, Cl, Na, Ca and Mg indicating common source (Tab- 4.8).

4.3.3 Calcium and Magnisium

Calcium and Magnesium in surface waters are derived from weathering of rocks in the catchment. The calcium concentration in Vembanad Lake varies from 2.4 to 590 mg/L. There is a strong seasonal variation seen. Magnesium concentration varies from 9.15 to 2626 mg/L. It also follows the salinity gradient of the lake. Calcium shows strong correlations with HCO3, SO4, Cl, Na, K and Mg showing a common marine origin. This is further confirmed by ratio of $(Ca+Mg)/(Na+K)$. This ratio is used as an index to understand silicate and carbonate weathering. Low $(Ca+Mg)/(Na+K)$ ratio i.e. less than unity, suggests no significant contribution from carbonate weathering.

4.3.4 Bicarbonate

Bicarbonate is a major ion in surface waters. In Vembanad Lake, it shows a irregular treand and ranges from 3.29 to 114.5 mg/L. There is an appreciable variation in pre and post-monsoon values. Bicarbonate shows good correlation with Cl, Na, Ca, Mg and K, indicating marine origin. The average pCO_2 value for Vembanad Lake is less than the atmospheric value of $10^{-3.5}$ atmosphere, which is in confirmation to the global trend (Bajpayee, 1998).

Higher values in pre-monsoon in Vembanad Lake are due to extensive evaporation and low discharge of fresh-water into the lake during summers.

4.3.5 Sulphate

Sulphate in water is mainly due to dissolution of gypsum or through seawater intrusion. The range of sulphate in Vembanad Lake is from 13.56 to 3112 mg/L. The concentration increases towards the opening to the sea (Fig- 4.6). Pockets of high sulphate concentrations are due to coconut husk fermentation, which releases H2S, which gets oxidized to sulphate in surface waters. Sulphate shows strong correlations with HCO3, Na, K, Cl, Ca and Mg.

4.3.6 Dissolved Silica

Dissolved silica has its source entirely from silicate rocks. Silica occurs in the form of H_4SiO_4 at pH values lower than 9. The range of dissolved silica in the Vembanad Lake is from 2.33 to 8.21 mg/L. The dissolved silica concentration decreases appreciably at the opening to the sea (Fig- 4.7). There is a removal of silica in high salinity region due to consumption of silica by organisms as diatoms and radiolarians (Kanatini and Takona, 1984). It doesn't show any correlation with any other parameter.

4.3.7 Phosphate

Phosphate in natural waters is derived mainly from agricultural practices, industrial effluent and domestic sewage. It is a major limiting nutrient in any aquatic system.

The range of phosphate in the Vembanad Lake is from 0.06 to 0.71 mg/L. There is no regular trend in the concentration and not much seasonal variation is seen. Higher concentrations occur in areas of human interference (Fig- 4.8). It also doesn't show any correlation with any other parameter.

4.3.8 Nitrate

Nitrate concentration in Vembanad Lake varies from 1.03 to 51.8 mg/L. There is no specific trend in its distribution across the lake (Fig- 4.9). Pockets of high concentration reflect areas of coconut husk fermentation where anoxic conditions prevail. Nitrate doesn't show any good correlation with any other parameters indicating its
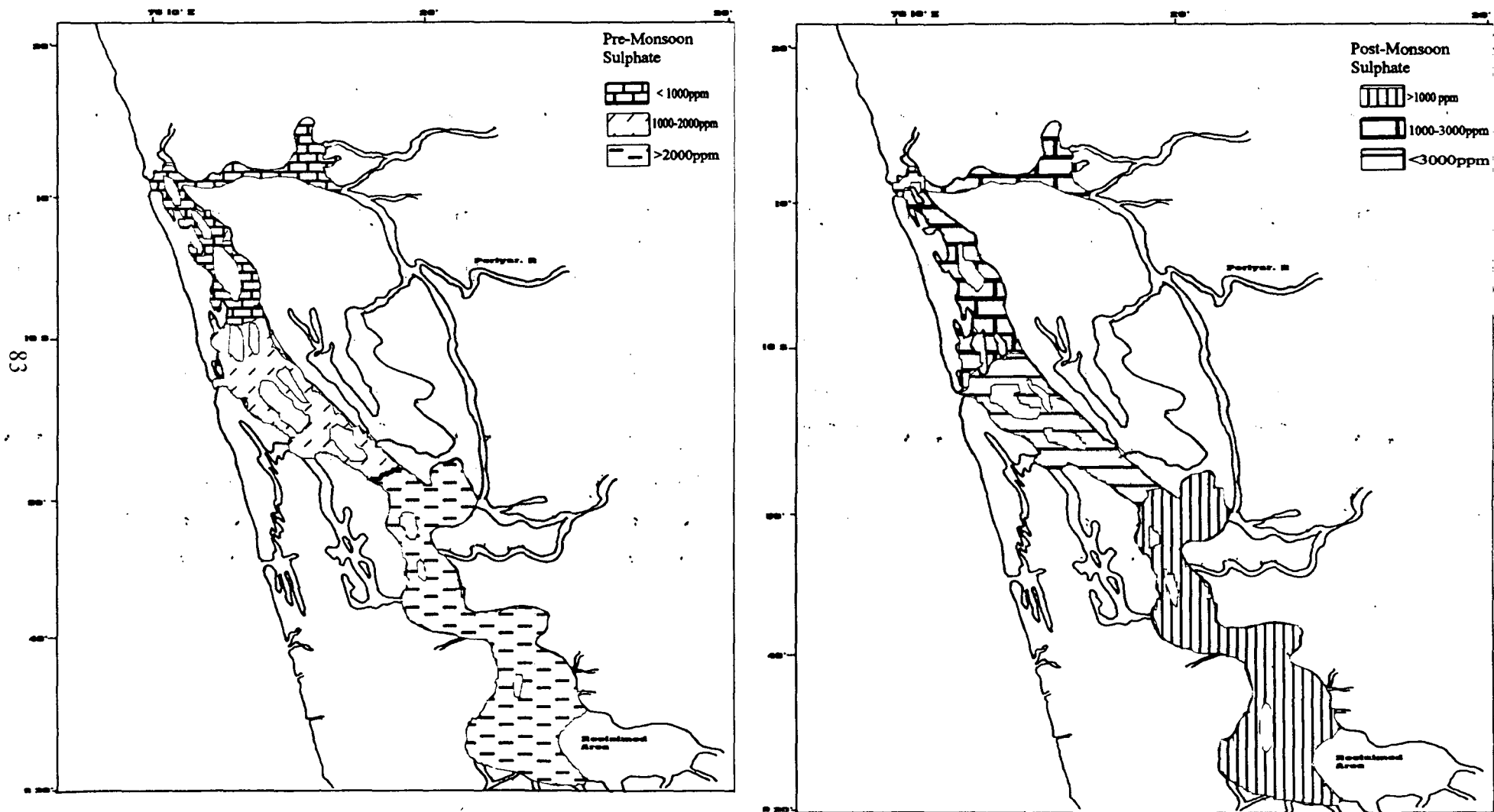
Figure 4.6: Seasonal and spatial variation in Sulphate concentration in Vembanad Lake
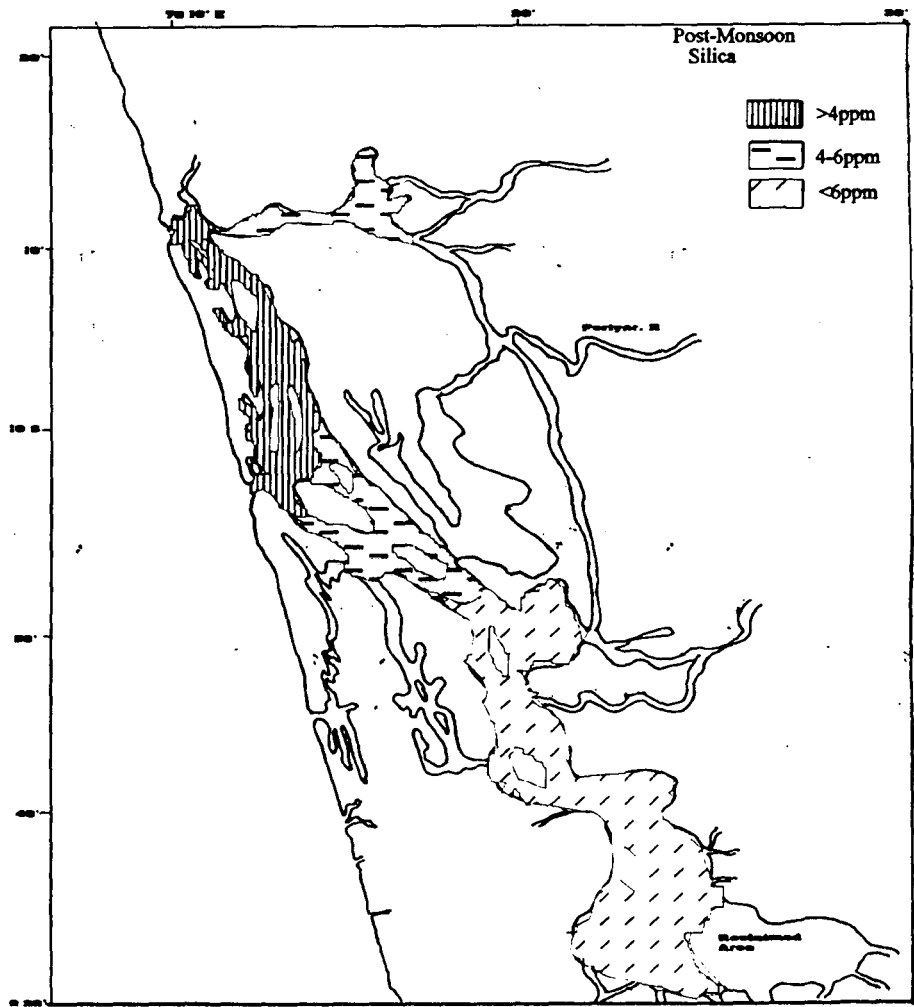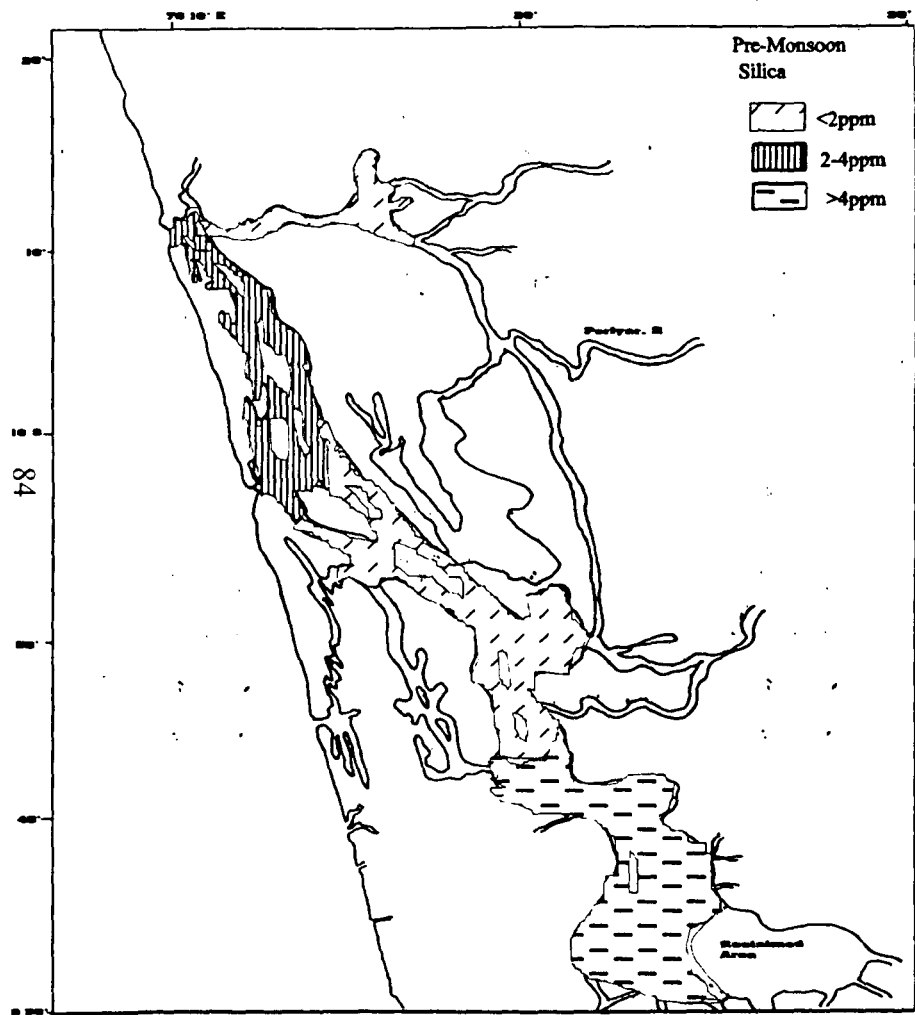
Figure 4.7: Seasonal and spatial variation in silica in Vembanad Lake.
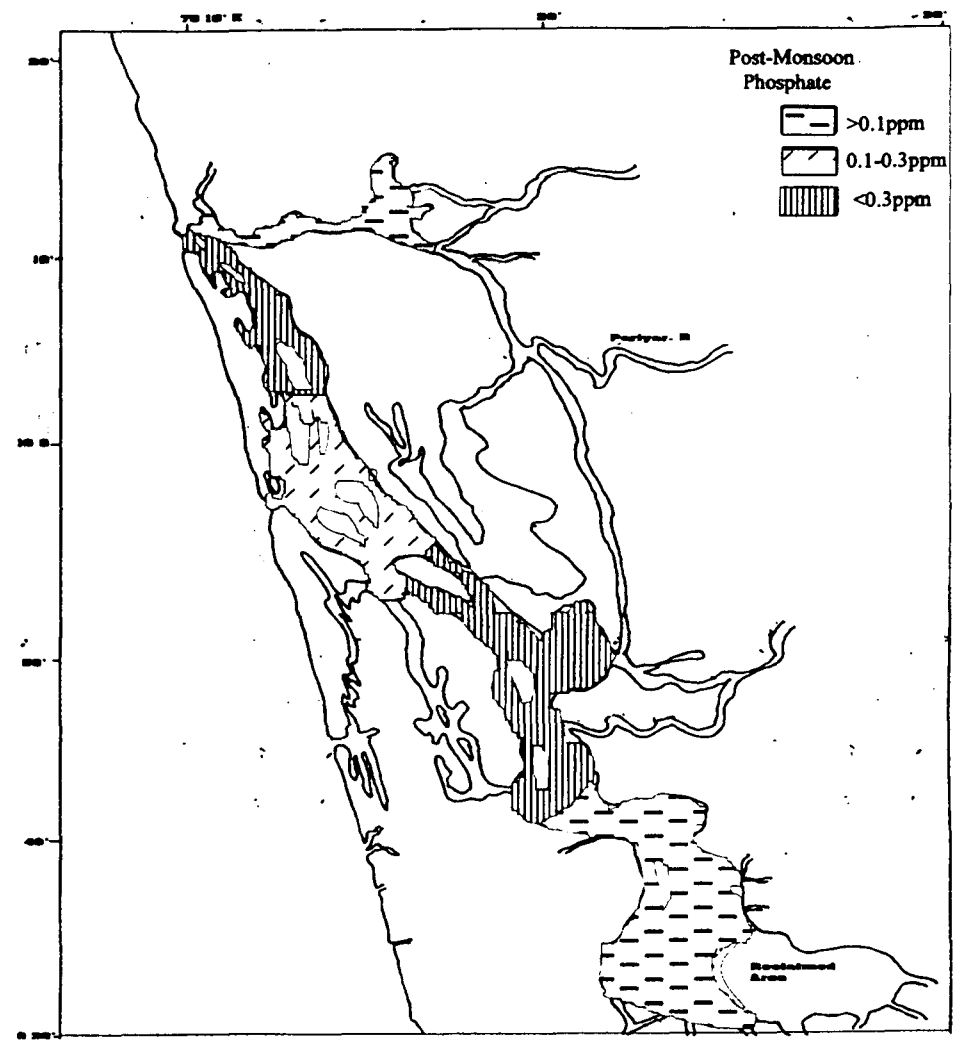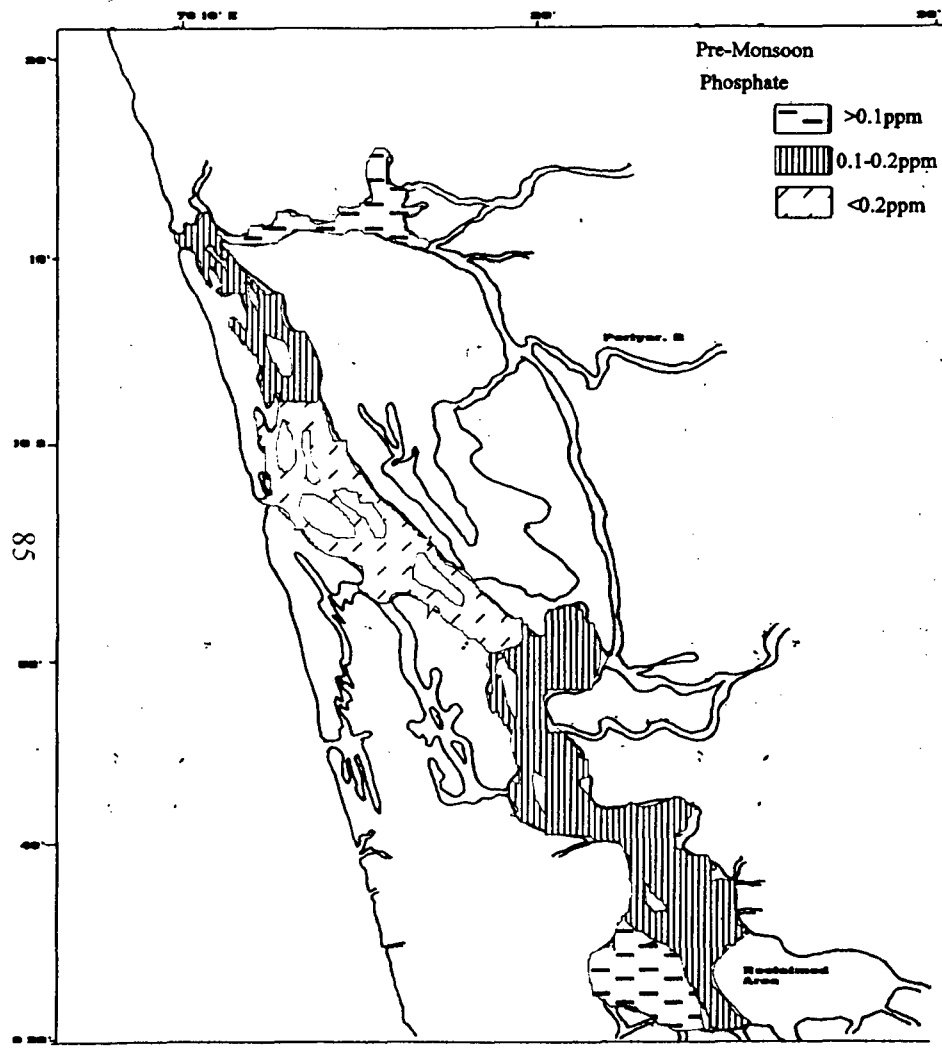
Figure 4.8: Seasonal and spatial variation in phosphate in Vembanad Lake.
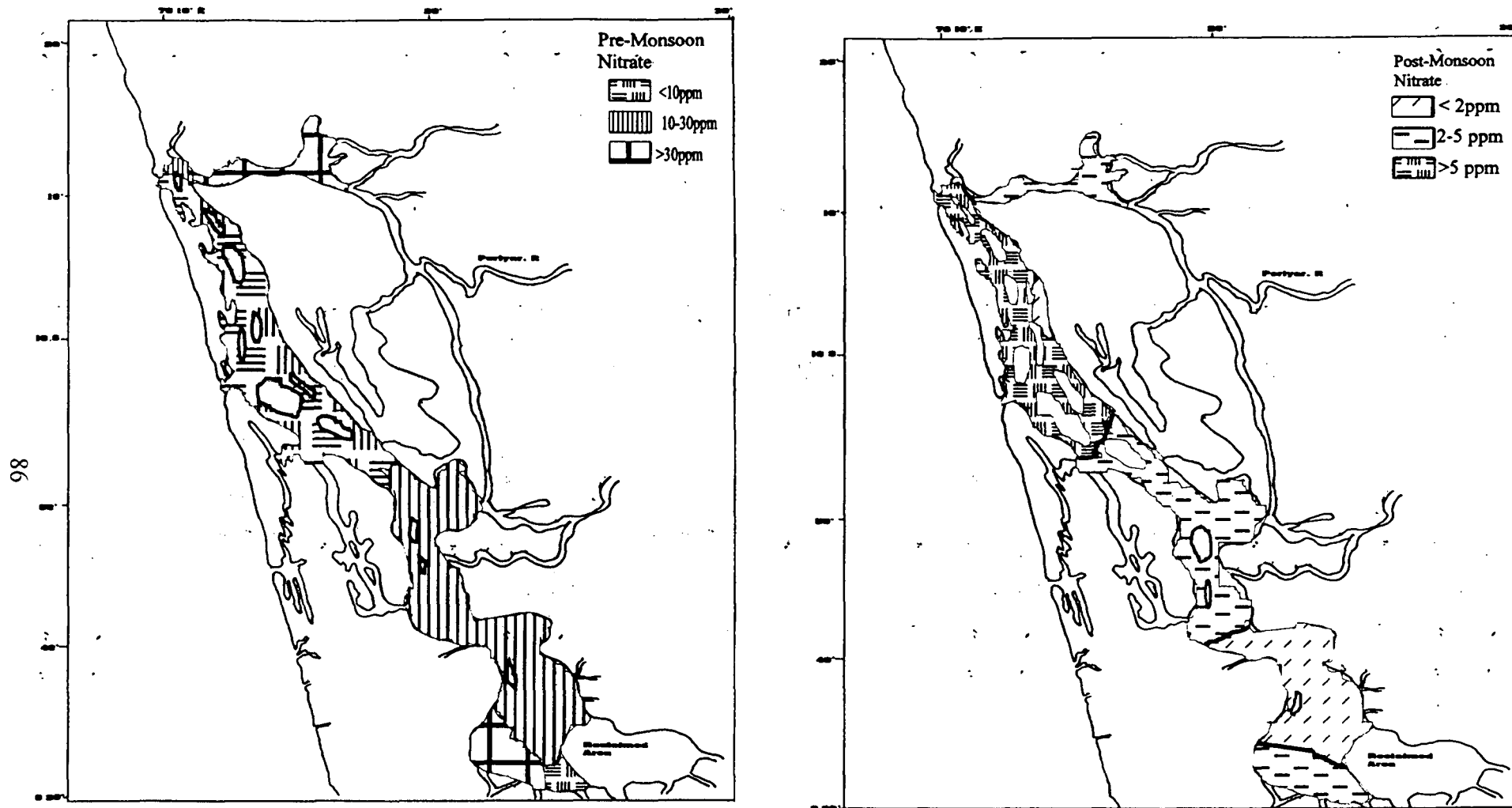
Figure 4.9: Seasonal and spatial variation in nitrate in Vembanad Lake.

independent mobility with respect to other dissolved species in the system. Nitrate behaves non-conservatively in Periyar Estuary was reported by Sarla Devi et. al, 1991 and in Mahanadi Estuary (Upadhayay, 1989).

4.4 PARTICULATE MATTER

Rivers transport land derived matter to the oceans in dissolved and suspended forms. The relative high stability and low nutrient values of particulate matter allows its accumulation in the deep-sea (Ittekkot et al. 1986). The transport of particulate organic carbon by Himalayan rivers is about 9 million tonnes per year. The flux of particulate organic and inorganic phosphorous from Indian rivers to oceans is 0.2 to 1.5 million tonnes per year, respectively (Ramesh et al. 1995). The estimated transport of nitrogen as particulate to coastal seas by rivers is 41 million tonnes per year (Galloway et al. 1995). Lakes and estuaries act as sinks for most of the particulate matter being transported by rivers. In lakes and estuaries the particulate matter undergoes changes in nutrient content and degradation, only the highly stable forms as humics are transported to the oceans. There is cycling to nutrients as nutrients are released from particulates to the water during decomposition.

4.4.1 Particulate Organic Carbon (POC)

Particulate Organic Carbon in the lake can be derived from authochthonous sources as phytoplanktons and periplanktons or from land-derived materials. The POC content in Vembanad Lake varied from 7.8% to 14.4% during the Post-Monsoon and from 0.06% to 4.8% during the Pre-Monsoon (Tab- 4.9). The large variation could be due to the nature of organic matter of the particulate matter.

4.4.2 Particulate Nitrogen (PN)

The Particulate Nitrogen in the rivers and lake are from mostly land derived sources or from phytoplanktons, hence good correlation with N/P (Tab- 4.10). The PN content in the particulate of Vembanad Lake varied from 0.143 to 0.722% during the Post-Monsoon and from 0.385 to 1.210% during the Pre-Monsoon.

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Table- 4.9: Nutrient variation in particulate matter during pre-monsoon and post-monsoon

Post-Monsoon

L.No	C%	N%	P%	C/N	C/P	N/P	Salinity	TSM
1	10.80	0.347	0.07	31.1	154.3	4.96	4.59	18.9
2	16.80	0.722	0.08	23.3	207.3	8.91	6.94	364.2
3	10.80	0.500	0.03	21.6	390.3	18.07	9.47	27.5
4	14.40	0.211	0.05	68.4	316.8	4.63	8.96	2151.0
5	9.02	0.250	0.72	36.1	12.5	0.35	6.27	56.0
6	7.80	0.292	0.08	26.7	94.0	3.51	10.98	1300.0
7	0.60	0.286	0.62	2.1	1.0	0.46	0.04	146.7
8	12.00	0.161	0.07	74.5	161.9	2.17	0.02	2.0
9	13.80	0.143	0.48	96.6	28.8	0.30	0.03	13.2
10	11.40	0.261	0.55	43.7	20.9	0.48	0.03	34.0
Mean	10.74	0.317	0.27	42.42	138.77	4.38	4.73	411.34
Std Dev	4.42	0.174	0.28	28.84	134.73	5.55	4.41	729.12
Std Err	1.40	0.055	0.09	9.12	42.61	1.76	1.39	230.57

Pre-Monsoon

L.No	C%	N%	P%	C/N	C/P	N/P	Salinity	TSM
1	4.80	0.385	0.05	12.5	96.0	7.70	14.21	140.00
2	0.48	0.533	0.07	0.9	6.9	7.61	15.62	13.21
3	0.30	0.600	0.04	0.5	7.5	15.00	17.99	15.09
4	0.06	1.210	0.08	0.05	0.8	15.13	15.62	33.33
5	0.30	0.692	0.64	0.4	0.5	1.08	12.14	26.67
6	1.80	0.400	0.06	4.5	30.0	6.67	12.66	115.00
7	0.06	0.571	0.72	0.1	0.1	0.79	3.51	23.33
8	1.80	0.471	0.1	3.8	18.0	4.71	3.19	3.77
9	0.54	0.660	0.65	0.8	0.8	1.02	0.07	5.66
10	0.12	0.400	0.59	0.3	0.2	0.68	0.07	2.00
Mean	1.03	0.592	0.30	2.39	16.07	6.04	9.51	37.81
Std Dev	1.48	0.243	0.30	3.88	29.74	5.54	6.99	48.71
Std Err	0.47	0.077	0.10	1.23	9.41	1.75	2.21	15.40

Table- 4.10: Correlation table for nutrients in particulate matters during pre-monsoon and post-

Post-monsoon

	C%	N%	P%	C/N	C/P	N/P	Salinity	TSM
C%	1.00							
N%	0.26	1.00						
P%	-0.46	-0.37	1.00					
C/N	0.57	-0.60	-0.05	1.00				
C/P	0.46	0.43	-0.81	-0.01	1.00			
N/P	0.27	0.69	-0.63	-0.33	0.85	1.00		
Salinity	0.18	0.43	-0.54	-0.31	0.60	0.59	1.00	
TSM	0.16	-0.11	-0.40	0.12	0.37	0.01.	0.60	1.00

Pre-monsoon

	C%	N%	P%	C/N	C/P	N/P	Salinity	TSM
C%	1.00							
N%	-0.47	1.00						
P%	-0.46	-0.01	1.00					
C/N	1.00	-0.46	-0.45	1.00				
C/P	0.98	-0.43	-0.47	0.99	1.00			
N/P	0.08	0.46	-0.81	0.08	0.16	1.00		
Salinity	0.18	0.28	-0.70	0.20	0.29	0.79	1.00	
TSM	0.81	-0.28	-0.42	0.83	0.85	0.19	0.41	1.00

4.4.3 Total Particulate Phosphorous (TPP)

The Total Particulate Phosphorous in the Vembanad Lake varied from 0.03 to 0.72% during the Post-Monsoon and from 0.04 to 0.72% during the Pre-Monsoon (Fig- 4.10).

4.5 SEDIMENT CHEMISTRY

Sediment chemistry is essential to calculate the individual element fluxes and their mass balance. Lake and estuaries act as sediment traps for sediments in the rivers. Ten surface sediments were collected from various parts of the Vembanad Lake and were analyzed for various elements.

4.5.1 Silica and Aluminum

Silica content in Vembanad Lake sediments varies from 21.4% to 35.6% (Tab- 4.11). Considerable heterogeneity was observed with respect to Si distribution in the Lake Basin. High Si is due to quartz domination in the bed sediments; lower values in certain regions are in the areas of clay dominance.

Aluminum content varies from 1.6% to 4.5%. No significant fluctuation is observed across the lake basin. Thus aluminum content can be said to be not affected by other chemical processes in the lake-estuary. Aluminum and silica show a negative correlation of $r = -0.49$. Lower aluminum values as respect to other estuaries as 16.5% for Cavery Estuary and Chilka Lake with average Al of 8.67%, is due to absence of bauxite in the area (Fig- 4.11).

4.5.2 Sodium and Potassium

The sodium content in bed sediments of Vembanad Lake varies from 0.25% to 16.96%. According to the distribution of sodium in the lake basin, it can be divided into two regions: a. Low Sodium region in the southern part of the lake and b. Sodium rich region in the northern brackish and saline area. Sodium content is higher near the opening to the sea, which may be due to flocculation and sodium gets aggregated into clays and deposits in the sediments.

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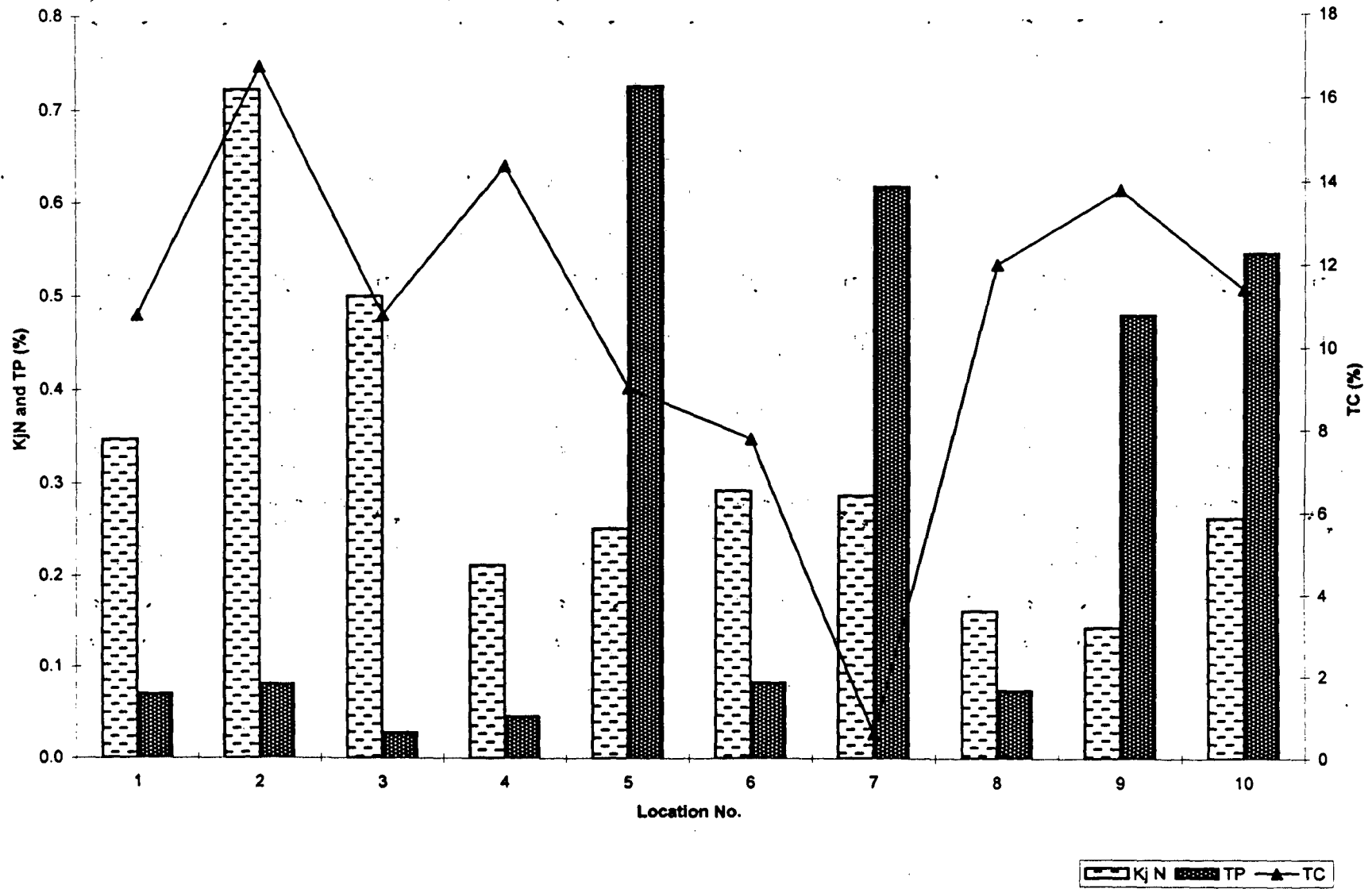
Figure 4.10: Spatial variation of TC, KjN and TP (%) in particulate matters of Vembanad Lake during Post-Monsoon

Table- 4.11: Sediment Chemistry for bulk sediments of Vembanad Lake, Kerala

All variables in mg/g except Si, Al and Fe which are in %

L.No.	Si	Al	Fe	Mn	Na	K	Ca	Mg	Cu	Ni	Pb	TC%	P%
1	30.10	2.46	3.22	198	11440	10600	6167	3902	14	74.5	3.5	1.58	0.290
2	32.95	2.09	0.07	396	7709	4789	40700	1586	7	39.5	7	0.20	0.108
3	33.03	2.84	0.59	297	14126	24863	34533	2870	14	79.5	7	0.18	0.035
4	33.66	2.15	2.20	297	15220	19123	35767	5639	14	64.5	10.5	0.25	0.118
5	30.50	2.31	2.30	692	12957	14263	25900	4544	14	119.5	14	0.28	0.116
6	26.55	4.51	4.75	593	16961	17961	20967	6470	56	174.5	17.5	2.75	0.146
7	35.63	1.68	0.69	593	3507	1373	16033	1926	14	79.5	3.5	0.35	0.006
8	21.41	2.86	0.35	198	2512	563	9867	1485	14	79.5	10.5	0.18	0.002
9	35.32	2.52	1.91	396	4601	3346	18500	2291	7	69.5	3.5	0.31	0.040
10	34.37	3.18	2.43	396	6764	7184	11100	3411	14	119.5	14	4.08	0.169
Mean	31.35	2.66	1.85	405	9580	10407	21953	3412	16.8	90.0	9.1	1.02	0.103
Std Dev	44484	7824	14640	171	5216	8348	11912	1720	14.1	38.1	5.0	1.37	0.088
Std Err	14067	2474	4630	54	1649	2640	3767	544	4.5	12.1	1.6	0.43	0.028
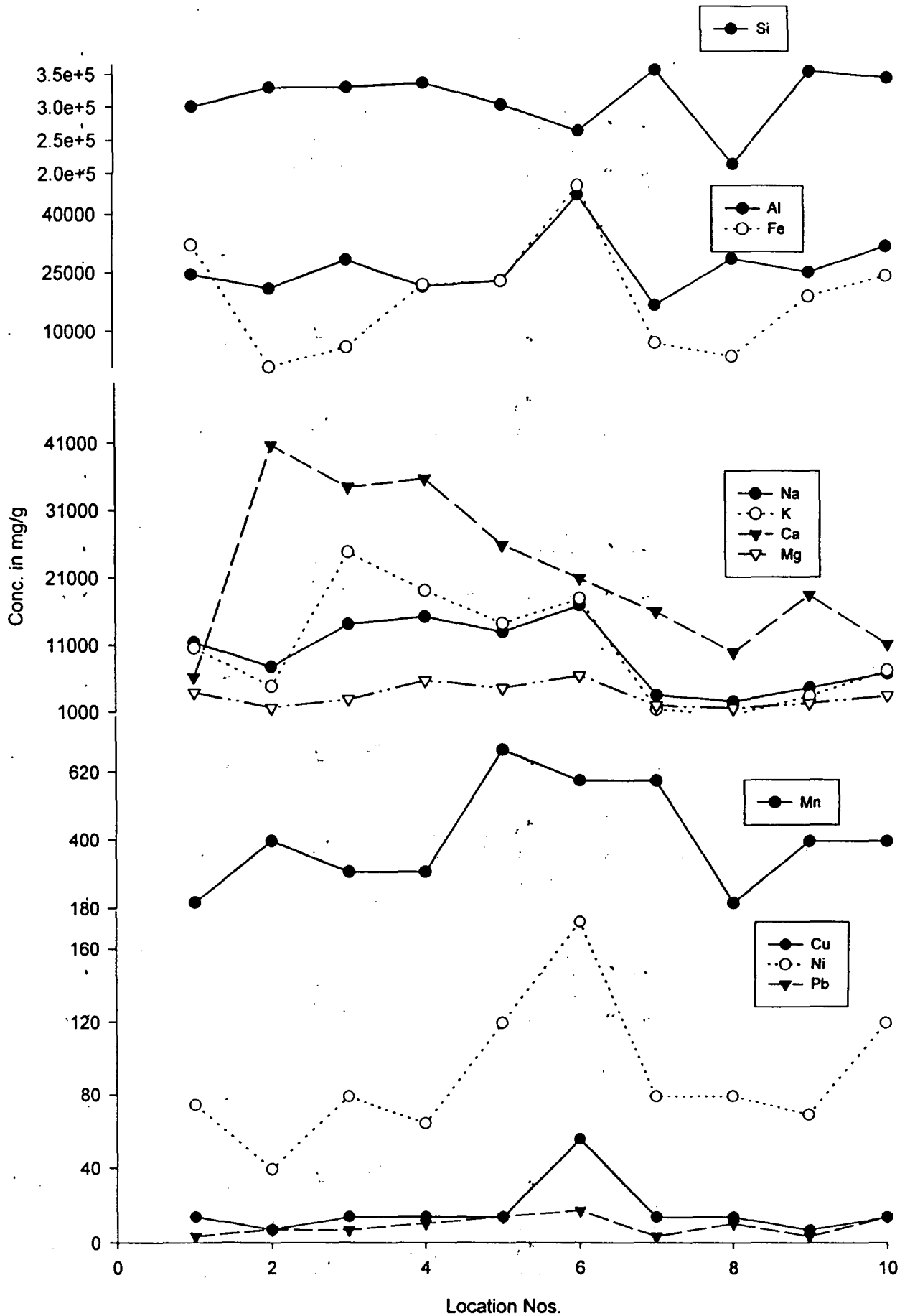
Figure 4.11: Spatial variation of elemental concentrations in bed sediments of Vembanad Lake

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Potassium content in bed sediments varies from 0.05% to 24.86%. Higher content in the brackish part of the Vembanad Lake is due to flocking and deposition. It also follows the same trend as that of sodium in the lake basin.

4.5.3 Calcium and Magnesium

The calcium content in the bed sediments range from 0.62% to 3.57% and that of magnesium varies from 0.15 to 0.65%. These elements are easily soluble i.e. chemically more active and hence vary depending on the geology of the basin. Careful scrutiny of Ca data indicates that Ca content is higher in the northern parts and low Ca zone in the center of the lake basin. Higher content of Ca and Mg in the northern part of the lake can be attributed to their flocculation and aggregation with montmorillonite and chlorite in brackish waters. Lower values of calcium and magnesium as compared to Cavery estuary 2.1% and 1.8% respectively, can be attributed to lack of carbonate rocks in the catchment.

Magnesium shows good correlation with Fe (r= 0.85) and Al (r=0.51), this could be due to adsorption/ absorption of Mg on Fe-Al clay minerals (Tab- 4.12).

4.5.4 Iron and Manganese

Iron content in bed sediments of Vembanad Lake ranges from 0.07% to 4.7%. High percentage in lake sediments in certain patches is due to presence of lateritic patches in the catchment and also the presence of minerals as pyrite or iron hydroxide in the system. Very low content (<2% Fe) is found in certain locations. Manganese content ranges from 198 to 692 ppm. There is no clear trend in Mn content in the lake. However, higher content of Mn is found in areas close to the opening to the sea as compared to other regions.

Iron and manganese don't show any good correlation (r= 0.121), indicating that iron and manganese form geochemically different phases. Iron and aluminum show good correlation (r= 0.64). Thus their source can be suggested to be riverine detrital material. Higher concentration of both in brackish waters can be due to flocculation. Fe shows

Table- 4.12: Correlation Table for Bed Sediment chemistry parameters for Vembanad Lake, Kerala

	Si	Al	Fe	Mn	Na	K	Ca	Mg	Cu	Ni	Pb	TC%	P%
Si	1.00												
Al	-0.49	1.00											
Fe	-0.14	0.65	1.00										
Mn	0.21	0.08	0.26	1.00									
Na	-0.03	0.40	0.59	0.16	1.00								
K	0.05	0.34	0.38	0.04	0.93	1.00							
Ca	0.32	-0.20	-0.31	0.15	0.44	0.48	1.00						
Mg	-0.10	0.51	0.85	0.29	0.85	0.69	0.11	1.00					
Cu	-0.43	0.83	0.72	0.37	0.54	0.38	-0.10	0.68	1.00				
Ni	-0.33	0.80	0.75	-0.55	0.42	0.32	-0.30	0.65	0.84	1.00			
Pb	-0.43	0.69	0.50	0.38	0.46	0.36	0.07	0.63	0.64	0.78	1.00		
TC%	-0.02	0.65	0.64	0.10	0.15	0.05	-0.45	0.40	0.48	0.65	0.51	1.00	
P%	0.00	0.21	0.66	-0.14	0.46	0.25	-0.23	0.52	0.20	0.22	0.15	0.56	1.00

good correlation with Mg (r= 0.85), Cu (r= 0.72) and Ni (r= 0.74). This can be due to deposition of flocs with these elements as hydroxide coatings.

4.5.5 Copper

Copper is extracted from silicates, sulphides and oxides during weathering of rocks. The copper content in the bed sediments of Vembanad Lake ranges from 7 to 56 mg/g. The copper content is constant over the lake, except in one pocket with exceptionally high Cu concentration (56 mg/g) associated with high concentration of iron (4.75%). This may be due to presence of chalcopyrite in the sediment sample of this area.

Cu shows good correlation with Al (r= 0.83), Fe (r= 0.72), Ni (r= 0.84) and Pb (r= 0.64) indicating co-precipitation of these elements in clays or flocculation.

4.5.6 Nickel and Lead

Nickel content ranges from 39.5 to 174.5 mg/g. Higher concentration in brackish water region and good correlation with Al (0.80), Fe (0.75), Cu (0.84) and Pb (0.64), indicated that copercipation or flocculation occurs.

Lead content in the sediments of Vembanad Lake varies from 3.5 to 17.5 mg/g. Higher content in the southern parts of the lake is observed. Negative correlation of Pb, Ni, Cu, Mg with Ca rules out biogenic removal of these elements from surface waters.

4.5.7 Phosphorus and Nitrogen

Phosphorus in sediments comes from P-bearing minerals as apatite and fluroapatite. The phosphorus in the sediments ranges from 0.016 to 0.954 mg/g. P does not show any good correlation with Ca (r= -0.23) (Table- 4.13), indicating that the major source of P is from use of fertilizers and not rocks. This is also supported by the higher concentration of phosphate in surface waters. The phosphorus is precipitated and mineralised in the sediments. This is supported by the good correlation of P with Fe (r= 0.66), indicating that Fe-P are bounded together and Fe is responsible for removal of P from the surface waters (Tab- 4.14).

Table- 4.13: Nutrients in Bulk Sediments, VL

L.No.	TC%	TIC%	TOC%	P%	N%	C:N	C:P	N:P	Salinity
1	1.58	0.20	1.38	0.290	0.103	15.35	5.45	0.36	4.59
2	0.20	0.12	0.08	0.108	0.004	50.48	1.87	0.04	6.94
3	0.18	0.16	0.02	0.035	0.007	26.31	5.26	0.20	9.47
4	0.25	0.10	0.15	0.118	0.015	16.69	2.12	0.13	8.96
5	0.28	0.17	0.11	0.116	0.018	15.48	2.40	0.16	6.27
6	2.75	0.43	2.32	0.146	0.257	10.70	18.83	1.76	10.98
7	0.35	0.19	0.17	0.006	0.014	25.15	58.68	2.33	0.04
8	0.18	0.09	0.08	0.002	0.006	29.35	88.05	3.00	0.02
9	0.31	0.14	0.17	0.04	0.017	18.15	7.71	0.43	0.03
10	4.08	0.23	3.85	0.169	0.241	16.93	24.14	1.43	0.03
Mean	1.02	0.18	0.83	0.103	0.068	22.46	21.45	0.98	4.73
Std Dev	1.37	0.10	1.30	0.088	0.100	11.42	29.18	1.07	4.41
Std Err	0.43	0.03	0.41	0.028	0.032	3.61	9.23	0.34	1.39

Table- 4.14: Correlation Table for nutrients in bed-sediments of Vembanad Lake, Kerala

	TC%	TIC%	TOC%	P%	N%	C:N	C:P	N:P	Salinity
TC%	1.00								
TIC%	0.70	1.00							
TOC%	1.00	0.67	1.00						
P%	0.56	0.37	0.56	1.00					
N%	0.96	0.85	0.95	0.55	1.00				
C:N	-0.44	-0.49	-0.43	-0.35	-0.50	1.00			
C:P	-0.05	-0.10	-0.05	-0.52	-0.07	0.13	1.00		
N:P	0.22	0.22	0.21	-0.39	0.24	-0.05	0.94	1.00	
Salinity	-0.06	0.34	-0.09	0.27	0.11	-0.06	-0.59	-0.49	1.00

The Kjeldahl Nitrogen includes ammonical nitrogen and organic nitrogen. Nitrogen content in the bed sediments ranges from 0.007 to 0.257%. Nitrogen shows a good correlation with total carbon and phosphorus, indicating they could have a common source. Very high concentration at Venapady Bridge is due to discharge of domestic sewage at this point into the Vembanad Lake. Lower concentration of nitrogen at the opening to the sea may be due to the tidal flushing.

The N:P ratio in the sediments of Vembanad Lake varied from 0.04 to 1.62. This is lower than that for plankton N:P::13.3:1. The low N:P ratio in Vembanad Lake indicates that the major portion of phosphorus in the sediments of Vembanad Lake is of abiogenic origin. This further supports that phosphate must be from fertilizers coming into the lake through surface runoff.

4.5.8 Carbon

Carbon in sediments is a major pool for carbon in the biogeochemical cycle of carbon. The carbon pool exists in the form of carbonate, bicarbonate and organic matter. Carbonate and bicarbonate are supplied by weathering of rocks in the catchment or as carbonates in shells. Organic matter in the sediments can have different origins: i) allochthonous, ii) autochthonous, and iii) anthropogenic forced.

The organic matter in sediments gives valuable information regarding the source, nature and kind of depositional environment.

$$TC = TOC + TIC$$

Where TC= Total Carbon; TOC= Total Organic Carbon, and TIC= Total Inorganic Carbon.

Total Organic Carbon (TOC)

Rivers transport on a world average 0.5 gigatons of organic carbon annually (Gupta et al. 1997). The total organic carbon content in sediments of Vembanad Lake varies from 0.012 to 3.845% (Tab- 4.13). High content at certain locations is due to coconut husk fermentation and domestic sewage discharge points.

Carbonate Carbon (TIC)

The major sources of inorganic carbon in aquatic systems are weathering of rocks and calcarious shells of organisms. The TIC in sediments of Vembanad Lake varies from 0.092 to 0.425. There is an overall low values but form a major part of the sediments. Relative higher content of TIC in certain regions of the lake is due its input through riverine sources. This is supported by relative higher values in North at entry of Periyar River, in the south due to Pamba River and in central region due to Muvattupuza river contribution (Fig- 4.12).
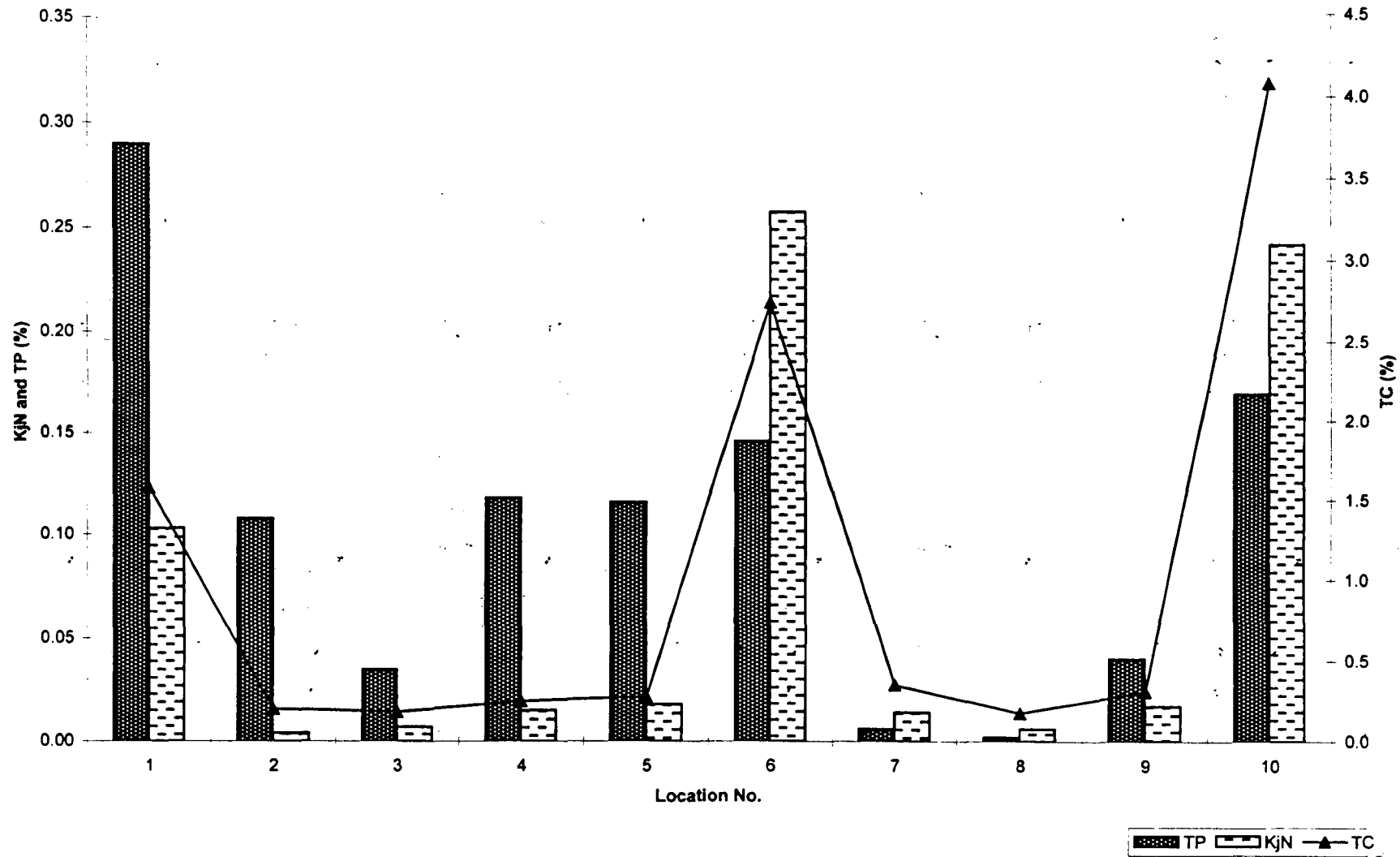
Figure 4.12: Spatial variation of TC, KjN and TP in bed sediments of Vembanad Lake

Chapter 5

GENERAL DISCUSSION

GENERAL DISCUSSION

INTRODUCTION

Kerala is one of the most populated state of India, with a population density of 640 to 1500 people per km^2 in coastal areas (Censes, 1991). Vembanad Lake is the largest lagoon system of Kerala and is surrounded by many rural and urban settlements. People depend on this lake for fisheries, aquaculture and coir as large-scale coconut husk fermentation is done in the lake waters. Treated and untreated sewage finds its way into the lake. Thus, it is interesting to study the overall nutrient behavior in the Vembanad Lake, Kerala, West Coast.

5.1 METHANE

Wetlands are the largest natural source of methane and account for about 20% of the total global emissions (IPCC, 1992). Several environmental forcing factors as temperature, salinity, sulphate, organic matter, Dissolved Oxygen, substrate etc. along with human additions control methanogenesis and CH_4 emissions to the atmosphere.

Kerala has abundance of paddy fields and wetlands. The estimated CH_4 emissions from Kerala based on paddy field estimations is 0.1 Tg/y (Gopalakrishnan et al. 1993). Coconut husk retting in the backwaters is also important source of methane. It has been observed that about 11 m^3 of gas is emitted in five months during retting of which 64% is methane (Zachariah et al. 1993). But the actual values and contributions from these wetlands have to be worked out.

The CH_4 emission values from Vembanad Lake has been studied and discussed in section-4.1. The values are very high as compared to the CH_4 emissions from East Coast as obtained by Ramesh et al. 1998 and Verma et al. 1999.

The higher values of CH_4 emissions in Vembanad Lake can be due to various environmental factors.

Floods, ebbs of tides and storms, influence coastal wetlands. Near coastlines, the salinity of the waters approaches to that of the ocean and in the inland salinity is closer to freshwater. In saline environment, methanogenesis and sulphate-reducers compete for substrates.

Sulphate content in Adyar Estuary and Bay of Bengal ranges from 600-4600 mg/L, due to tidal influence and partially due to pollution from sewage. In contrast the sulphate concentration in Vembanad Lake ranges between 14-3887 mg/L. Thus, lower sulphate concentrations can account for higher CH_4 values in Vembanad Lake, West coast to Adyar Estuary, East Coast.

Organic matter content also effects methane production and emissions. The substrate for methane production are H_2 plus CO_2, formate, acetate, methanol and methylated amines (Oremland, 1988). Wetland soils in tropics show rapid mineralization and weak himification, which favors CH_4 formation (Ramesh et al. 1998).

In high sulphate environment, part of organic carbon is used for processes other than methanogenesis. In Adyar Estuary, organic carbon ranged from 0.9 to 6.5% and in Vembanad Lake varies from 0.17 to 4.10%. Higher CH_4 emissions despite lower carbon indicates a coexistence of methanogens and sulphate-reducers in the sediments in the West Coast. Dr. R. Ramesh, Anna University, Chennai, in a personal discussion indicated that TMS (Tri-Methyl Sulphide) as an alternative substrate for methanogenesis, which does not have competitors, and can be responsible for high methane emissions in West Coast. No analysis for TMS was done, hence the extent of its contribution to methanogenesis cant be said with any certainty.

Thus, these are possible reasons for overall higher CH_4 emissions from the West Coast than from the East Coast of India. So to work out the overall CH_4 emissions from the wetlands of India, it is important to account for spatial variations that can occur due to difference in the environmental conditions and factors.

5.2 NUTRIENT BIOGEOCHEMISTRY

Nutrients are contributed to coastal waters by continental weathering, land runoff and human activities. Nutrient utilization, regeneration, remineralization and geochemical cycling are important to understand nutrient biogeochemistry in coastal estuarine and lagoonal environments.

5.2.1 Salinity

Salinity plays an important role in the behavior of nutrients in the estuarine and lagoonal environments. The salt content in the water column increases with depth, flow pattern, however indicates a uni-directional water movement, reversing with the reversal of tides.

In order to relate the dilution factor to average salt input to the estuary as an approximate measure of the degree of mixing, the simple mixing relation can be applied:

$$F = 1 - \frac{S_1}{S_2}$$

Where F is the fraction of fresh water in the sample,

S_1 is the salinity of the sample,

S_2 is the salinity of the 'source water'.

The results are presented in the tab- 5.1, the freshwater and seawater fractions are given. It indicates that there is more freshwater discharge during the post-monsoon than in the pre-monsoon. Thus, there is less percentage of seawater percentage in the post-monsoon than in the pre-monsoon. Further, it is indicated that the salt water intrudes till almost Tameermukham (location-8) during the pre-monsoon. Further extent of salt water is avoided by the presence of the Thaneermukham Bund. Thus, it can be said that the so-called 'salt front' lies close to location-8 during the pre-monsoon.

5.2.2 Nutrient Status

Nutrient status of any water body is essential to know the productivity of the system. Carbon, nitrogen, phosphorus, silica and sulfur with other elements are biogeochemically cycled through the aquatic system. The rate of cycling depends on the relative proportion of the biota. Adding either an excess of organic compound or an excess of inorganic nutrients as phosphorus and nitrogen may perturb the delicate balance between photosynthesis and respiration in the lake. In most inland water

Table- 5.1: Average values of fresh water fractions (F)
in Vembanad Lake, Kerala

Post-Monsoon

L.No.	Salinity	F	Dilution Factor	Sea Water %
1	4.59	0.860	1.16	14.04
2	6.94	0.788	1.27	21.24
3	9.47	0.710	1.41	28.96
4	8.96	0.726	1.38	27.42
5	6.27	0.808	1.24	19.19
6	10.98	0.664	1.51	33.59
7	0.04	0.999	1.00	0.13
8	0.02	0.999	1.00	0.07
9	0.03	0.999	1.00	0.09
10	0.03	0.999	1.00	0.10
Sea	32.69			

Premonsoon

L.No	Salinity	F	Dilution Factor	Sea Water %
1	14.21	0.571	1.75	42.88
2	15.62	0.529	1.89	47.12
3	17.99	0.457	2.19	54.28
4	15.62	0.529	1.89	47.12
5	12.14	0.634	1.58	36.63
6	12.66	0.618	1.62	38.19
7	3.51	0.894	1.12	10.60
8	3.19	0.904	1.11	9.61
9	0.07	0.998	1.00	0.20
10	0.07	0.998	1.00	0.21
Sea	33.15			

phosphorus and nitrogen act as limiting nutrient in determining the productivity. In estuaries and many marine coastal waters, concentration of nitrogen and phosphorus can be used to act as limiting.

5.2.2.1 Element Behavior in the lake

The elements are transported in estuaries and lagoons in dissolved and particulate form. The dissolved substances can behave as conservative or non-conservatively in the system. Elements that are generally unreactive and have no influence of mixing on traveling through the water mass are considered to be conservative in nature.

When elements change their concentration with time by mechanisms other than dilutions then complications arise and elements are considered to be non-conservative in nature. In general, nutrients as N, P and Si show non-conservative behavior in estuaries and lagoons (Gibbs, 1977).

Figure 5.1, shows that Nature, K, Ca and Mg show conservative behavior in Vembanad Lake whereas NO3, SiO2 and PO4 show non-conservative behavior in Vembanad Lake, this is similar to the findings of Sarla Devi et al. (1991) for Periyar Estuary.

To calculate the concentration of nutrients on the basis of standard one dimensional estuarine model on basis of mixing with saline water is given by Gupta et al. (1987) as:

$$X_{sample} = X_{riv} + \frac{(X_{sw} - X_{riv})}{S_{sw}} \times S_{sample}$$

Where

X Sample= Calculated concentration of the sample

X riv= Concentration of nutrient in river water

X sw = Concentration of nutrient in sea water

S sw = Salinity of sea water

S sample = Salinity of sample.

The values obtained are given in Tab- 5.2. It indicates that different nutrients behave in a different manner in the estuaries.
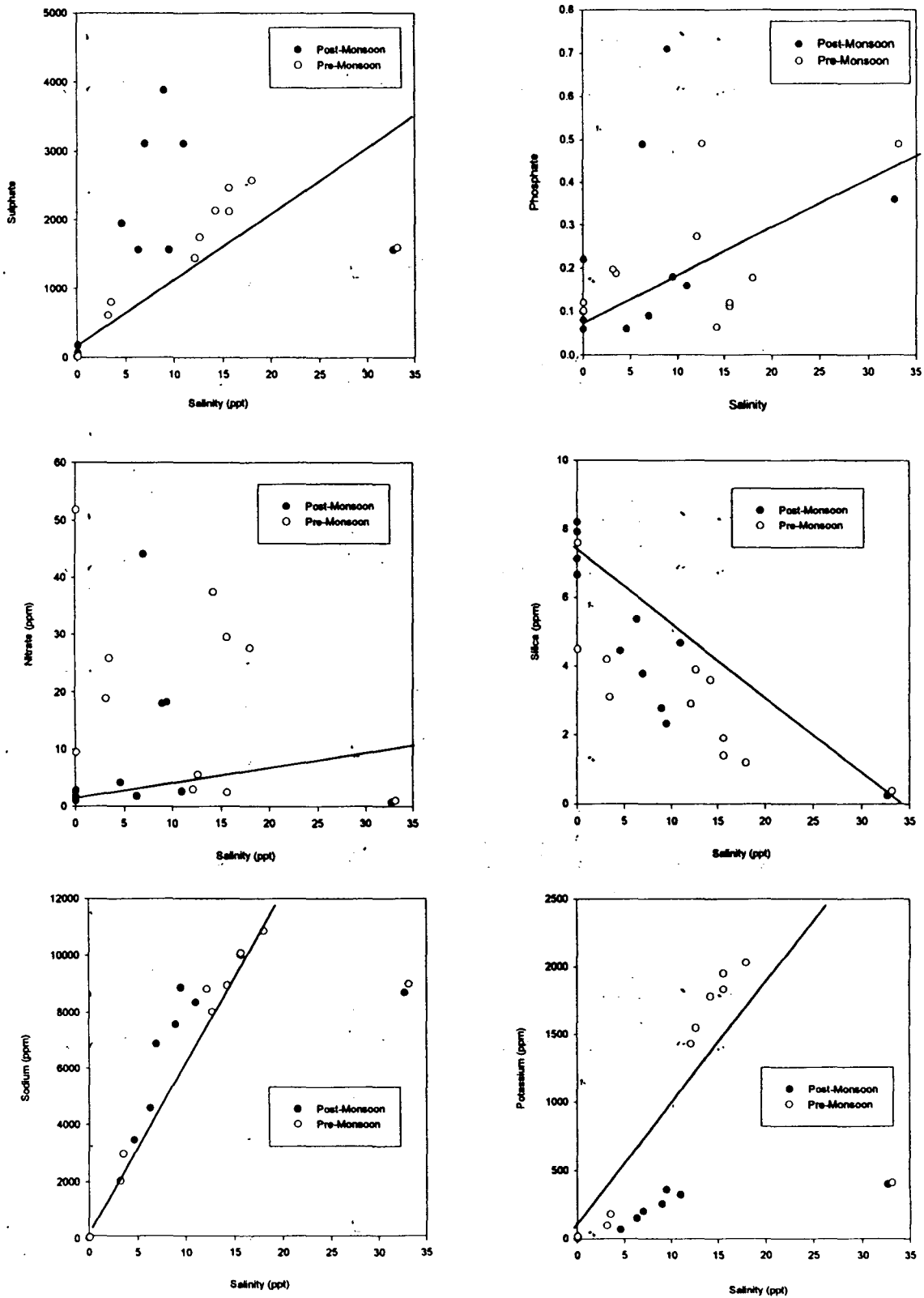
Figure 5.1: Element Vs Salinity graphs for pre-monsson and post-monsoon seasons in Vemband Lake.

Table- 5.2: Observed concentrations of nutrients and their expected values in Vembanad Lake waters

Post-Monsoon

L.No.	Salinity	$PO_{4\,obs}$	$PO_{4\,calc}$	Diff %	$NO_{3\,obs}$	$NO_{3\,calc}$	Diff %	$SiO_{2\,obs}$	$SiO_{2\,calc}$	Diff %
1	4.59	0.06	0.14	-127.5	4.14	2.35	43.3	4.45	7.09	-59.3
2	6.94	0.09	0.16	-72.5	44.09	2.22	94.9	3.79	6.52	-71.9
3	9.47	0.18	0.18	2.6	18.22	2.07	88.6	2.33	5.90	-153.3
4	8.96	0.71	0.17	75.9	17.96	2.1	88.3	2.78	6.03	-116.7
5	6.27	0.49	0.15	69.4	1.74	2.25	-29.5	5.37	6.80	-24.4
6	10.98	0.16	0.19	-17.1	2.61	1.99	23.9	4.68	5.53	-18.23
7	0.04	0.22	0.1	54.4	2.80	2.61	6.87	6.66	8.20	-23.1
8	0.02	0.06	0.1	-66.9	1.03	2.61	-153.3	7.13	8.21	-15.1
9	0.03	0.08	0.1	-25.3	1.70	2.61	-53.4	7.91	8.20	-3.7
10	0.03	0.10			2.61			8.21		
Sea	32.69	0.36			0.75			0.24		

Pre-Monsoon

L.No.	Salinity	$PO_{4\,obs}$	$PO_{4\,calc}$	Diff %	$NO_{3\,obs}$	$NO_{3\,calc}$	Diff %	$SiO_{2\,obs}$	$SiO_{2\,calc}$	Diff %
1	14.21	0.06	0.28	-336.2	37.4	5.8	84.5	3.6	4.50	-25.0
2	15.62	0.11	0.29	-163.3	29.5	5.5	81.5	1.9	4.19	-120.7
3	17.99	0.18	0.32	-80.5	27.6	4.9	82.4	1.2	3.68	-206.4
4	15.62	0.12	0.29	-143.7	2.4	5.5	-127.3	1.4	4.19	-199.5
5	12.14	0.27	0.26	6.2	2.9	6.3	-118.4	2.9	4.95	-70.8
6	12.66	0.49	0.26	46.7	5.5	6.2	-12.8	3.9	4.84	-24.1
7	3.51	0.19	0.16	14.7	25.9	8.5	67.1	3.1	6.83	-120.5
8	3.19	0.20	0.16	20.5	18.8	8.6	54.3	4.2	6.90	-64.4
9	0.07	0.10	0.12	-19.4	51.8	9.4	81.9	4.5	7.58	-68.5
10	0.07	0.12			9.4			7.6		
Sea	33.15	0.49			1.03			0.37		

Phosphate shows an overall erratic behavior both in pre-monsoon and post-monsoon. It is held in the system in the brackish water region, which can be due to adsorption and flocculation under these conditions. Phosphate is released near the opening to the sea, which may be due to desorption of phosphate form the sediments due to wave action and churning.

Nitrate also shows an overall release to the surface waters in both pre-monsoon and post-monsoon. There is takeup of nitrate in brackish region, which may be due to biological uptake since abiological removal processes for nitrate are not all that prominent. The release in the regions close to the mouth could be due to anthropogenic additions or regeneration as oxidation product of ammonia.

Silicate shows a strong removal mechanism with in the lake-lagoon-estuary environment of Vembanad Lake. The removal can be due to biological uptake of silica by diatoms coupled with its burial into the sediments. This leads to little or no silicate flow out from the Lake to the sea.

5.2.2.2 N:P Ratio

In general, the ratio of Dissolved Inorganic Nitrogen (N) and Phosphate (P) is used to assess the nutrient status of the water body (Howarth et al. 1996). It is found that average cellular N: P ratio is 16:1 (Hecky and Kilam, 1988). In most marine, estuarine and coastal ecosystems are limited by N, P, Si and Fe (Martin et al. 1994). Although N and P are major limiting factors for primary productivity and dissolved N and P may be cycled at different rates in the system (Hoegh-Goldberg, 1994). Dissolved N and P are cycled so rapidly by living organisms that they are often difficult to detect in the soluble inorganic phase, hence both organic and inorganic forms of N and P are taken together by organisms (Sakamoto, 1966).

If the N:P ratio is < 16:1 then the waters are N-Limiting but if N:P ratio is > 16:1 than they are P-Limiting. Total N concentration in marine ecosystem from estuaries to oligotropic seas varies by about 30-folds and that of Total Phosphorous varies 650 fold. Thus, total N: P ratio varies from 5 to 310, average at about N:P=37. N:P for average living marine organism is ~ 16 (Elser and Hassett, 1994). The open seas have N:P ratio greater than 16 indicating the P or some other nutrient other than N limits the productivity. Low N:P ratios have been found for estuaries and coastal

ecosystems (Downing, 1997) (Tab- 5.3), but most of the coastal waters have nitrogen as the primary limiting nutrient, especially those heavily loaded by human influence (Howarth et al. 1995).

Table 5.3: Frequency of total N:P molar ratios in various environments (Downing, 1997).

Environment	Frequency to N:P ratio	
	<16	≥ 16
Open Sea, <50m depth	14	104
Open Ocean, Surface films	3	6
Estuaries, harbors, bays	11	17
Deep, open Ocean, >50m depth	23	13
Total	51	140

The N:P ratio for Vembanad Lake varies from 3.5 to 579.9. There are higher ratios at all locations during pre-monsoon than for post-monsoon. Thus, the Lake is mostly P limiting for most time of the year (Tab- 5.4).

Table: 5.4: Nutrient limitation of water bodies on basis of N:P ratio. N+P indicates N and P both together are limiting for the primary productivity of the water body, N or P indicates they alone influence productivity, * indicates changes seasonally.

Place	Limiting Element	Reference
Vembanad Lake	**P**	**Present Study**
Gulf of Morbihan, France	N, N+P	Le Rouzie et al. 1992
Chesapeake Bay	N, P*	Fisher et al. 1992
Chesapeake Bay	N	D'Elia et al. 1992
Neuse River Estuary	N, N+P	Rudek et al. 1991
New York Harbor	N	Ryther et al. 1971
Mediterranian Sea	P, N+P	Berland et al. 1987
Sargasso Sea	P	Laponite 1986
Mediterranian Sea	P	Bonin et al. 1989

5.2.2.3 Nutrient Eutrophication Index

An index was designed to test the relationship between nutrient at a point to total loading and area surveyed. Logarithmic transformation smoothes the minor random fluctuations. Karydis et al. (1983) has formulated a simple method to calculate the nutrient index for each nutrient and evaluate eutrophication levels in marine and coastal environments. The Index was calculated for Vembanad Lake waters using the formula:

$$I = (C/ (C\text{-}\log X)) + \log A$$

Where, I= Nutrient Eutrophication Index,

   C= Log of the total (annual) loading of a given nutrient in a area,

   X= The nutrient loading at a station (mmol m^{-2}),

   A= Number of stations in the area.

If   I > 5, than the waters are eutrophic,

   I is between 3 and 5, waters are mesotrophic,

   I < 3, than the waters are oligotrophic.

Calculation of the Eutrophication Index for Vembanad Lake is shown in Table:5.5. It shows that the lake is oligotrophic with respect to phosphate for most locations and for both seasons. Except for few locations, the waters of the lake are mesotropic to eutrophic with respect to nitrate. Thus, phosphorous is the major limiting nutrient for primary productivity of Vembanad Lake.

5.2.2.4 Silica

Silica is an important nutrient for the growth of phytoplanktons and diatoms in estuarine and coastal marine environment. Besides diatoms, silicoflagellates, radiolarians and siliceous sponges need silica for their growth (Aston, 1980, Ittekkot, 1998, Smetacek, 1999).

Silicon is abundant in earth crust but the seawater is under-saturated with respect to silicon. The silica in water comes mainly through weathering of silicate

Table- 5.5: Nutrient Eutrophication Index (I) , calculated for N and P for waters of Vembanad Lake, Kerala

Postmonsoon

L.No.	PO4	X	Log X	I
1	0.06	0.68	-0.17	2.2
2	0.09	0.93	-0.03	2.4
3	0.18	1.93	0.29	2.8
4	0.71	7.44	0.87	4.9
5	0.49	5.18	0.71	4.0
6	0.16	1.68	0.22	2.7
7	0.22	2.30	0.36	2.9
8	0.06	0.68	-0.17	2.2
9	0.08	0.80	-0.10	2.3
10	0.10	1.05	0.02	2.4
Sum	2.15	22.66	1.36	

L.No.	NO3	X	Log X	I
1	4.14	234	2.37	3.7
2	44.09	2489	3.40	11.9
3	18.22	1028	3.01	6.1
4	17.96	1014	3.01	6.1
5	1.74	98	1.99	3.1
6	2.61	147	2.17	3.4
7	2.80	158	2.20	3.4
8	1.03	58	1.77	2.9
9	1.70	96	1.98	3.1
10	2.61	147	2.17	3.4
Sum	96.90	5470	3.74	

Premonsoon

L.No.	PO4	X	Log X	I
1	0.06	2.38	0.38	2.3
2	0.11	4.12	0.62	2.5
3	0.18	6.57	0.82	2.8
4	0.12	4.47	0.65	2.5
5	0.27	10.06	1.00	3.2
6	0.49	18.10	1.26	4.2
7	0.19	6.92	0.84	2.8
8	0.20	7.27	0.86	2.9
9	0.10	3.77	0.58	2.5
10	0.12	4.47	0.65	2.5
Sum	1.85	68.12	1.83	

L.No.	NO3	X	log X	I
1	37.4	2110	3.32	6.4
2	29.5	1665	3.22	5.8
3	27.6	1556	3.19	5.6
4	2.4	134	2.13	3.1
5	2.9	166	2.22	3.2
6	5.5	313	2.50	3.6
7	25.9	1462	3.16	5.5
8	18.8	1063	3.03	4.9
9	51.8	2926	3.47	7.7
10	9.4	529	2.72	4.0
Sum	211.2	11924	4.08	

minerals as quartz and feldspar on land and enters into the aquatic environment as orthosilicic acid (H_4SiO_4). Workers as Lal (1978), Spencer (1975), indicated that fate of silica in estuaries, lagoons and oceans depends upon many factors. The behavior of silica in estuaries depends on the physical mixing of the natural waters of different concentrations. The factors directly involved with silica distribution are adsorption, opal dissolution and chemical interactions with clay minerals (Lal, 1978; Aston, 1980; Gouda and Panigrahy, 1991). Subba Rao (1984), Kamatani and Takono (1984), Gouda and Panigrahy (1991) and Choudhary and Panigrahy (1992) have documented role of biological removal of silica. Removal of silica in estuaries by flocculation and precipitation depends on salinity gradient.

Silicate contribution in the estuary is dependent on external sources such as river discharge and land drainage. The influence of seawater mixing is seen in the northern part of the Vembanad Lake.

Coefficient of correlation shows a negative correlation between salinity and silica, indicating conservative behavior of silica in the estuary. The distribution of silica is higher (12 mg/L, Bajpayee, 1998) which gradually decreases seawards (1.2 mg/L). Thus, silica is limiting in the waters of Vembanad Lake.

In some regions, open sea and coastal seas, silicic acid is in short supply relative to major nutrient nitrate and phosphate (Smetacek, 1999). For instance the N:P ratio across the southern ocean varies less than 10% but Si:N ratio ranges from 0.15 to 3. The diatoms demand for Si:N ratio is about 1, the discrepancy in dissolved nutrient ratio indicates that N is recycled more effectively than Si (Dugdale, 1995).

In Vembanad Lake Si:N ratio varies from 0.09 to 6.91 during the post-monsoon and ranges from 0.04 to 0.98 during the pre-monsoon (Tab- 5.6). Thus besides N and P, Si is also limiting especially during the pre-monsoon when the silicic acid contribution from the weathering through the runoff and river discharge is less during pre-monsoon.

5.3 AMINO ACIDS

Organic matter is an important fraction of estuarine, lagoonal sediments. In these environments there is a wide changes in the chemical composition of waters due

Table- 5.6: N:P & Si:N ratio for waters of Vembanad Lake.

Postmonsoon

L.No.	N:P	Si:N
1	44.68	1.07
2	347.12	0.09
3	68.91	0.13
4	17.61	0.15
5	2.45	3.08
6	11.33	1.8
7	8.87	2.38
8	11.13	6.91
9	15.48	4.65
10	18.07	3.15

Premonsoon

L.No.	N:P	Si:N
1	401.7	0.096
2	182.7	0.064
3	107.1	0.044
4	13.6	0.589
5	7.5	0.986
6	7.8	0.704
7	95.6	0.12
8	66.1	0.223
9	350.7	0.087
10	53.5	0.811

to mixing with seawater and hence a variety of processes occur which can degrade organic matter to different extents and hence change the nature of organic matter.

Amino acids (AA) and hexosamine (HA) are the most easily degradable constituent of organic matter. The decrease in bulk protein AA's relative to bulk non-protein AA's in samples may result from the preferential decomposition of protein AA's, that are easily digestible. Non-protein AA's β–ala (β-ala) and γ- aminobutyric acid (γ-aba) in sediments are enzymatically-decomposed products of aspartic acid and glutamic acid (Lee and Cronin, 1982).

The overall composition of the amino acids in the Vembanad Lake sediments is similar to that of Godavari Basin (Gupta et al. '1997). The organic matter has not undergone much degradation, that can be seen from the Fig- 4.3, which shows lower mole% of g-aba and b-ala.

On comparison of the values of bed sediment amino acids of Vembanad Lake with the mangroves leaves, there is a close resemblance (Tab- 5.7). These plants grow in abundance along the coastline. This indicates that organic matter has not undergone much degradation within the top 5 cm. of the sediments of the Vembanad Lake. It can also be said that the lake sediments act as a trap for organic matter entering the lake and retaining. It also indicates that there is slow recycling of organic matter in the lake and there are chances of humicification of organic matter.

5.4 BED SEDIMENT CHEMISTRY

The chemical composition of sediment serves as a good tool for delineating the source and transport of sediments in a basin. The concentration of heavy metals reflects the contamination load of the bed sediments. The distribution of elements in the lake seems to be associated with lithogenic origin, anthropogenic inputs and

Table 5.7: Amino acid composition of Vembanad Lake sediments, fresh leaves of Aviceni and Rhizophoa mangle, phytoplankton and Zooplankton (data from Crowie and Hedges, 1

Amino Acid	Vembanad Lake sediments (mole-%)	Fresh leaf, A. schaueriana (mole-%)	Fresh leaf, R. Mangle (mole-%)	Phytoplankton	Zooplankton
Asp	12.5	9.0	10.6	7.9-15.1	8.9-13.3
Thr	6.7	6.4	6.3	4.6-5.8	3.8-5.3
Ser	7.2	6.9	7	2.7-5.7	3.3-4.9
Glu	10.2	12.9	11.8	9.8-20.8	12.4-19.9
Gly	15.7	10.7	10.4	8.4-12.0	10.1-13.2
Ala	11.5	8.5	8.8	7.2-13.0	10.4-11.7
Val	7.1	6.9	6.6	5.5-7.3	4.7-6.8
Met	0.8	1.9	1.1	1.4-2.4	1.2-2.3
Ile	4.3	5.7	5.5	4.1-5.4	3.5-5.2
Leu	7.3	10.2	9.7	6.0-8.8	6.6-7.9
Try	1.1	3.3	3.1	2.1-3.1	1.6-3.6
Phe	3.9	5.2	5.0	1.6-4.3	2.4-2.8
b-ala	0.6	0.1	0.1	<0.1-1.0	0-0.9
g-aba	0.6	1.7	1.4	0.3-0.8	0.3-1.2
His	1.7	1.7	2.3	0.8-1.8	0.5-2.0
Orn	0.4	0.3	0.2	0.0-1.9	0.2-2.7
Lys	3.9	4.3	5.8	5.0-15.2	7.7-11.7
Arg	4.4	4.3	4.4	2.3-5.5	2.7-5.5

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physical and chemical forces associated with transport of materials within the lagoons.

5.4.1 Metal – Aluminium Ratio

Silica is a major element in the earth's crust and forms a part of all rocks. Bostrom et al.(1972) contented that Si/Al ratio $\approx$ 3, when alumino-silicate sediments serves as main source. Higher Si/Al ratio encountered in sediments when sediments contain excess amount of silica derived either from detrital quartz or biogenic sources. Lower than normal (<3) in sediments occur when it contains more Al due to presence of higher amounts of clay minerals. Thus, high Si/Al ratio in sediments of Vembanad Lake can be attributed to presence of excess of quartz in the basin. Sands dominate regions of higher Si/Al ratio. Addition of silica from biogenic sources is difficult to account for. Dertital alumino-silicate clays are the major source of Al in aquatic system.

Iron is next abundant element in the sediments. It occurs as minerals-oxides, hydroxides and sulphides as well as associated with silicates. Iron mainly comes through clay minerals and hence is called lithogenic Iron. Iron oxides, hydroxides, sulfides and precipitates are formed geochemically under estuarine conditions. The major controlling factors for diagenisis of iron are redox potential and pH. Relative higher concentration of iron in certain parts of Vembanad Lake indicates fluvial discharge of iron from iron rich lateritic catchment. Higher Fe/Al ratio in the estuarine region may be due to iron coating or adsorption onto clay minerals or due to flocculation (Tab- 5.8).

Manganese into the coastal system is from lithogenic sources, either as sediment debris or in the form of colloids. Higher Mn concentration in certain pockets can be due to its physico-chemical flocculation in estuarine regions. Negative correlation with iron indicates that they form geochemically different phases. The high Mn/Al ratios indicates that under the conditions existing in the Vembanad Lake, Mn is removed through surface adsorption and desorption of Mn is a slow process taking months to years.

Calcium in sediments is fixed in clays either in the matrix or as shells or calcium phosphate. A negative correlation with phosphorus indicated that calcium

Table- 5.8: Metal/Al ratio for bed sediments of Vembanad Lake.

x10-3

L.No.	Si/Al	Fe/Al	Mn/Al	Na/Al	K/Al	Ca/Al	Mg/Al	TC/Al	P/Al
1	12.25	1.31	8.05	0.466	0.432	0.251	0.159	0.643	0.118
2	15.74	0.04	18.89	0.368	0.229	1.944	0.076	0.096	0.052
3	11.62	0.21	10.44	0.497	0.875	1.215	0.101	0.065	0.012
4	15.63	1.02	13.77	0.707	0.888	1.660	0.262	0.116	0.055
5	13.23	1.00	30.03	0.562	0.619	1.124	0.197	0.121	0.050
6	5.88	1.05	13.15	0.376	0.398	0.465	0.143	0.609	0.032
7	21.24	0.41	35.37	0.209	0.082	0.956	0.115	0.210	0.004
8	7.47	0.12	6.90	0.088	0.020	0.344	0.052	0.061	0.001
9	13.99	0.76	15.67	0.182	0.133	0.733	0.091	0.122	0.016
10	10.80	0.76	12.43	0.213	0.226	0.349	0.107	1.282	0.053

can't get precipitated as calcium phosphate in the system. In most cases, calcium is held as interlayer cation in clay minerals. Na and K are not precipitated by hydrolysis in aquatic system. They are tied up in clay minerals either by cation exchange and/or adsorption. In general, distribution of clay minerals and texture of sediments (Toyoda and Masoda, 1990) govern distribution of Na, K and Mg in marine and estuarine system. In addition exchange of calcium and adsorption process causes fixation of Mg, Na and K in clays when they come in contact of seawater (Drever, 1974). This could be the reason for higher Mg, Na and K at opening of Vembanad Lake to the sea.

5.4.2 Nutrients

The organic matter in the sediments undergoes decomposition with the help of microbes. The organic matter is transformed to another form due this thus when diganesis occurs the nature of organic matter is transformed. The decomposition releases and/or absorbs nutrients and metals. There is recycling of matter between surface water-pore water-sediments. Thus ratio of C,N and P can be helpful to assess the source, decompotional conditions for the organic matter in the lake.

5.4.2.1 N:P Ratio

The N:P ratio in the sediments of Vembanad Lake varied from 0.04 to 1.62. This is lower than that for plankton N:P::13.3:1. The low N:P ratio in Vembanad Lake indicates that the major portion of phosphorus in the sediments of Vembanad Lake is of abiogenic origin. This further supports that phosphate must be from fertilizers coming into the lake through surface runoff.

Grasshoff (1975) reported a value of 13.3 for N:P ratio on planktons and a value of 13.8 in cultured planktons. The N:P ratio observed for Vellar Estuary sediments is 12.5 (Shivkumar et al. 1983) and that for Vishakapatanam Harbor is 0.14 (Venketaramana, 1990). The N:P ratio obtained for Cochin Backwaters by Shankaranarayanan and Panampunnayil (1979) was 1.51. The value obtained for the same region in the present study is much lower i.e. 0.98 (Tab- 5.9). This lowering in N:P ratio indicates that a considerable fraction of phosphorous in the sediments is from abiogenic origin and comes mainly through sewage discharge into the lake.

Table: 5..9: Sediment Total Organic Carbon(TOC), Total Inorganic carbon (TIC), Total Nitrogen(TN), Total Phosphorous (TP) and C/N, C/P and C/N ratios for some estuaries, sea and lakes.

	TOC%	TIC%	TN%	TP%	C:N	C:P	N:P	Reference
Vembanad Lake	**0.83**	**0.18**	**0.068**	**0.10**	**22.4**	**21.4**	**0.98**	**Present Study**
Cochin Backwaters	1.62	-	0.32	0.15	5.06	10.8	2.1	Nair et al, 1984
Asthamudi Lake	2.5	-	0.76	0.39	3.29	6.4	1.9	-do-
Mandovi Estuary	1.60	-	-	-	-	-	-	Shirodkar et al, 1988
Cauvary Estuary	0.59	-	-	0.21	-	2.8	-	Mohanchandran, 1992
Krishna Estuary	1.79	-	-	0.25	-	7.16	-	-do-
Godavari Estuary	1.97	-	-	0.27	-	7.29	-	-do-
Ganges Estuary	0.65	0.32	0.05	-	13.0	-	-	Jose, 1995
Vishakapatnam harbor	3.03	-	0.005	0.12	264	0.17	32.7	Venketaraman, 1990
Pulicat Lake	0.57	-	-	-	-	-	-	Rao et al. 1974
Bay of Bengal	1.47	-	-	0.05	-	34.1	-	Venketaraman, 1990
Arabian Sea								
Inner Shelf	2.45	-	-	0.11*	-	20.5	-	Venketaraman, 1990
Outer Shelf	1.25	-	-	0.12	-	9.4	-	Venketaraman, 1990
Deep Sea	1.89	-	-	0.09	-	10.4	-	Venketaraman, 1990

5.4.2.2 C:N Ratio

The C:N ratio of sediments is used to characterize various types of organic matter. The C:N ratio for the sediments of the Vembanad Lake varies from 10.72 to 48.07. The average C:N ratio for sediments of estuaries, lagoons and oceans throughout the world has been found to be between 8 and 12 (Trask, 1932). Sea water containing humic material of fresh water origin exhibit high C:N ratio (about 10). The C:N ratio for zooplanktons and phytoplanktons are 5.9 and ~6, respectively. Bacteria and benthic animals may contain upto 80% protein and show C:N ratio of order of 4-5 (Bordowskiy, 1965). Higher plants are the main contributors of terrestrial organic matter. They contain >20% protein hence show high C:N ratios.

The high C:N ratio for sediments of Vembanad Lake indicates terrestrial origin of organic matter in the lake sediments with detritus brought in by rivers. High C:N ratio (2.48 to 37.5) has been obtained for self sediments of Arabian Sea by

Bhosle et al. 1977, this is attributed to degradation of complex proteins and humics in the sediments. For cochin backwaters, Quasim and Sankaranarayan (1972) reported a value of 7.6, while Shankaranarayanan and Panampunnayil (1979) reported a value of 6.4, the present study fives the average value of C:N ratio to be 22.4. The higher ratio now could be due to excess input of organic matter through sewage and also humicification of organic matter in the lake sediments. Shivkumar et al (1983) found the C:N ratio for sediments of Vellar Estuary to be 30.4 on an average. The values obtained for Vishakapatanam Harbor is 264.

5.4.2.3 C:P Ratio

The C:P ratio for the sediments of Vembanad Lake varies between 0.6 to 22.7. For detritus of Cochin Backwaters the average C:P ratio is 41.1 (Quasim and Sankaranarayanan, 1972). Low C:P ratio observed in the present study indicates that the increase in phosphorous content in sediments is probably due to anthropogenic effect as discharge of domestic sewage. From the study of various chemical constituents of detritus and sediments, the uppermost layer of sediment is mostly detritus. The C:P ratio for Vishakapatanam Harbor is 0.17. The lower values is due to input of phosphorous from sewage and industrial effulents.

On the basis of behavior of carbon, nitrogen and phosphorous in the sediments of Vembanad Lake, it can be inferred that humics play an important role in controlling the cycling of nutrients from the sediments. Low N:P and C:P ratio of the sediments of Vembanad Lake indicates that the contribution of phosphorous is by sewage and other sources as surface runoff bringing in fertilizers.

5.5 FACTOR ANALYSIS

Factor analysis aims to explain observed relations among numerous variables in terms of simpler relations. It is also a way of classifying manifestations or variables. (Cattel, 1965). In simpler terms, "the primary aim of factor analysis is to achieve a parsimonious description of data matrix ..... that is, to determine of the table of numbers can be simplified in some way" (Klovan, 1975).

After the correlations between every pair of variables have been computed both PCA and PFA determine a set of factors called an original solution. In this, an initial factor that does the best job of representing all of the variables is determined first. Then the second is found. The second factor is required to be uncorrelated to first one. Similarly other factors are found. The three factors were extracted from Principal Factor matrix (Eigen value > 1). Factors gives values closer to - 1, 0 and - 1 for factor (Briz Kishore and Murali, 1992).

Factor loading is related to degree of correlation between variable and a factor. Higher the correlation between a variable and a factor, the higher the loading of that variable on the factor (Jaeger, 1983). Extreme negative values reflect essentially unaffected by the process and positive values reflected most effected.

Eigen values are associated with factors. They indicate how much of the variation in the entire set of original variable is "accounted for" by each factor. The first factor will always have the largest Eigen value; the second factor the next largest Eigen value and so on. (Jaeger, 1983).

5.5.1 Factor Analysis for methane emission four factors have been identified (Tab- 5.10).

Factor -1 -This factor has an Eigen value of 6.016 and accounts for 54.7% of variance in the data matrix. It comprises of Salinity, Sulphate, Dissolved Iron, Nitrate, Carbon and Nitrogen. These show a negative relation with methane. So these can be termed as factors responsible for inhibition for methane production. Since, salinity and sulphate are known to be major inhibitors of CH_4 production followed by Diss. Fe and nitrate in any sedimentary environment.

Factor-2 - This factor has an Eigen value of 3.06 and accounts for 27.8% of variance in the data matrix. It comprises of Sedimentary Iron, Phosphate, Nitrate and dissolved manganese. A relation between sedimentary iron and phosphorous indicates they are

Table- 5.10: Principal Factor Matrix for Methane Emission with various Water and Sediment Chemistry Parameters in Vembanad Lake, Kerala.

	Factor 1	Factor 2	Factor 3	Communality
Methane	-0.351	-0.824	0.445	1.00
Salinity	0.906	-0.147	0.396	1.00
Sulphate	0.972	-0.114	0.206	1.00
Phosphate	-0.116	0.718	0.686	1.00
Nitrate	0.649	0.631	-0.425	1.00
Carbon	0.993	0.063	-0.099	1.00
Nitrogen	0.976	-0.088	0.199	1.00
Sed. Iron	-0.147	0.946	-0.289	1.00
Sed. Mn	0.119	0.545	0.830	1.00
Fe	0.983	0.131	-0.128	1.00
Mn	-0.867	0.464	0.184	1.00
Factor	1	2	3	
Eigen Value	6.016	3.063	1.921	
Pct. Of Var.	54.7	27.8	17.5	
Cum. Pct.	54.7	82.5	100.0	

correlated and are in the same phase. Iron may be responsible of binding phosphorous.

These components can be considered as secondary factors controlling methane emissions from Vembanad Lake. It is known that sedimentary iron followed by nitrate control methane emissions in wetlands.

Factor-3 - This factor has an Eigen value of 1.921 and accounts for 17.5% of variance in the data matrix. It comprises of sedimentary manganese, Phosphorous and Methane. This factor indicates that after all limiting components are depleted then methane emissions is related to phosphorous that is indirectly indicating that the nature of organic matter effects methane emissions.

5.5.2 Factor Analysis for water chemistry of Vembanad Lake three factors were identified (Tab – 5.11).

Factor-1 –This factor has an Eigen Value of 12.088 and accounts for 75.5% variance in the data matrix. This factor is due to seawater intrusion in the Lake. The main contituents are sulphate, chloride, fluoride, sodium, potassium, calcium, magnesium, salinity, bicarbonate and TDS. Thus, it indicates strong marine influence on the water chemistry of Vembanad Lake.

Factor-2 - This factor has an Eigen Value of 1.655 and accounts for 10.3% variance in the data matrix. The variables in this factor are Phosphate and TSM. Thus, this factor can be considered to anthropogenic induced factor. The primary source of phosphate in the system is domestric sewage put into the lake. A relation with TSM also supports this.

Factor-3 - This factor has an Eigen Value of 1.095 and accounts for 6.8% variance in the data matrix. The main variables in this factor are nitrate and TSM. This factor could be due to fixation of nitrogen in the system through biological activity.

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Table- 5.11: Principal Factor Matrix for Water Chemistry of Vembanad Lake, Kerala.

Variable	Factor-1	Factor-2	Factor-3	Communality
Ph	0.754	-0.318	-0.323	0.774
EC	0.995	0.011	0.040	0.992
Bicarbonate	0.928	0.130	-0.125	0.894
Sulphate	0.982	-0.103	0.061	0.979
Phosphate	0.158	0.881	-0.039	0.802
Nitrate	-0.241	-0.723	0.521	0.852
Chloride	0.998	-0.025	0.022	0.997
Silica	-0.781	0.259	0.081	0.683
Flouride	0.962	0.015	-0.192	0.962
Sodium	0.994	0.006	0.008	0.988
Potassium	0.991	-0.011	0.059	0.986
Calcium	0.988	-0.024	0.099	0.988
Magnesium	0.990	0.018	0.078	0.986
TDS	0.998	-0.018	0.027	0.997
TSM	0.408	0.397	0.795	0.957
Salinity	0.998	-0.025	0.021	0.998
Factor	1	2	3	
Eigen Value	12.088	1.655	1.095	
Pct. Of Vari.	75.5	10.3	6.8	
Cum. Pct.	75.5	85.9	92.7	

These three factors taken together explains about 92.7% of the total variance in the data matrix. This indicates that the variables determined are related to each other not only linearly but also otherwise. For instance, water chemistry is not only controlled by marine influence but also by anthropogenic activities in the watershed.

5.5.3 Factor Analysis for sediment chemistry of Vembanad Lake, Kerala four factors were extracted given in Tab- 5.12.

Factor-1: This factor has an Eigen Value of 6.11 and accounts for 47.0% of variance in the data. It comprises of aluminum, iron, magnesium, copper, potassium, sodium, nickel and carbon. Although silica is not included in the factor, Factor-1 stands for clay mineral influence. It stands for clay mineral as mountmorillonite and keolinite dominating the sediments and metals are associated due to adsorption/desorption from the clay. Carbon indicates a likely association of organic matter with there clay minerals.

Factor-2: This factor has an Eigen Value of 2.37 and accounts for 18.3% of variance in the data. It consists of calcium, potassium, sodium, silica and magnesium. This factor emphasizes the role of weathered materials i.e. river detritus in controlling the sediment chemistry of the Vembanad Lake.

Factor-3: This factor has an Eigen Value of 1.59 and accounts for 12.3% of variance in the data. It consists of phosphate, iron, silica and carbon and a negative relation with manganese. This factor signifies the relationship of iron and phosphorous in the system and that iron and manganese exists as two separate phases geochemically in the sediments. This also emphasizes the role of iron on the availability of free phosphorous in the system.

Factor-4: This factor has an Eigen Value of 1.30 and accounts for 10.0% of variance in the data. The factor consists of silica, manganese and carbon. This factor theoretically signifies that manganese is deposited as oxide coating on clay minerals

or associated with organic matter. It also signifies that manganese is not easily mobilized due to its association with silica.

Table- 5.12: Principal factor Matrix for Bed Sediment Chemistry of Vembanad Lake, Kerala

Variable	Factor-1	Factor-2	Factor-3	Factor-4	Communality
Silica	-0.308	0.432	0.316	0.705	0.878
Aluminum	0.823	-0.282	-0.169	-0.241	0.844
Iron	0.881	-0.097	0.306	0.149	0.902
Manganese	0.334	0.118	-0.502	0.735	0.918
Sodium	0.720	0.651	0.139	-0.157	0.986
Potassium	0.566	0.712	0.077	-0.230	0.887
Calcium	-0.101	0.874	-0.276	-0.042	0.852
Magnesium	0.875	0.328	0.149	0.032	0.897
Copper	0.871	-0.106	-0.267	-0.062	0.846
Nickel	0.891	-0.252	-0.267	0.191	0.966
Lead	0.783	-0.046	-0.368	-0.052	0.754
Carbon	0.653	-0.453	0.316	0.249	0.793
Phosphate	0.491	-0.023	0.788	0.025	0.793
Factor	1	2	3	4	
Eigen Value	6.113	2.375	1.597	1.303	
Pct.of Var.	47.0	18.3	12.3	10.0	
Cum. Pct.	47.0	65.3	77.6	87.6	

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Chapter 6

CONCLUSION

CONCLUSION

Vembanad Lake, Kerala, is one of the largest backwater lakes in India. Its importance increases due to the inflow of a number of rivers into it. It also supports a wide range of fisheries, aquaculture activities, with coir industries etc. apart from navigation.

Methane is emitted from the lake as a result of degradation of organic matter under the low-level anoxia existing in the lake. The emission rates vary drastically seasonally and spatially. Spatial variation is due to the salinity gradient across the lake due to seawater intrusion. Strong seasonal variation is observed due to concentration of salts and organic matter during the pre monsoon when the fresh water input from the rivers is low. Salinity and sulfate were found to be main controller of methane emissions. The methane emissions are significant and large as compared to that from East Coast of India. (Verma & Subramanian, 1999 and Ramesh et al., 1998). This could be due to anthropogenic activities.

The waters of Vembanad Lake are eutrophic and have mostly P-limiting except in few locations where it is N-limiting. This is against the conventional belief that most estuaries and lagoons are N-limiting.

The C/N, N/P and C/P ratios of particulate matters and bed sediments indicate that the organic matters are of detrital origin.

Amino acid spectra for surface layer of bed sediments indicate that most of the organic matters in the sediments are fresh. This is supported by low gluam/ galam ratio. On observing the amino acid spectra it is evident that the amino acids are of land origin that is detrital, which is in confirmation with the ratios discussed above. Low Asp/b-ala and Glu/ g-aba ratios indicate that the organic matter in the sediments have not undergone significant degradation.

But there are certain other points to be considered. We can summarise them as follows:

1. Study of effect of TMS on methane emissions should be understood as it is now considered to be a major substrate for methanogenesis.

2. The loading of nutrients have to be calculated which will help us to understand how much of the nutrient enters the lake and part that actually reaches the coastal seas.

3. Study of phytopigments would also be interesting, as it will help in understanding eutrophication and also the history of eutrophication in the lake.

4. Amino acid analysis for the cores will also be useful to understand the fraction of organic matter being trapped in the sediments.

5. Analysis of humic and fulvic acids in water and sediments will also be helpful in complete understanding of nature of organic matter in the Vembanad Lake.

A more comprehensive and extensive study, based on extensive sampling, covering space and seasons, will help in complete understanding of methane emissions, nutrient dynamics and nature of organic matter in Vembanad Lake- a complex river-estuary-lagoon system.

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APPENDIX-I

Calculation for Nutrient Eutrophication Index (I)

(Adapted from Kaydis et al. 1983)

The Index was calculated for Vembanad Lake waters using the formula:

$$I = (C / (C - \log X)) + \log A$$

Where, I= Nutrient Eutrophication Index,

C= Log of the total (annual) loading of a given nutrient in a area,

X= The nutrient loading at a station (mmol m^{-2}),

A= Number of stations in the area.

Eg.

PO4= 0.06 ppm

X= (PO4/ 94.966) x 1000 x av. Depth

X= (0.06/94.966) x 1000 x 3.5

 = 0.68 mmol m^{-2}

logX= -0.17

C= log of sum of all X = 1.36

A= 10

So calculated value form the above formula is I= 2.2

For N

NO3 = 4.14 ppm

X= (NO3/62.004) x 1000 x av. Depth

 = (4.14/62.004) x 1000 x 3.5

 = 234 mmol m^{-2}

Log X = 2.37

C= 3.74

A= 10

So, I= 3.7

APPENDIX- II

Calculation for Degree of Mixing
(Adopted from Gupta et al. 1987)

S_1 = Salinity of sample

S_2 = Salinity of sea water

Eg.

S1 = 4.59 ppt

S2 = 32.69 ppt

F= 1 - (S1/S2)

F = 1 - (4.59/32.69)

  = 0.86

Sea Water %

F% = F x 100

    = 0.86 x 100

    = 86 %

SW% = 100 - F%

      = 100 - 86 = 14 %

ABBREVIATIONS

		C/N ratio (atomic)
Asp	Aspartic acid	3.43
The	Threonin	3.43
Ser	Serine	2.57
Glu	Glutamin	4.28
Gly	Glycine	1.71
Ala	Alanine	2.57
Val	Valanine	4.28
Met	Methionine	4.28
Ile	Isoleusine	4.28
Leu	Leusine	5.14
Tye	Tyrosine	7.71
Phe	Phenylalanine	7.71
His	Histidine	1.71
Lys	Lysine	2.57
Arg	Arginine	1.28
Orn	Ornithine	
b- ala	b- alanine	
g- aba	g- aminobutyric acid	
Gulam	Glucoseamine	
Galam	Galactoseamine	
TC	Total Carbon	
TN	Total Nitrogen	
THAA	Total hydrolysable amino acid	
THHA	Total Hydrolysable hexosamine	
AA	Amino acid	
AS	Amino Sugar	
HA	Hexosamine (Amino Sugar)	

THAA-C	Total hydrolysable amino acid carbon
THAA-N	Total hydrolysable amino acid nitrogen

Mole% = ((nmole/g concentration of a particular AA)/ (nmole/g concentration of all AA)) x 100

MTF	Methanofuran
MPT	Methanopterin
HS-CoM	coenzyme M
HS-HTP	Mercaptoheptanovithreonine phosphate
CoM-S-S-HTP	heterodisulfide coenzyme M
PIC	Particulate Inorganic Carbon
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
POC	Particulate Organic Carbon