WATER QUALITY ASSESSMENT AND ISOTOPE STUDIES OF VEMBANAD WETLAND SYSTEM

A THESIS

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By

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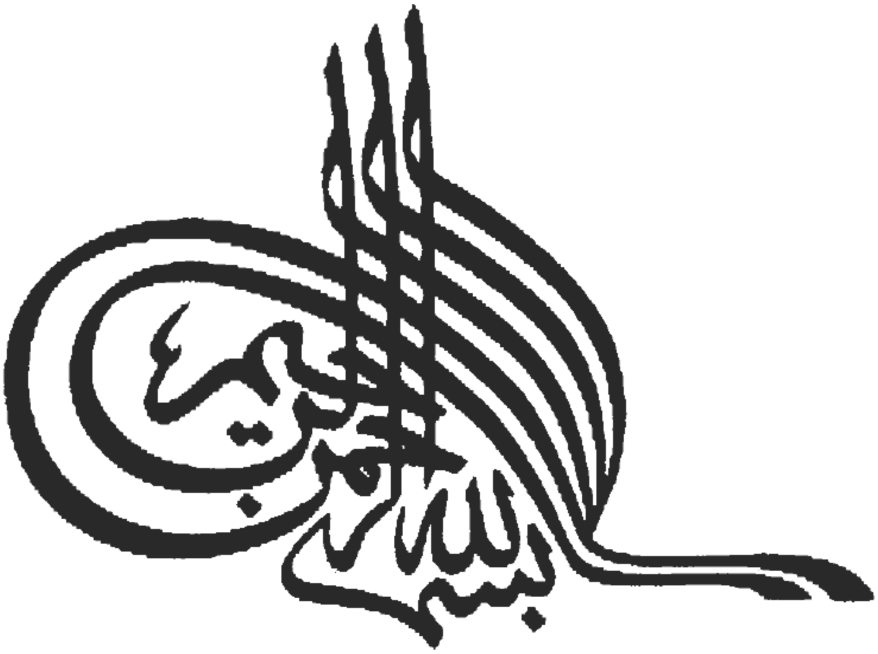

IN THE NAME OF ALLAH THE COMPASSIONATE THE MERCIFUL

Most surely in the creation of the heavens and the earth and (in) the alternation of the night and the day there are signs (of His sovereignty) for men who understand-those who remember Allah standing and sitting and lying on their sides and reflect on the creation of the heavens and the earth (and say): Our Lord! Thou has not created this vain! Glory be to Thee; save us from the chastisement of fire.

* * *

(AL- QURAN, 3:190-191)

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CERTIFICATE

This is to certify that the thesis entitled “Water Quality Assessment and Isotope studies of Vembanad Wetland System” is an authentic record of work carried out by Mr. U P Nasir under my supervision and guidance, in partial fulfillment of the requirements for the award of degree of Doctor of Philosophy in Chemistry under the Faculty of Science, University of Calicut. The contents of this thesis, in full or in parts, have not been presented before for the award of any degree or diploma

Place: CWRDM
Date:

P S Harikumar
(Research Guide)

DECLARATION

I, U P Nasir do hereby declare that this thesis entitled “Water Quality Assessment and Isotope studies of Vembanad Wetland System” submitted by me to the University of Calicut for the award of the degree of Doctor of Philosophy in Chemistry under the Faculty of Science is the result of the bonafied research carried out by me under the guidance of Dr. P S Harikumar, Scientist & In charge, CWAL, CWRDM, Calicut. I further declare that the results presented in thesis have not been submitted previously for any degree.

Place: CWRDM

Date: (U P Nasir)

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ABSTRACT

The indiscriminate exploitation of wetlands beyond its supportive capacity, and input of residues exceeding its assimilative capacity, pollutes the wetland system of Kerala state of India, the magnitude of which is very alarming. The Vembanad wetland system is a complex aquatic system of coastal backwaters, lagoons, marshes, mangroves and reclaimed lands with an intricate network of natural and man made channels and its associated drainage basins are situated in the humid tropical region on the south west coast of the Indian peninsula. Numerous studies have demonstrated that wetlands in general are sinks for various pollutants. Pollution in the wetland is attributed to industrial, urban and agricultural effluents from the city of Kochi and adjoining areas. The environmental status of this wetland including the water and sediment quality had been carried out in the present study. The wetland is an important water body formed by backwaters, estuaries, lagoons and canals, spreading over 196Km in the north-south direction and 29Km in the east-west direction, play an important role in hydrologic functions. Hence the study also focuses on the distribution of various natural isotopes in the wetland system and its use in identifying the source of pollution.

The study on the spatial and temporal variation in water quality of Vembanad Lake indicated that the physico-chemical and microbiological status of the wetland system had been worsened by pollutants. The source of major cations and anions in the system is mainly from the saline contribution of Cochin estuary. Nutrient level in water is as high to cause eutrophication in the system, which is reflected by hypereutrophic stage in many parts of the water body. The sewage running through the open canals of Alappuzha contributed high amount of inorganic and organic components to the water body. The dewatering from the agricultural areas also causes damage to physical and chemical quality of water. The improper management of Thanneermukkom bund flushes high concentrations of ions to the fresh water region which poses threat to the paddy fields. Absence of dissolved oxygen in some sites in the southern part of Thanneermukkom bund is a major threat to the aquatic organisms. The microbiological contamination of the lake is caused by domestic sewage, tourist boats and other anthropogenic activities. In monsoon no stations were free of Escherichia coli. The uncontrolled playing of house boats discharges organic wastes, which is threatening the system with very high amount of oil and grease. With respect to the drinking water guidelines, most of the groundwater samples in the basins of Vembanad Lake were not found to be good for drinking.

Chemical classification of wetland system based on Wilcox and USSL diagrams were carried out. The different chemical characteristics such as sodium absorption ratio, sodium percentage, soluble sodium percentage, Kelly’s ratio, magnesium hazard ratio, residual sodium carbonate, chloro-alkaline index and permeability index of the surface and groundwater samples were calculated. Hydrochemical facies showed sodium-calcium-chloride-bicarbonate type for most of the groundwater and sodium-chloride for most of the surface water. Indices of Base Exchange indicated cation exchange in groundwater samples.

The geochemical analyses of different core sediments collected from Vembanad Lake revealed that the lake is blanketed with highly nutrient rich sediments, which are polluted by heavy metals like manganese, nickel, copper, zinc, cadmium, lead, mercury and chromium. Determination of the texture of the sediment indicated various proportion of silt and sand in different regions of the wetland system. There was high accumulation of organic matter. The variation of C/N ratios in the sediment core indicated maximum contribution of terrestrial sources and a few aquatic sources towards organic matter. Determination of nutrient concentrations revealed a hypereutrophic stage of the lake with vertical increase in the deposition of major anions. The relative concentration of major exchangeable cations indicated the variability in ion exchange capacity of sediments in different regions of wetland system. Phosphorous fractionation study revealed more contribution of organic phosphorous in the region close to Alappuzha town and more inorganic phosphorous near the agricultural area. Examination of pesticides in sediments revealed high concentration of chlorinated pesticides in the wetland system.

Most of the heavy metals reported enrichment towards the surface of the core sediment and its concentration is very alarming in the Cochin side. Quality of the sediments were evaluated based on Sediment Quality Guidelines, Pollution Load Index, sum of Toxic Units and with Effect Range Low/Effect Range Median and Threshold Effect Level/Probable Effect Level values of Environmental Protection Agency guidelines. The degree of contamination for each station was determined. The concentrations of different heavy metals were compared with world average concentration of shale values. Statistical analysis showed correlation among different parameters. The analysis of the core collected from the estuarine region of the wetland confirmed the role of Cochin industrial belt in determining the pollution status of the southern region of the wetland system. The concentration of heavy metals in some stations exceeded the effect range median levels, which represents a probable effect range with in which adverse biological effects frequently occur. The spatial variation of heavy metals showed more contamination in the downstream at Pathalam industrial site. The present study highlighted severe heavy metal contamination of wetland system with increased rate of deposition.

The heavy metals (iron, manganese, nickel, cadmium, copper, zinc, mercury, lead and chromium) were quantified in certain native aquatic macrophytes *(Eichornia crassipes, Sacciolepis interrepta, Alternanthera pheloxeroides, Salvenia molesta and Pistia stratiotes*) of Vembanad wetland system. The results indicated that the concentration of all the heavy metals were high with maximum concentration in the roots of *Alternanthera pheloxeroides* except mercury which is high in leaves, and minimum value in the stem of *Sacciolepis interrepta*. Comparison of the heavy metals with the background concentration of sediment showed more chromium and mercury in *Alternanthera pheloxeroides.* The species *Sacciolepis interrepta* and *Pistia stratiotes* reported minimum uptake of heavy metals. The concentration factor calculated showed the comparative suitability of different macrophytes among the selected plants as biomonitor for specific heavy metal. *Eichornia crassipes* is the suitable biomonitor for iron, *Alternanthera pheloxeroides* for manganese, nickel, lead, cadmium, chromium and mercury and *Salvinia molesta* for copper and zinc.

Seasonal and spatial variations in the stable isotopic composition of natural water were investigated in Vembanad wetland system. The precipitation samples of the area follows the equation $\delta D = 5.32\delta^{18}O+9.0$. The stable isotopic composition of precipitation showed seasonal and amount effect. The lake water has the most enriched values of $\delta^{18}O$ and $\delta^{2}H$ in the pre-monsoon season. But in the monsoon season the water samples were relatively depleted in isotopic composition. The spatial variation of $\delta^{18}O$ showed most enriched value at the station Thanneermukkom north, through which saline water enters to the fresh water region. The highest enriched value of $\delta^{2}H$ was observed at the station Kanavattinkara, where the lake is stagnant with high rate of evaporation. The slope of the best fit line to all groundwater data in $\delta^{18}O$-δD plot is 6.5 with a *d*-excess of 7.3‰. The study to understand interconnection between surface and subsurface water identified three groups of samples. The $\delta^{34}S$ value of sulphate showed a disparity from +10.5‰ to +23.9‰. A plot of sulphate concentration against $\delta^{34}S$ revealed that, the station Thanneermukkom has marine contribution whereas the station Cherukarakayal has marked difference from the range of other stations. Recent sedimentation rate of the lake determined using ^{137}Cs dating technique was found to be 0.51cm/year.

Key words: Vembanad wetland system, Aquatic macrophytes, Heavy metals, Delta values, Precipitation, Sedimentation rate.

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PREFACE

Lakes and wetlands have been playing a crucial role in maintaining the ecological balance in their surrounding ecosystems. Their importance has been recognized in the maintenance of biodiversity, ecology hydrology and recreation. They provide habitat for wide variety of flora and fauna and help maintain the life cycle of many species. They are sinks for incoming contaminants and recycle and maintain the impaired conditions. Lakes and coastal wetlands all over the world are ideal places for human habitation, fisheries, industries, shipping and recreation. Habitat environment of lakes and coastal wetlands are deteriorating due to their exploitative use and improper management. As rapid development and population growth continue in coastal areas, environmental degradation and over-exploitation will further erode the biodiversity and undermine the productivity of these unique ecosystems.

Lakes and coastal wetlands are transitional areas between dry terrestrial and permanent aquatic ecosystems and are recognized as highly productive. Their importance in socio-economic frontiers has been increasingly felt. These have been used as main source of water supply, food, fodder, fuel, fishery, aquaculture, timber production, transport, ecotourism, culture and heritage, research and educational values. They influence significantly the lifestyle and the livelihood of the community, which lives in and around the lake and wetlands. Over 200 rivers and lakes in the world are shared by two or more countries. This envisages their international importance.

Due to increased use of lakes and wetlands and exploitation of their resources for various economic growths, these ecosystems are under severe stress. The stress may further increase in coming years because of urbanization, industrial growth, transportation, agriculture, housing etc. The most wide spread problems that lakes and wetlands face are sewage from domestic sector, effluents from industrial sector (point sources), and agricultural non-point runoff of silt and associated nutrients and pesticides. Unless timely corrective measures are taken, over-exploitation and environmental degradation will erode these ecosystems which in turn will affect their productivity.

Various efforts are currently underway to develop technologies and systems for successful management of lakes and coastal wetlands-both at national and international levels. However conflicting interest in the use of their resources have led to further worsening of the problems facing lakes and coastal wetlands. Therefore it is very important to involve all of those concerned in the process of restoration, conservation and management of lakes and coastal wetlands. Thus there is an imminent need to promote regional linkages, develop strategic partnership and follow good practices in the conservation and management of lakes and wetlands. It is also essential to establish new, strengthen ongoing regional and international co-operation, linkages and strategic partnership between governments, international agencies, universities, research institutions, non-governmental organizations, private sectors, local communities, and individuals.

Kerala, notwithstanding its limited geographical size supports a rich diversity of wetland ecosystem. Wetlands of Kerala comprise the coastal wetland ecosystems such as backwaters and estuaries with the associated mangroves, mudflats, swamps and marshes and the inland ecosystems like natural fresh water lakes and swamps and man made reservoirs. The wetlands in Kerala are currently subjected to acute pressure of rapid developmental activities. Efforts at every level are needed to ensure that these environmentally crucial ecosystems are projected and preserved against the onslaught of developmental fallout.

In the above context the present study entitled “***Water Quality assessment and isotope studies of Vembanad wetland system***” was undertaken to understand the various problems faced by Vembanad wetland system with special reference to water & sediment quality and variation of different natural isotopes in the wetland system as a whole.

The first chapter comprises of some general aspects of the wetlands and the current problems faced by Vembanad wetland system and the objectives of the present study. In the second chapter the important studies carried out in wetlands of India with special reference to wetlands of Kerala is reviewed. The various methodologies adopted are explained in chapter three. The surface water quality of the wetland system is explained in chapter four and groundwater threats are mentioned in chapter five. The historical quality of the wetland system is explained in detail by using sediment cores from different parts of the wetland system in chapter six. Chapter seven gave an easier way of underrating the pollution problems using aquatic macrophytes in biomonitoring studies. The general variation of different natural isotopes in various waters of wetlands and use of other isotopes for pollution studies are explained in detail in chapter eight. The major conclusions and the recommendations are given in chapter nine.

There is case to be made for wetland science as a unique multidisciplinary, with support in ecology, chemistry, hydrology, and engineering. Wetland management, as the applied side of wetland science, also requires an understanding of the scientific aspects of wetlands, balanced with legal, institutional, and economic realities, to ensure protection of these valuable ecosystems.

1.0 Wetlands

1.1 Introduction

India with its annual rainfall of over 1,300 mm, having varied topography and climatic regimes, support and sustain diverse and unique wetland habitats. Natural wetlands in India consist of the high-altitude Himalayan lakes, followed by wetlands situated in the flood plains of the major river systems, saline and temporary wetlands of the arid and semi-arid regions, coastal wetlands such as lagoons, backwaters and estuaries, mangrove swamps, coral reefs and marine wetlands. With the exception of bogs, fens and typical salt marshes, Indian wetlands cover the whole range of wetland ecosystem types elsewhere. In addition to the various types of natural wetlands found, a large number of man-made wetlands also contribute in sustaining the faunal and floral diversity.

1.2 Wetlands definition

Wetland is defined differently by individuals/agencies depending on the objectives and their need. There is world-wide confusion about ‘what constitutes a wetland?'. In spite of global attention currently focused on wetland ecosystem, there is yet no single universally accepted definition for wetland. Wetlands are historically defined by scientists working in specialized fields such as botany or hydrology. A botanical definition would focus on the plants adapted to flooding and/or saturated soil conditions, while a hydrologist's definition would emphasize the position of the water table relative to the ground surface over a period of time. A more complete definition of wetlands involves a multidisciplinary approach. The following paragraphs narrate some standard definitions used officially by Government department and institutions.

1.2.1 Ramsar Convention

Wetlands are areas of marsh, fen, peat land 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 meters. It is globally the most widely accepted definition. However, in the Indian context, paddy fields are not to be viewed as covered by this definition (Anon 1994, 1999, 2002 and website of Ramsar/MoEF 2005/2006).

1.2.2 US Fish and Wildlife Services

Wetlands are lands transitional between terrestrial and aquatic systems, where the water table is usually at or near the surface or the land is covered by shallow water level. For purposes of this classification, wetlands must have one or more of the following three attributes: (i) at least periodically the land supports predominantly hydrophytes; (ii) the substrate is predominantly undrained hydric soil; and (iii) the substrate is non-soil and is saturated with water or covered by shallow water level al some time during the growing season of each year (Cowardin et al. 1979).

1.2.3 Asian Wetland Bureau

The Asian Wetland Bureau (1991) broadly defines the wetlands of South and West Asia as: "Estuaries and deltas, salt marshes, mangroves, and mudflats, coastal lagoons, freshwater lakes and marshes, oasis, seasonal flood plain wetlands, swamp forests, rivers and streams, man-managed systems such as rice fields, fish ponds and reservoirs" (Asian Wetland Bureau 1991).

1.2.4 Soil Conservation Services (SCS) of the U.S. Department of Agriculture

In defining wetlands from an ecological standpoint, the SCS emphasizes three key attributes: (i) hydrology - the degree of flooding or soil saturation; (ii) wetland vegetation (hydrophytes); and (iii) hydric soils. All areas considered wetlands must have enough water at some time during the growing season to stress plants and animals not adapted for life in water or saturated soils present. Accordingly, "Wetlands are defined as areas that have a predominance of hydric soils and are inundated or saturated by surface or groundwater at a frequency and duration sufficient to support, and under normal circumstances do support, a prevalence of hydrophytic vegetation typically adapted for life in saturated soil conditions".

1.2.5 U.S. Environmental Protection Agency (EPA) and Army Crops of Engineers (ACE)

"Those areas that are inundated or saturated by surface or groundwater at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions, Wetlands generally include swamps, marshes, bogs and similar areas".

1.2.6 International Biosphere Programme (IBP)

"Part of the surrounding ecological structure and several stages in the succession from open water to dry land or *vice versa*, occurring at a sites situated as a rule between the highest and lowest water levels as long as the flooding or water logging of the soil is of substantial ecological significance".

Another simple definition is that the wetlands are areas where, for part of the year at least, water stands naturally from 2.5 cm to around 300 cm.

1.3 Classification of wetlands

In the present context, the Ramsar Classification System for Wetland and the Ministry of Environment and Forests Classification for Wetland are examined.

1.3.1 Ramsar classification system

The Ramsar Classification is exhaustive, given under three broad groups as Marine/Coastal Wetlands, Inland Wetlands and Human-made Wetlands. There are twelve categories under Marine/Coastal Wetlands, twenty categories under Inland Wetlands and ten categories under Human-made Wetlands, as given below. The codes are based on Ramsar Classification System for Wetland as approved by Recommendation 4.7 and amended by Resolutions VI.5 and VII.11 of the Conference of the Contracting Parties.

The categories listed herein are intended to provide only a very broad framework to aid rapid identification of the main wetland habitats represented at each site.

i. Marine/Coastal wetlands

A-Permanent shallow marine waters (in most cases less than 6m deep at low tide; includes sea bays and straits).

B-Marine sub-tidal aquatic beds (sea-grass beds, tropical marine meadows)

C-Coral reefs.

D-Rocky marine shores (includes rocky offshore islands, sea cliffs)

E-Sand, shingle or pebble shores; includes sand bars, spits and sandy islets; includes dune systems and humid dune slacks.

F-Estuarine waters; permanent estuaries and estuarine systems of deltas.

G-Intertidal mud, sand or salt flats.

H-Intertidal marshes; includes salt marshes, salt meadows, raised salt marshes; includes tidal brackish and freshwater marshes.

I-Intertidal forested wetlands; includes mangrove swamps and tidal freshwater swamp forests.

J-Coastal brackish/saline lagoons; brackish to saline lagoons with at least one relatively narrow connection to the sea.

K-Coastal freshwater lagoons; includes freshwater delta lagoons.

Zk(a)-Karst and other subterranean hydrological systems, marine/coastal.

ii. Inland wetlands

L-Permanent inland deltas.

M-Permanent rivers/streams/creeks; includes waterfalls.

N –Seasonal/intermittent/irregular rivers/streams/creeks.

O-Permanent freshwater lakes (>8 ha); includes large oxbow lakes.

P-Seasonal/intermittent freshwater lakes (>8 ha); includes floodplain lakes.

Q-Permanent saline/brackish/alkaline lakes.

R–Seasonal/intermittent saline/brackish/alkaline lakes and flats.

Sp-Permanent saline/brackish/alkaline marshes/pools.

Ss-Seasonal/intermittent saline/brackish/alkaline marshes/pools.

Tp-Permanent freshwater marshes/pools; ponds (<8 ha), marshes and swamps on inorganic soils; with emergent vegetation, water-logged for at least most of the growing season.

Ts-Seasonal/intermittent freshwater marshes/pools on inorganic soils; includes sloughs, potholes, seasonally flooded meadows, sedge marshes.

U-Non-forested peatlands; includes shrub or open bogs, swamps, fens.

Va-Alpine wetlands; includes alpine meadows, temporary waters from snowmelt.

Vt-Tundra wetlands; includes tundra pools, temporary waters from snowmelt.

W-Shrub-dominated wetlands; shrub swamps, shrub-dominated freshwater marshes, shrub carr, alder thicket on inorganic soils.

Xf-Freshwater, tree-dominated wetlands; includes freshwater swamp forests, seasonally flooded forests, wooded swamps on inorganic soils.

Xp-Forested peatlands; peatswamp forests.

Y -Freshwater springs; oases.

Zg(a)-Geothermal wetlands.

Zk(b)-Karst and other subterranean hydrological systems, inland.

Note: "floodplain" is a broad term used to refer to one or more wetland types, which may include examples from the R, Ss, Ts, W, Xf, Xp, or other wetland types. Some examples of floodplain wetlands are seasonally inundated grassland (including natural wet meadows), shrub lands, woodlands and forests. Floodplain wetlands are not listed as a specific wetland type herein.

iii. Human-made wetlands

1 - Aquaculture (e.g., fish/shrimp) ponds.

2 - Ponds; (farm ponds, stock ponds, small tanks-generally below 8 ha).

3 - Irrigated land; (includes irrigation channels and rice fields).

4 - Seasonally flooded agricultural land (grazed wet meadow or pasture).

5 - Salt exploitation sites; (salt pans, saline’s, etc.)

6 - Water storage areas; (reservoirs/barrages/dams/impoundments (>8 ha).

7 - Excavations; (gravel/brick/clay pits; borrow pits, mining pools).

8 - Wastewater treatment areas; (sewage farms, settling ponds, oxidation basins, etc.

9 - Canals and drainage channels, ditches.

Zk - Karst and other subterranean hydrological systems, (human-made).

1.3.2 Ministry of Environment and Forests Classification System

The Classification System for Wetlands in India was evolved under the National Wetland Mapping Programme sponsored by Ministry of Environment and Forests, Government of India, executed by the Space Application Centre, ISRO, Ahmedabad with the exhaustive use of the Indian Remote Sensing Satellite-IA/B, LISS I & II, Geocoded Database, pertaining to 1988/89/90 in the scales of 1:2,50,000 and 1:50,000. The classification is developed for each one of these scales. For 1:2,50,000 scale mapping, two broad groups as Inland Wetlands and Coastal Wetlands were identified and in each group Natural and Man-made sub-groups of Wetlands were also identified. There are 14 categories of wetlands in the Inland Wetland, and 19 categories in the Coastal Wetland group.

1.4 Importance of wetlands

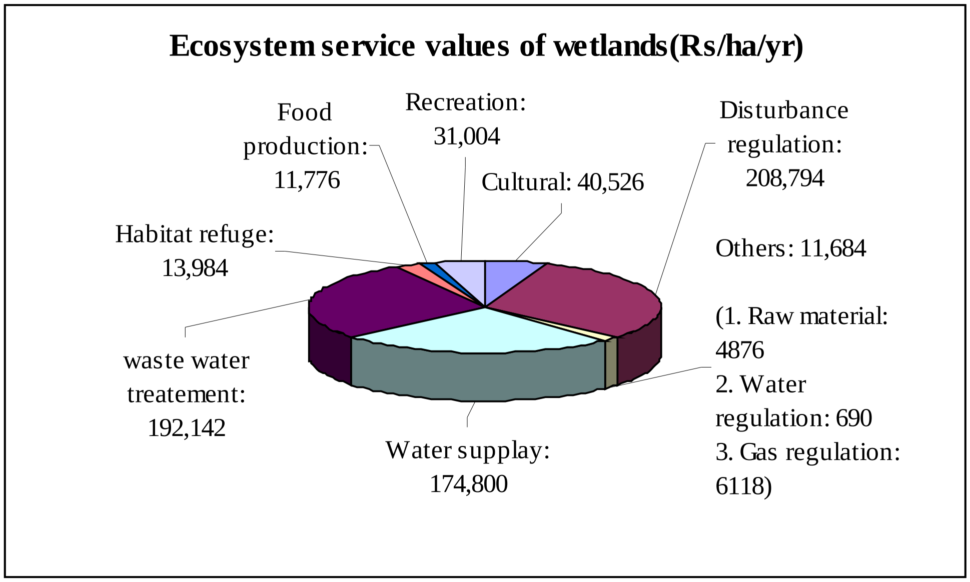
Wetlands provide many services and commodities to humanity. Regional wetlands are integral parts of larger landscapes, their functions and values to the people in these landscapes; depend on both their extent and their location. Each wetland thus is ecologically unique. Wetlands perform numerous valuable functions such as recycle nutrients, purify water, attenuate floods, maintain stream flow, recharge groundwater, and also serve in providing drinking water, fish, fodder, fuel, wildlife habitat, control rate of runoff in urban area, buffer shorelines against erosion and recreation to the society. The interaction of man with wetlands during the last few decades has been of concern largely due to the rapid population growth accompanied by intensified industrial, commercial and residential development further leading to pollution of wetlands by domestic, industrial sewage, and agricultural run-offs as fertilizers, insecticides and feedlot wastes. The fact that wetland values are overlooked has resulted in threat to the source of these benefits.

Wetlands are often described as “kidneys of the landscape” (Mitsch & Gosselink 1986). Hydrologic conditions can directly modify or change chemical and physical properties such as nutrient availability, degree of substrate anoxia, soil salinity, sediment properties and pH. These modifications of the physiochemical environment, in turn, have a direct impact on the biotic response in the wetland (Gosselink & Turner 1978). When hydrologic conditions in wetlands change even slightly, the biota may respond with massive changes in species composition and richness and in ecosystem productivity. Traditional limnological methods of assessment of water quality are time consuming and uneconomical, but using remote-sensing data assessment of water quality and productivity in surface impoundment is both cost effective and fast. The indicators useful for such an assessment include suspended materials visible to the human eye, which include suspended inorganic material, phytoplankton, organic detritus and dyes.

1.4.1 Ecosystem service values of wetlands

It has been reported that wetlands are the most productive ecosystem, and that in terms of economic and ecosystem service values they outweigh forest ecosystems by almost seven times. While the ecosystem service value of a forest is estimated at US $ 2,007 ha^{-1}, that of a wetland is US $ 14,785 ha^{-1} (Costanza et al. 1997). The ecosystem services considered in the above calculation are a) gas regulation, b) disturbance regulation such as flood control, c) water storage and supply, including groundwater recharge, d) habitat refuge, e) food production, f) raw material, g) recreation, including tourism, and h) cultural (Figure 1.1).

The ecosystem services should be considered as an income to the national budget. It would be clearer in a situation where such ecosystems are absent and consequently their services are not available, thereby forcing the State to incur huge expenditures to compensate the services of ecosystems. It is reported that the New York City Council needed $6 billion for water filtration to provide safe drinking water for its 9 million customers, as against $ 1 billion for managing river banks, forests, agriculture and other ecosystems to reduce pollution (Vidal 2005). In Georgia, around 1,022 ha wetland saves $1 million, annually, in water control costs (OTA 1993). The quantity of pollutants removed by a swamp in South Carolina is equivalent to that by a water treatment plant costing $5 million (USEPA 1995).



(Source: - Modified from Costanza 1997, Nature Vol. 387)

Figure 1.1 Different ecosystem values of wetlands

Wetland values could also be recognized by comparing the output from other land use practices. An intact wetland in Canada is found to be worth $6,000 ha^{-1}, while it is only

\$2,000 ha^{-1} for one cleared for intensive agriculture. Tropical mangroves are found to be worth around \$1,000 ha^{-1}, while the cleared one for shrimp farms, values only around \$200 ha^{-1} (Vidal 2005).

Only limited data is available from India. However, it is estimated that the loss of the number of tanks and ponds for the last ten years in the country is about 0.277 million to 0.292 million. Considering that a minimum of five families, each having an average five members use one wetland, such a loss would have amounted to loss of water and other ecosystem services to 6.925 to 7.3 million people! These estimates are certainly quite conservative (Vijayan et al. 2004).

1.4.1.1 Ecosystem service values of wetlands in India

India has, according to a very conservative figure, around 13.1 million ha of wetlands, including inland, coastal, mangroves and rivers. Total intangible service values of these ecosystems, using the global average as reported by Costanza et al. (1997), would be around Rs. 7,151.08 billion per year. Including the ecosystem service values of the 55.1 million ha of paddy fields in the country, the total values go up to Rs. 14,396.80 billion per year. In other words, if we just protect and maintain the country's wetlands as they are today, we get indirect services/benefits worth Rs 14,396.80 billion. It is to be noted that this is much higher than the annual receipt shown in the national budget (Rs. 5,639.91 billion) for 2007 - 2008.

1.4.1.2 Ecosystem service values of wetlands in Kerala

The available data show that Kerala has around 328,402 ha of wetlands covering lakes and reservoirs, rivers, estuaries, prawn fields, kole wetlands, Kuttanad, ponds and tanks (Mohan 2004, Gopalan 2002, Vijayan et el. 2004). The aggregate minimum ecosystem service values of these wetlands would be around Rs. 157.97 billion (Costanza 2007).

1.4.1.3 Annual service values of wetlands of Kerala

Types of wetlands	Area in ha	Values (Rs. in billion)
Rivers	85,000	32.50
Lakes & Reservoirs	47,345	18.11
Estuaries	65,500	67.30
Prawn fields	12,511	2.77
Kole wetlands	11,000	2.45
Kuttanadu	82,000	18.18
Ponds, tanks. etc	25,046	16.66
Total wetland area	328,402	157.97

Since the ecosystem services of the paddy fields are also similar to those of wetlands, it is logical to consider them also as wetlands. Kerala has 330,000 ha of paddy fields (Mohan 2004) and the total ecosystem service values of which would be around Rs.73.18 billion per year. It makes the total annual wetlands services worth Rs.231.15 billion. Again, if we add the ecosystem service values of the forests that we have in the state, the total ecosystem service values would be around Rs. 375.63 billion per year.

It may be noted that the revenue receipt of Kerala, as per the budget of 2007 -2008 is only 214.56 billion. It shows that the annual receipt from the forests and wetlands are much more than that from all other sources. Again, the expenditure in the budget is projected as Rs. 266.97 billion for 2007 -2008. It is pertinent to note that the expenditure would have been several times high, if we have not received the services of the forests and wetlands. In other words, the expenditure is limited to Rs. 266.97 billion only because of the forests and wetlands which determine and ensure the availability of water for agriculture and drinking.

1.5 Problems faced by the wetlands

In spite of such vital roles being played by the wetlands, they are under serious anthropogenic threats which appear to be remarkably similar across the country. One of the major reasons for the drastic decline is the failure to consider wetlands as a productive unit of land. They have been considered as "wasteland". To a certain extent, these issues reflect the situation wetlands face in a global context. Conversion of wetlands for various other land uses such as agriculture, reclamation for development projects, institutionalized dumping of wastes (from Municipalities and Corporations), overgrazing, invasion of weeds such as water hyacinth, formation of silt consequent to anthropogenic activities in the catchments, and over exploitation of a) fish and other animal, and plant resources, b) water for irrigation, c) bore wells in the adjacent areas of wetlands, are some of the major reasons for the decline of wetlands. Compounding the loss of wetlands is the serious issue of pollution in the existing wetlands. It is a cause for great concern that not even one of the 1,700 fishes studied from 170 wetlands from 14 States was free from pesticides/heavy metal (Vijayan et al. 2004). As a result of rapid developmental activities and indiscriminate utilization of land and biomass the wetland system all over is destroyed especially in the tropics (Brij Gopal 1993).

Wetlands appear to be one of the most preferred landfills for dumping solid wastes from a variety of origins, and an ultimate end point for discharging untreated industrial and domestic effluents. In one of the wetlands studied in Tamil Nadu (Pallikaranai), most of the 3,500 tones of municipal wastes from Chennai city are dumped everyday! This particular wetland harbors the most precious germplasm of *Oryza ruifipogon,* a wild variety of rice. Blissfully ignorant of this fact, 32 million liters of domestic effluents are also discharged everyday! Apart from filling the wetland and contaminating the water body, such wastes pollute the air; and waste containing plastic origin is burnt in many cases. One of the studies shows that the human milk in some such areas contains dioxin, a deadly carcinogenic chemical, which got into the air because of the burning of plastics.

Though there exists no quantitative estimate of the destruction of wetlands of Kerala, the reports indicate that the wetlands in Kerala are facing many environmental problems (Nair 1994, 1997, Ouseph 1987, Nair and Unni 1993, Laksmmanan et al. 1982). The reclamation of wetland for urban development, agricultural practices, construction of barrages and bunds, discharge of industrial effluents, dumping of municipal wastes without proper treatment, drainage of fertilizer, pesticide residues, tourism, coconut husk retting and such other activities are contributing to the loss and degradation of wetlands of Kerala(Muraleedharan Nair and Ajaykumar Varma 2002).

Restoration is quite a task, once the wetlands are occupied for non-wetland uses. Hence, attempts should be made to prevent conversion of wetlands. The loss of one km^2 of wetlands in a high population area as in India, will have much greater impacts than that in a low population area. Therefore, it is high time that the country conceives a determined, proactive National Wetland Conservation and Sustainable Use Strategy and Action Plan with adequate support of legal instruments, and implement it with all seriousness and priority to arrest further erosion of its most precious life support system, the wetland - the ultimate insurance for drinking water and food security.

The exploitation of these fragile ecosystem and dumping of untreated waste into the system exceeding its assimilative capacity. This will finally cause ecological imbalance leading to deleterious effects such as harm to living resources, hazards to human health, hindrance to aquatic activities, impairment of water quality etc.

1.6 Wetland pollution

The feverish tempo of wetland reclamation for urban constructions and undesirable agricultural practices, construction of levees and dykes for hydrologic manipulation, discharge of industrial effluents, dumping of municipal wastes in the absence of reuse, recycling and disposal facilities, drainage of fertilizer-pesticide residues, overexploitation of resources and domain utilization for mining, construction, tourism, coconut husk retting and such other activities are contributing to the loss and degradation of wetlands of Kerala (Nair and Varma 2002). These are in addition to the natural causes such as erosion, storm surge, siltation, drought, eutrophication and biotic interferences. The major sources of pollution of the wetlands of Kerala and the pollutant characteristics, are given hereunder.

1.6.1 Industrial effluents

It is a general practice to establish industries on the banks of streams, rivers and backwaters, mainly to avail the ease of discharge of effluents. The flowing water bodies which contain, rich flora and fauna, has enormous capacity to assimilate most of the pollutants generally contained in the effluents, if the discharge is controlled spatially and temporally, and limited within the physical, chemical and biological saturation levels. However, such controls and regulations are often absent, leading to pollution of water bodies. The backwaters, being the repository of river discharges, are characteristically the hotspots of aquatic pollution, especially due to industrial discharges. It is estimated that industrial effluents of the order of 6.5 Mm3 are discharged into the water bodies of Kerala (Anon 2003). The Eloor- Edayar region of the Kochi estuary provides a typical example of wetland pollution due to industrial discharges.

The Eloor-Edayar region on the banks of River Periyar, near the river-estuary confluence region, houses Kerala's largest industrial cluster with about 50 industries including major ones like Fertilizers and Chemicals Travancore Ltd. (FACT), Hindustan Insecticides Ltd (HIL), Indian Rare Earths Ltd., Travancore Cochin Chemicals etc. Some of the major industries, their products, pollutants and permitted effluent discharge to the Kochi estuary are given in Table 1 as an example. Many of these industries are more than 50 years old and their effluent treatment and management systems are mostly not attuned to the present day pollution control norms. These industries take large amounts of fresh water from River Periyar and in turn, discharge effluents containing large toxic ingredients such as acids, alkali, heavy metals, suspended solids and a number of other chemicals, having immediate and long-term effects on the ecosystem. The input of acids and alkalis lead to drastic imbalances in the ionic status of water, upsetting the living environment of organisms. The suspended solids cause turbidity maxima leading to productivity impairment.

1.6.2 Municipal sewage and solid wastes

Most of the cities, towns and other urban centers are on the banks of water bodies. None of the urban centers in Kerala has a sewerage system, except Thiruvananthapuram with a partial coverage. Therefore, the analysis of almost all river and estuarine water samples from any part of the State generally indicate high fecal coliform counts. For example, a major source of pollution in Vembanad Lake is the domestic sewage generated in the urban areas and tourism locations of Alappuzha, Kochi, Vaikom, Cherthala, Chenganasseri, Kottayam, Kumarakom etc, and the operation of houseboats in large numbers. About 10,000 people are added every year to the urban population of the city of Kochi alone. Kochi city generates about 3 Mm^3 per day of wastewater that enters the lake directly, through major canals, such as Padiyathubalam, Kavathi, Rameswaram, Pulimutu, Thevara etc. The pollution load of Kochi Corporation is estimated to be around 200 tons/day of BOD (Nair and Unni 1993). The total dissolved solid content near the sewage discharge site in Kochi estuary was as high as 53,750 mg/l during summer. It lowers drastically during the rainy season, to 160 mg/l. Similarly, the coliform counts observed in River Pamba, near Sabarimala were of the order of 240 to 46,000 MPN/100ml. The quantum of pollution caused by the discharge of untreated sewage into wetland system is alarming. The domestic sewage containing oxygen demanding wastes, infectious agents, organic chemicals and inorganic minerals, often affect the water quality of wetland system (Lakshmanan et al. 1982, Unnithan et al. 1976).

Table 1.1 Major industries and their effluent discharge to Cochin estuary

SI. No.	Industry	Products	Production (Tones/ moth)	Effluent Discharge (m3/day)	Major pollutants
1	FACT	Ammonium chloride, Ammonium sulphate, Ammonium phosphate, Ammonia, Phosphoric acid	2250 18000 16500 10200 3750	25400	Free Ammonia, Ammonia Nitrogen, Fluorides, Phosphates, Suspended solids
2	FACT Petrochemical	Caprolactum, Nitric acid, Soda ash	--	5040	--
3	Travancore Cochin Chemicals	Caustic Soda, Liquid chlorine & Hydrochloric acid Sodium H sulphate Sodium sulphate	2775 2487 10 54	6680	Mercury Free chlorine Suspended Solids
4	Indian Rare Earths Ltd	Rare Earths Chloride Trisoidum Phosphate	375 465	3000	Fluorides, Phosphates, Radio active Substances
5	Binani Zinc Ltd.	Zinc slabs Cadmium	1400 3	550	Zinc & Lead
6	United Catalysts India, Ltd.	Metallic Catalysts	--	537	Hexavalent Chromium
7	Periyar Chemicals Ltd.	Formic Acid Sodium Formate	85 165	330	--
8	Hindustan Insecticides Ltd.	DDT BHC Hydrochloric acid Sulphuric acid	336 500 140 100	1000	Insecticides
9	Travancore Chemicals Manufacturing Co.Ltd.	Copper sulphate Copper oxy chloride Sodium aluminate Sulphate of alumina Alumino Ferric . Pot. Chlorate	250 75 85 100 150 100	720	--

Contd...

10	Indian Aluminium Company	Aluminium extrusions	3760	13700	--

(Source: Environmental Status Report, Kerala State Pollution Control Board, 2000)

1.6.3 Fertilizers and Pesticides

The residues of chemical fertilizers and pesticides, wherever they are used, ultimately reach the water bodies through the dense drainage system of the State. The intensive agricultural practices have resulted in the input of large quantities of agrochemicals and pesticides in the State. In the wetland bodies of Kerala, especially in Vembanad Lake, the pesticide pollution is acute (Nair and Unni 1993). The application of fertilizers and bio-degradation of organic wastes has also led to the enrichment of nitrogen in the lake waters.

Pesticides are used in increased quantities than the recommended dosage by the farmers to avoid annual damage to crops by fungi, insects and noxious weeds and rodents. At least 46 different formulations of pesticides are commonly being used in Kuttanad area. The annual usage of pesticides/fungicides/weedicides in Kuttanad is reported to be 117 tons during *virippu* season and 368 tons during the *Mundakan* and *puncha* season (Nair & Unni 1993). The excessive use of these substances has led to the serious contamination of both land and aquatic environment of the area. The problem of pollution in Kuttanad is extremely grave as the entire population depends on rivers for their water requirements including drinking purposes.

The degradation rate of pesticides is very slow after entering into the environment. The studies by Rajiv Gandhi Centre for Biotechnology (Roy Mathew 2000) confirmed serious deterioration of the ecosystem of Kuttanad, the rice bowl of Kerala as there were high concentrations of heavy metals and organochlorine pesticide residues in water and sediment. High levels of bioaccumulation of these chemicals are taking place in humans and animals living in the area. The studies also showed the presence of virulent strains of poliovirus I and other viruses like hepatitis viruses in water. It was observed that water and sediment in the Kuttanad system acted as sources for bioaccumulation in the faunal compartments. High concentrations of residues were found in plankton, benthos, earthworm, clam, fish, prawn, frog, cow's milk and human blood from the area.

1.6.4 Tourism and Fisheries

Water Pollution in wetlands of Kerala is mounting as the number of houseboats and fishing boats increases. At present there are more than 500 houseboats operating in Alappuzha alone. There is considerable increase in the number of backwater tourism centers as well as houseboats operating from such centers. The Pollution problems created by houseboats are numerous. Houseboats often release sewage and kitchen wastewater directly into the lake. As a result, the presence of total coli form, E.coli and Fecal streptococcus is very high in the lake waters. The organic pollution is also found high in many locations of Ashtamudi Lake due to fisheries and direct input of sewage.

One of the reasons for pollution is careless filling of fuel. Oil and fuel from two-stroke engines is being released through motorized boating activity. Between 25 and 30 percent of the fuel and required oil that conventional two strokes use is ejected unburned through the tailpipe and enter in to the water body. Numerous oil tankers and fishery vessels plying through the waters are also major source of pollution. The areas in Ashtamudi estuary near the fishing harbor at Neendakara exhibited very high concentrations of petroleum hydrocarbon (19 μg/l) when the safe level is only 2 μg/l. Oil is found mostly in the form of unburned fuel and the tarry nature of these residues adheres to the respiratory system of aquatic organisms. The aromatic hydrocarbons like benzene, toluene etc. associated with oils and lubricants are also poisonous to the aquatic organisms. It is found that hydrocarbons subjected to bioaccumulation in an organism are stable regardless of their structure and remain in the food chain without alteration. Chemosensory disruption, narcasia, cell damage etc. are some of the effects of oils on organisms.

Petrochemicals released from two-stroke engines float on the surface layer and settle within the estuarine and shallow ecosystems of bays, lakes, rivers, and oceans, where marine life is youngest and most vulnerable. These areas are the base of the food chain, inhabited by fish eggs, larvae, algae, crab, lobster, shrimp, and zoo-plankton. The gills, through which the fish breathe, get coated with oil and grease. The fish shows a tendency to migrate en masse to areas of lake where the film is thin or absent. If the situation goes unchecked, fish and other aquatic organisms will perish. The oil spread as film over the water in Akkulam- Veli Lake system inhabits free exchange of oxygen from atmosphere and light penetration resulting in impairment of primary production (Nair et al. 1998).

1.6.5 Retting of coconut husks

Retting of coconut husk has transformed the highly productive estuarine environment in to virtual cess-pools of foul smelling sulfide rich stagnant waters. A study conducted by Central Inland Fisheries Research Centre (ICAR), Alappuzha in 10 'hot spots' of the wet land ecosystems viz. Neeleswaram, Valapattanam, Mahe, Ponnani, Chettuva, Kodungallur, Kayamkulam, Ashtamudi, Anchuthengu and Kadinamkulam, has revealed that Coconut husk retting is converting the wetland ecosystem into a peculiar and complex eco-system of micro aerobic and anaerobic properties. Kadeeja et al. (2004) indicated acidic nature of water and significant deterioration of transparency, dissolved oxygen, plankton and benthos population in retting zones. All the retting zones are characterized by very high concentrations of dissolved hydrogen sulfide of the order of 10 to 41 mg/l compared to 1 to 4 mg/l in the non-retting zones. The large scale reclamation of the wetlands due to dumping of husk, coir pith and related materials has resulted in horizontal and vertical shrinkage of the water bodies.

It has been estimated that in Kuttanad, about 157 million coconut husks are subjected to retting annually covering an area of 242 ha. The consequent anoxic conditions, excess hydrogen sulfide and increased turbidity drastically reduces the primary productivity of the lake leading considerable decline in fishery resource. Likewise, large quantities of organic substances like pectin, petosan, fat and tannin are liberated into the water by the activity of bacteria and fungi. Retting activity has also led to acidic pH conditions coupled with high carbon dioxide values leading to drastic reduction in the incidence and abundance of Plankton, benthic fauna. The retting yards also act as breeding grounds for mosquitoes.

1.7 Vembanad Wetland System

The Vembanad wetland system is a complex aquatic system of coastal backwaters, lagoons, marshes, mangroves and reclaimed lands with an intricate network of natural and man made channels and its associated drainage basins are situated in the humid tropical region on the south west of the Indian peninsula (Figure 1.2). The total area of the wetland system is 2195 km^2. It is believed to have been formed by an upheaval of the shoreline subsequent to the advance and recession of the coastal waters in the past. This system includes the Vembanad backwaters and the lower reaches of the five rivers draining in to it. The five rivers which drain in to the Vembanad Lake are Muvattupuzha, Meenachil, Manimala, Pamba and Achenkoil. All these rivers originate from the Western Ghats, flow westwards through the wetland system and join the Lakshadweep / Arabian Sea. The wetland is typically divided into two distinct segments, the freshwater dominant southern zone and the salt-water dominant northern zone. The estuarine zone and organically rich sedimentary substratum of the inshore region makes it a highly preferred and desirable habitat for shrimps breeding. Vembanad is renowned for its live clam resources and sub-fossil deposits. Vembanad Wetland has been designated as a Ramsar Site in November 2002.

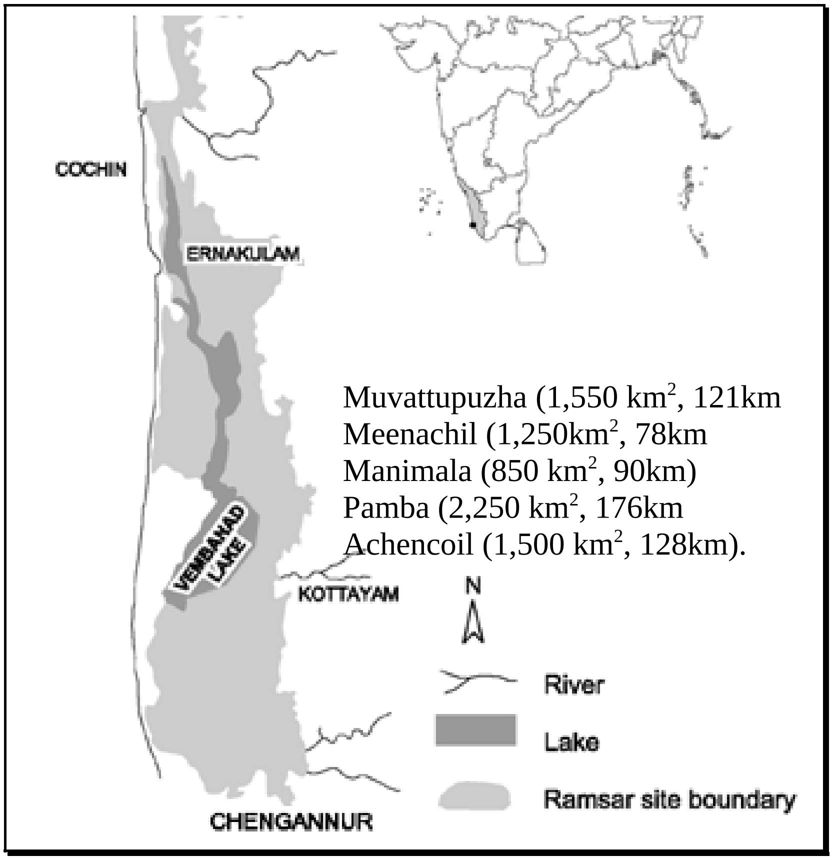


Figure 1.2 Vembanad wetland system and associated drainage basins

The wetlands are important from the point of view of their flora and fauna as well as their water quality. Seasonal rainfall followed by excessive flooding leaves extensive portions of these wetlands inundated for certain periods of the year. When the floodwaters recede gradually, nutrient-rich alluvial soils are deposited, rendering them highly fertile agricultural land.

Nowadays the wetland is facing so many threats like, land reclamation for agriculture and plantations, pollution due to industrial effluents, agrochemicals, sewage, over-exploitation of lime shell, reclamation and bunding activity in the river mouth which affects the natural facility for breeding and migration of species etc. The environmental problems faced by the lake are due to industrial effluents, municipal solid wastes and sewages, fertilizers and pesticides, oil spillage, retting of coconut husks, eutrophication, aquatic weeds etc.

Because of the valuable roles played by the Vembanad wetland system and the major threats faced by the wetland, a study has been conducted to understand the status of the wetland in terms of water quality and sediment characteristics. It was also aimed to understand the variation of isotopic composition of precipitation, lake water and groundwater. The sedimentation rate and the possible source of sulfate to the lake were investigated. The significance of the present study and the main objectives are discussed in the next section.

1.8. Scope and Objectives

The goal of the present study is to understand how anthropogenic activities affected the environmental conditions of the Vembanad wetland system. The main objectives of the study include:

1) To assess the water quality status of Vembanad wetland system spatially and temporarily.
2) To study the sediment quality of the wetland
3) To determine the pollution level of the selected aquatic macrophytes in the wetland
4) To assess the groundwater quality of the wetland system
5) To study the stable isotope characteristics of water samples
6) To determine the sedimentation rate of the system using ^{137}Cs

2.0 Literature review

2.1 Studies on Indian wetlands

According to study conducted by Chopra (1985), more than 50,000 small and large lakes in India were polluted to the extend that, it is being considered as dead. The degradation of water quality is a direct consequence of pollution making them unfit for drinking, fishing, bathing or any other recreational activities. Unaware of the ecological consequences, the wetland system have been subjected to uninterrupted reclamation for the past 150 years, for various purposes such as, agriculture, aquaculture, harbor development, urbanization and industrialization. As a result, the system is being destroyed at an alarming rate of one percent per year (Gopal et al. 1993).

Factors that cause wetland deterioration like vegetational changes, deterioration of water quality, siltation, cattle grazing and poaching were recorded in India by Vijayan (1986), Anjaneyulu et al. (1990) and Trisal (1993). Status of wetlands in India was assessed by Anon (1990). A number of studies on various physico-chemical and biological aspects of wetlands were done in India. Important contributions were made by Huthinson (1937), George (1964), Khan and Siddiqui (1982), Kulshreshtha and Gopal (1982), Seshavatharam and Chandramohan (1982), Adoni and Saini (1984), Vyas et al. (1990), Khatri (1984) and Ramalinkam and Jayaraman (1985). Mohanty and Bhunya (1990) studied various physico-chemical properties in relation to faunistic composition of Ansupa lake, Orissa. A brief description of fishes and macro and micro invertebrates were also included in their study. Studies on one of the biggest wetland in the northern region of India, the Harike wetland and its management were carried out by Singh (1990).

Various physico-chemical features of Kawar Lake, a natural wetland of Bihar have been discussed in detail by Ahmad and Singh (1990). Other important contributions include those by Sheshavatharam (1990), in Kolleru lake, Andra Pradesh and Sheshavatharam et al. (1990) in lake Kodakaria, near Visakapatnam.

Physico-chemical properties of water in Keolandeo National Park were studied in detail by Ali and Vijayan (1986), Mittal et al. (1990) and Vijayan (1991). Akram (1992) studied the physico-chemical environment of Wular lake Kashmir. Abbasi (1997) conducted studies on the ecology of wetlands of India.

In a recent attempt at prioritization of wetlands for conservation, Samant (1999) noted that as many as 700 potential wetlands do not have any data to prioritize. Many of these wetlands are threatened

2.2 Status of wetlands of Kerala

The state of Kerala has a total of 217 wetland units, of which 157 units are greater than 0.6 km2 and has a total area of about 1279 km2 (Anon 1990). The wetland of Kerala, especially along the coastal stretch are also polluted to the extend that their fishery and recreational values are fast declining. The major interventions include fishing, over harvesting, subsistence activities, effluents from industries, solid waste and effluents from human habitation, coconut husk retting, stagnation, intensive shrimp farming, lime shell mining, wetland reclamation, construction of roads, railways, weirs, embankments, shrimp farms, mangrove cleaning, alteration of shoreline environment etc. (Nalini et al. 2000).

Details of wetlands of Kerala have been provided by Nayar and Nayar (1997). Various threats faced by wetlands of Kerala and its impact and the need for their conservation was studied by Nair et al. (1998). Geochemical classifications of wetlands in Kerala were also given by IRRI (1985).

The wetlands of Kerala are subjected to severe quality degradation (Ouseph 2003&2006, Nair and Unni 1993, Nair 1994, Remadevi and Abdul Aziz 1995, Anil Kumar and Abdul Aziz 1995, Sreejith 1996, Vasu et al. 1998, Harilala et al. 2000, Gopalan 2002, Ouseph and Pillai 2004, Krishnakumar et al. 2005, Mahesh and Omana 2006, Sabitha and Nagaraj 2007).

The indiscriminate exploitation of wetlands beyond its supportive capacity, and input of residues exceeding its assimilative capacity, pollutes the wetland system of Kerala, the magnitude of which is very alarming. This if continued will cause harm to living resources, hazards to human health, hindrance to aquatic activities, impairment of water quality and reduction of amenities and finally ecological imbalance leading to catastrophic effects (Ajaykumar Varma et al. 2007).

The feverish tempo of wetland reclamation for urban construction and undesirable agricultural practices, construction of levees and dykes for hydrologic manipulation, discharge of industrial effluents, dumping of municipal wastes in the absence of reuse, recycling and disposal facilities, drainage of fertilizer-pesticide residues, over exploitation of resources and domain utilization for mining, construction tourism, coconut husk retting and such other activities are contributing to the loss and degradation of wetlands of Kerala (Nair and Varma 2002). These are in addition to the natural causes such as erosion, storm surge, siltation, drought, eutrophication and biotic interferences.

2.2.1 Environmental Problems Faced by Wetlands of Kerala

2.2.1.1 Industrial effluents

Industrial effluents discharged into the water bodies is a major threat to the wetlands of Kerala. It is a general practice to establish industries on the banks of streams, rivers and backwaters, mainly to avail the ease of discharge of effluents. It is estimated that industrial effluents of the order of 6.5Mm3 are discharged into the water bodies of Kerala (Anon 2003). The Eloor-Edayar region of the Kochi estuary provides a typical example of wetland pollution due to industrial discharge. Edayar region is identified as one of the toxic hotspots in the world by Green Peace, an international NGO campaigning against environmental destruction (Nair et al. 2001). The heavy metal pollution has a long-term impact which is evident from Beypore estuary where considerable amounts of mercury was found retained in the sediments even after the stoppage of industrial effluent discharge (Nair 1994).

2.2.1.2 Municipal effluents

Another important cause for wetland pollution in Kerala is the threat due to untreated municipal sewages and solid wastes. Most of the cities, towns and other urban centers are on the banks of water bodies. None of the urban centers in Kerala has a sewage system, except Thiruvananthapuram with a partial coverage. Kochi city generates about 3 Mm3 per day of waste water that enters the lake directly, through major canals and the pollution load of Kochi Corporation is estimated to be around 200 tones/day of BOD (Nair and Unni 1993). Similarly, the coliform counts observed in river Pumba, near Sabarimala were of the order of 240 to 46,000 MPN/100ml. The domestic sewage containing oxygen demanding wastes, infectious agents, organic chemicals and inorganic minerals, often affect the water quality of wetland system. It is reported that about 1,700 tones of wastes in the urban and about 6000 tones o f wastes in the rural areas are left to decay in the drains and on the road sides. It is also indicated that around 80% of the municipal solid waste contain organic matter and appreciable concentration of heavy metals (Anon 2003, Padmalal et al. 2002). The high nutrient content associated with sewage and solid wastes is attributing as one of the main causative factor for the high rate of eutrophication in the wetlands of Kerala. The domestic sewage, which contains oxygen demanding waste infecting waste, infectious agents, biotic organic chemicals and inorganic minerals affect the water quality of wetland system.

2.2.1.3 Fertilizers and Pesticide residues

The residues of chemical fertilizers and pesticides, ultimately reached to the water bodies is another problem in the wetlands of Kerala. The intensive agricultural practices have resulted in the input of large quantities of agrochemicals and pesticides in the state. In the water bodies of Kerala especially in the Vembanad Lake pesticide pollution is acute (Nair and Unni 1993). The analysis of water and sediment samples collected from the creek and adjacent wetlands near Udyogamandal Institute estate indicated high organic contaminants and heavy metals (Labunska et al. 1999). The study indicated that the sediments from the creek near Hindustan Insecticides Limited (HIL) containing more than 100 organic compounds

.2.2.1.4 Tourism

Tourism in Kerala have a direct and greater impact on wetland pollution. Water pollution in wetlands of Kerala is mounting as the number of houseboats and fishing boats increases. The pollution problems created by houseboats are numerous. Houseboats often release sewage and kitchen wastes to the lake. As a result the presence of total coliform, fecal coliform and E coli was very high in the lake waters (Harikumar et al. 2007). The organic pollution is also found to be high in many locations of Ashtamudi lake due to fisheries and direct input of sewage (Nair et al. 2001, Remadevi and Abdul Aziz 1995). Oil and fuel from two stroke engines is being released through motorized boating activity. Numerous oil tankers and fishery vessels playing through the waters are also major source of pollution. The oil spread as film over the water in Akkulam-Veli Lake system inhabits free exchange of oxygen from atmosphere and light penetration resulting in impairment of primary production (Nair et al. 1998). The bacterial contamination of Sasthamkotta Lake, one of the Ramsar site in Kerala is severe and shows high threat in monsoon season (Girijakumari and Abraham 2007).

2.2.1.5 Coconut husk retting

Retting of coconut husk in the backwaters of Kerala has transformed the highly productive estuarine environment into virtual cess-pools of foul smelling sulfide rich stagnant waters, is another pollution problem faced by the wetlands (Bijoy Nandan 2003). The retting of coconut husks results in production of hydrogen sulfide and release of organic substances such as pectin, petosan, fat and tannin by the biological degradation of algae and fungi. Retting of coconut husk, in the wetland ecosystem on the west coast of India, has lead to the creation of stressed ecosystems with aerobic/anoxic trends along the 590 km coastal belt of the state, tremendously affecting the eco-biological stability of these productive systems. The physico-chemical studies of the estuaries revealed that retting has been identified as a source of estuarine pollution (Sarthre Alex et al. 2002, Nandan and Abdul Aziz 1996)

It is revealed that retting activity has lead to acidic pH conditions with anoxia resulting in the production of high amounts of sulfide and an array of organic compounds like pectin, polyphenols, tannin and others, coupled with carbon dioxide values leading to a drastic reduction in the incidence and abundance of plankton, benthic fauna and the fishery resources. An outstanding observation was that the primary productivity of the retting zones totally collapsed. A study conducted by Central Indian Fisheries Research Centre (ICAR) in 10 hot spots of the wetland ecosystems viz Neeleswaram, Valapattanam, Mahe, Ponnani, Chettuva, Kodungallur, Kayamkulam, Ashtamudi, Anchuthengu and Kadinamkulam, has revealed the retting is converting the wetland ecosystem into a peculiar and complex ecosystem of micro aerobic and anaerobic properties. Kadeeja Beevi et al. (2004) indicated acidic nature of water and significant deterioration of transparency, dissolved oxygen, plankton and benthos population in retting zones.

The hydro-chemical studies have been carried out in wetlands like Vembanad, Kattampally, Ashtamudi, Akkulam Veli, Vellayini, Sasthamkotta, Chelur and Pookot (Harilal et al. 2000, Ouseph and Pillai 2004, Vasu et al. 1998, Remadevi and Abdul Aziz 1995, Nair et al. 1998, Krishnakumar 2005, Sreejith 1996). The geochemical studies of surface sediments of different wetlands like Vembanad, Kattampally, Akkulam Veli, Vellayini, Sasthamkotta, Chelur were also carried out (Vasu et al. 1998, Nair et al. 1998, Krishnakumar et al. 2005, Sreejith 1996). High degree of organic carbon was reported in most of the wetlands.

2.3 Vembanad wetland system

The Vembanad wetland system is a complex aquatic system of coastal backwaters, lagoons, marshes, mangroves and reclaimed lands with an intricate network of natural and manmade channels and associated basins. Of late the wetland is facing serious ecological problems due natural and man made activities. The main problems faced by the wetland include troubles due to man-made interventions such as barrages and bunds, land reclamation, pollution due to industrial, agricultural and domestic effluents, organic pollution due to coir retting, tourism activities, lime shell mining, and over exploitation of natural resources (Harikumar et al. 2007).

2.3.1 Problems Faced by Vembanad Wetland System

2.3.1.1 Wetland reclamation

The case study of Vembanad wetland may serve to illustrate the reclamation tendencies of wetlands in Kerala. Shrinkage of Vembanad wetland to 37% of its original area due to land reclamation has been the most important environmental consequence of human intervention in this water body (James 1996, Narayana and Priju 2006). Within the wetland system, the earliest human intervention was in the form of dredging for a major natural harbor at Kochi and subsequent reclamation for locating the port facilities. In Cochin harbor effects of dredging was pronounced in bottom waters leading to the ecological imbalance of benthic micro flora due to natural habitat loss (Rasheed et al. 1995&2000). The Thanneermukkom bund has been relatively successful in keeping the water in Kuttanad free from salinity. Several drawbacks have been noticed, the major ones: reduction in the upstream migration of marine fish and prawns and increase in weed growth in the upstream. The construction of Thanneermukkom bund and Thottappally spillway to prevent saltwater penetration into the paddy fields during pre-monsoon has lead to serious ecological problems by interrupting the natural ebb and flow of tides (Menon et al. 2000). The structure has severely restricted the natural flushing of pollutants. Another major intervention is the deforestation especially the mangroves (James 1998).

2.3.1.2 Industrial effluents

The Vembanad wetland system is a receptacle of a large variety of industrial effluents especially from Cochin industrial belt. A number of industries situated on the banks of rivers and backwaters in Kochi empty their effluents in to the wetland system. About sixteen major industries such as oil refineries, fertilizer plants and chemical industries discharges nearly 260 million m3 day-1 of wastes into backwaters (Anon 1990, Balachandran et al. 2003). These effluents contain a large number of toxic ingredients such as acids, alkali, heavy metals, suspended solids and a number of other chemicals, which have immediate and long-term effects on the organisms. The input of acids and alkalis lead to drastic imbalances in the ionic status of water upsetting the living environment of organisms. The suspended solids cause turbidity maxima leading to productivity impairment (Muraleedharan et al. 2002). The Cochin estuarine system receives effluents containing a large dose of heavy metals.

2.3.1.3 Domestic sewage

A major source of pollution in Vembanad wetland is the domestic sewage generated in the urban areas and tourism locations of Alappuzha, Kochi, Vaikom, Cherthala, Chenganssery, Kottayam, Kumarakom etc. and the operation of house boats in large numbers. The water quality deterioration due to sewage contamination in Vembanad Lake in the vicinity of Kumarakom tourist village was studied by Suchindan et al. (1999). He observed very high BOD and coliform contamination in the pre-monsoon season. The potential pathogenic hazards of organic pollution in Cochin estuary was studied by Sarthre et al. (2000). The increasing loads of sewage and industrial waste have created conditions that are extremely destructive to the flora and fauna. It is seen that the oxygen content is always low at the bottom which is attributed to oxygen consumption during decomposition of organic matter in deeper strata of water body (Sankaranarayanan et al. 1969). The higher COD values observed are due to domestic sewage and the waste discharged into the wetland (Saraladevi et al. 1979).

2.3.1.4 Fertilizers and Pesticide residues

Residue of chemical fertilizers and pesticides are causing greater problems to Vembanad Lake (Nair and Unni 1993). The studies by Rajiv Gandhi Centre for Biotechnology (Roy and Mathew 2000) confirmed serious deterioration of the ecosystem of Kuttanad, the rice bowl of Kerala as there were high concentration of heavy metals and organo-chlorine pesticides residues in water and sediment. The annual usage of pesticides/fungicides/weedicides in Kuttanad is reported to be 117 tones during Virippu season and 368 tones during the Mundakan and Puncha season (Nair and Unni 1993). Seasonal and temporal variation of cyclodiene pesticides in the sediments of Kuttanad backwaters was estimated by Babu et al. (2008). Annual fertilizer consumption in Kuttanad is 8409 tones of nitrogen, 5044 tones of potassium. Pesticides/fungicides/ weedicides are applied to the tune of about 500 tones/year (James 1998).

2.3.1.5 Coconut husk retting

It is reported that the retting and coir processing yards with in the proximity of the lake around Kuttanad, Alappuzha, Chittur and Vaduthala has converted the once productive lake in to non-productive anoxic areas. The retting yards also act as breeding grounds for mosquitoes. It has been estimated that in Kuttanad, about 157 million coconut husks are subjected to retting annually covering an area of 242 ha. The consequent anoxic condition, excess H_2S and increased turbidity drastically reduce the primary productivity of the lake leading to considerable decline in fishery resource (Muraleedharan et al. 2002). Fish kills have been recorded from several retting zones in the wetlands of the state resulting from extensive depletion of dissolved oxygen and associated deleterious changes occurring in the wetlands (Bijoy Nandan 2003).

2.3.1.6 Hydrochemistry

Heavy load of organic materials released into the backwaters is responsible for the decrease of dissolved oxygen in the backwaters, especially during periods when river runoff is minimal (Babu et al. 2006). The marginal variation observed in the concentration of phosphorous and iron between surface and bottom waters as well as between southern and northern sector is presumably due to the near freshwater (monsoon) character of the overlying waters (Padmalal and Seralathan 1991). The geochemical characteristics of Kuttanad water and sediment were studied by Mathew et al. (2001). They found that acidic nature of the sediment and accumulation of the toxic salts made this area less fertile for rice. Variation of DO content of coastal waters along the southwest coast of India in space and time has been extensively studied (Narayanapillai 1993). The BOD is also increased gradually with commencement of pre-monsoon and shows a decreasing trend with onset of monsoon period. The dissolved oxygen concentration in Cochin backwaters was found to remain under saturated during monsoon period. This may be due to the utilization of oxygen for the decomposition of dead planktonic organisms brought down by flood tide or silt loaded fresh water (Shyanamma and Balakrishnan, 1973). The higher COD values observed are probably due to domestic sewage and waste discharged into the harbor area (Saraladevi et al. 1979). Chemical oceanographic studies of the estuary were also carried by Balachandran, (2001).

2.3.1.7 Tidal study

Stratification and salinity distribution in relation to tides and freshwater discharge have been studied by Joseph and Kurup (1990). Hydrological conditions of Cochin backwaters are greatly influenced by sea water intrusion and influx of river water as shown by the distribution of salinity and temperature (Lakshmanan et al. 1982). The change in salinity has been found to have a profound effect on the sequence of fluctuation in the abundance and ecological succession of the fauna and flora in the estuary (Madhupratap et al. 1977). Distribution of salinity in the Cochin estuary shows marked seasonal variation. A distinct stratified layer is observed near Cochin bar mouth during monsoon and pre-monsoon and the estuary is well mixed throughout, whereas the post-monsoon is a transition period (Anirudhan and Nambeesan 1990). Hydrographic characteristics and tidal prism at the Cochin bar mouth was studied by Ramaraju et al. (1979). The overall change in salinity at the harbor region is in the range of 34.31ppt in April, to 1.11ppt in July. The change in salinity has been found to have a profound effect on the sequences of fluctuation in the abundance and ecological succession of the fauna and flora in the estuary (Madhupratap et al. 1977).

2.3.1.8 Nutrients

Distribution and variability of nutrients in Cochin backwaters have been extensively studied by Lakshmanan et al. (1987). Bindu and Harikumar (2007) studied the eutrophication of Vembanad Lake using a dynamic model. The eutrophication of the system is mainly determined to be phosphorous limited. Speciation of phosphorous in marine sediment of Cochin estuary revealed that aluminum bound phosphorous was maximum compared to iron, calcium and organic bound phosphorous. Phosphate fractions varied with locations and exhibited seasonal fluctuations (Ashraf et al. 2006). The organic phosphate polls play a crucial role, wherein it acts as an inducer in the triggering mechanism of aquatic life in coastal zone (Balchand and Nair 1994). Other studies in relation to phosphorous fractionation include Nair et al. (1993), Nair and Balchand (1993), Balchand and Nair (1994). In the Cochin back waters the nutrient distribution is largely dependent upon two main components, the marine influence and freshwater discharge (Shankaranarayanan and Quasim 1969). It is estimated that the backwater is receiving $42.4\text{x}10^{3}$ mol/d of inorganic PO_4 and $37.6\text{x}10^{3}$/d of organic nitrogen through Periyar. The export to coastal waters is only $28.2\text{x}10^{3}$mol/d inorganic PO_4 and $24\text{x}10^{3}$mol/d of inorganic NO_3. Thus estuary seems to act as a sink for nutrients. Associated with the diminishing of flushing rate, a nutrient build up is taking place for the backwater system. (Balachandran et al. 2003).

2.3.1.9 Heavy metals in water

Concentration of dissolved and particulate trace metals (Ni, Pb, Zn, Mn) and their partitioning behavior between the dissolved and particulate phases in Vembanad lake was studied by Unnikrishnan and Nair (2004). They found that lack of proper flushing of backwaters, which receive large amount of trace metals through the application of pesticides and agro-chemicals, due to the presence of salinity barrier has significantly affected the water quality of southern half. Other studies on the trace metal distribution of the water column include those of Babukutty (1991), Babukutty and Chacko (1995), Ouseph (1995), Ouseph (1987), Nair et al. (1991), Shibu (1992), Luther et al. (1986), Nair et al. (1990), Shibu et al. (1990), Senthilnathan and Balasubramanian (1997).

2.3.1.10 Geochemical studies of sediment

Geochemical studies of sediment with respect to organic carbon were done by Geetha et al. (2008). The results indicate that the main source of sediment organic carbon is plant remains. C/N ratio showed decrease towards the depth. Significant variations due to seasonal changes were observed (Lizen and Chandramohanakumar 2003). Textural characteristics of the sediment were also done by Nair et al. (1993). Surficial sediments indicated variation in texture resulting from detritus settlement influenced by mixing conditions in the estuary. Textural and geochemical studies in the southern half of Vembanad Lake were also carried out by Harikumar et al. (2007). Other geochemical studies include those of Nath et al. (2000) with regard of weathering and sedimentary process on the elemental ratios in Vembanad Lake. The coastal landforms of this region consist of Quaternary sediments, overlying a precambrian terrain consisting of granulites, gneisses and greenstones (Veerayya and Murthy 1974, Narayana and priju 1999).

Sediment distribution, grain size and suspended sediment characteristics of Cochin estuary have been reported by many scientists (Sundaresan 1990, Ajith 1996), but scanty reports by Sundaresan (1991) are available on sediment transport and related sedimentation process in this estuary. The sedimentation rate of the Cochin estuary was carried out by Rasheed and Balchand (2008) in an experiments using sediment trap. The surface sediments of the Vembanad Lake are mostly a mixture of clay, silt and sand. The northern part of the lake is covered with clay sand and silty sand, the central part with clay sand and sandy silt, and the southern part is covered with silty sand and clay silt (Veerayya and Murty 1974, Narayana and Priju 1999). Presence of desiccated clays beneath the peat deposits suggests arid climate prior to the humid climate during 40,000 yrs BP (Narayana et al. 2002).

2.3.1.11 Sediment organic carbon

A comparative evaluation of the organic carbon content of the Cochin harbor area indicated substantial increase during the last two decades (Seralathan et al. 1993). The anoxic conditions prevail in the Vembanad estuary for most part of the year (Padmalal and Seralathan 1991), favors the preservation of sediment organic carbon. Seasonal variation in the organic carbon with lower values post-monsoon was attributed to the constant tidal flushing, while higher values reflected seclusion of organic residues in sediment layers (Sunilkumar 1996). Variation of organic carbon due to sediment texture showed higher values in highly grained sediments (Bijoy Nandan and Abdul Aziz 1996). Tidal activity and sediment has a good role in the preservation and retention of organic matter (Rini Sebastian and Jacob Chacko 2006). The strong correlation of sediment iron and phosphorous with organic carbon suggests that the major source of these elements in the lake system is from the organic decay (Padmalal and Serelathan 1991). It has been shown that organic carbon in sediments is higher during monsoon due to contribution from land runoff (Remani et al. 1980). While organic associations for most of the metals with seasons are preferential, absence of any correlation for Zn and Mn with organic carbon and clay on all occasion is striking (Balachandran et al. 2003). The potential value of Allochthonous organic matter, accumulated in the estuary as a result of microbial decomposition of Salvenia has been pointed out.

2.3.1.12 Heavy metals in sediments

Priju and Narayan (2007) studied the variation of some trace elements in the core sediments in the estuarine region of the wetland and showed enrichment in the recent past. The concentrations of different metals in estuary are documented (Ouseph 1986,1987&1989). Studies on trace element distribution patterns in the sediments of Vembanad lagoon are a few (Moorthy and Veerayya 1981, Borakkar et al. 1984, Paul and Pillai 1986, Nair et al. 1990&1991, Padmalal et al. 1997, Manjunath et al. 1998, Nath et al. 2000, Nair and Balchand 1993). A seasonal analysis of particulate trace metals, viz.

iron, manganese, zinc, copper, cobalt and nickel in Cochin backwaters are being presented. The special trend for cobalt, iron and nickel was stationary at surface where as the metals copper, zinc and manganese showed special variations (Sankaranarayanan et al. 1998).

2.3.1.13 Studies on Lime shell

The occurrence and recovery of lime shell deposits of Vembanad Lake was studied by Maya et al. (2008). The study revealed that indiscriminate mining of shells over the years has imposed serious environmental problems to the lake system. The idea of subterranean flow through lime shell beds initiating formation of mud banks may apply globally to any coastal regions hugged by wetlands and of similar geological conditions (Balachandran 2004).

2.3.1.14 Biomonitoring

Biomonitoring in terms of hyperaccumulator plants were also done by Manorama Thampatti et al. (2007). They found that plants like Hydrilla Verticillate, Eichornia Crassipes and Cyperus Pangorci were found to poses hyper accumulation capacity for iron, manganese, zinc copper and aluminum in the wetlands of Kuttanad. The threat due to aquatic weed population in Vembanad Lake is quite alarming and these may dominate in future weed flora of Kuttanad (Joy et al. 1993). The study of aquatic weed, Salvenia molesta as a bio-pollutant for aquatic ecosystem has been carried out by Sydney et al. (1975). The fauna associated with the floating weeds as well as the influence of the floating weed mat on the estuarine benthos has been studied by Gopalan and Nair (1975).

The benthic organisms such as mussels and oysters are found to have high accumulation of Zn beyond the permissible limit. High concentration of Zn, Cu, Fe etc were also observed in Crassostrea madrasesnsis from Kochi region (Sankaranarayanan et al.1978). The distribution of trace metals (Cd, Cu, Fe, Mn, Zn and Hg) in the back water oyster, Crassostrea madrasesnsis (preston) of Kochi harbour was found to exhibit seasonal variation (Nair and Nair 1986). The oyster is found to be a suitable indicator organism for metal pollution in backwaters (Rajendran and Kurian 1986). The use of detergents add chromium, cobalt etc to the wastewaters. Sewage sludge, discharged in to the waters may be a significant source of copper, zinc and lead in aquatic weeds (Harikumar and Madhavan 2003). The possible role of cumulative deposition of macrophytic biomass in bringing about a gradual alteration in the estuarine benthic communities and its significance in food chain has been discussed in detail by Gopalan and Nair (1975).

The concentration level of copper, zinc, manganese and iron have been determined in marine fishes from Cochin area, which is one of the major fishing zones along the west coast of India. The concentration of heavy metals varied from species to species. Copper, zinc, iron and manganese showed increased level in the gills and alimentary canal compared to the muscle. Difference in heavy metal concentration in various species studied is attributed to the varying feeding habits. The observed levels were below the toxic limit (Nair et al. 1997).

The major studies reported above are mostly carried out in the northern region (estuarine region) of the Vembanad wetland system and hence the present study aimed to conduct in the southern part of the wetland with respect to water, sediment and aquatic macrophytes.

2.4 Groundwater studies of India

Groundwater constitutes 0.614% of earth's fresh water resources, compared to the 0.008% in lakes and 0.005% in rivers (Mandel et al. 1981). Groundwater is the major source of drinking water in both urban and rural India. Besides, it is an important source of water for the agricultural and the industrial sector. Till recently it had been considered a dependable source of uncontaminated water.

The geological survey of India (GSI), for first time in 1969, setup a basic network of 410 hydrologic stations in different hydrological settings. The central groundwater board (CGWB) has increased the number to 3640 by 1981 and by now the number is much more. In this monitoring program water levels are monitored five times a year water qualities are monitored twice a year. Most of the state government has also set up groundwater departments and they have their own network stations.

2.4.1 Major water quality problems of India

The subsurface water quality is degraded mainly due to natural reasons along with over withdrawal of water, insanitary conditions in rural and urban areas and increased application of fertilizers and POP’s. The parameters of concern in subsurface water are higher level of Fluoride in several pockets of the country (about 200 districts are being affected); Arsenic problem in parts of West Bengal, specially in 24 paragna’s of West Bengal; Nitrate problems observed in many parts of the country especially in intensively irrigated and high productivity regions from agriculture point of view; and in urban areas due to improper and inadequate sewage collection; Salinity problems in intensive irrigated (command areas) and coastal areas of the country; Micro pollutants, especially pesticides due to their intensive applications in certain parts of the country; and Pathogenic pollution in urban areas, due to in-sanitary conditions.

2.4.1.1 Fluoride

The incidence of fluoride above permissible levels of 1.5ppm occur in 14 Indian states, namely, Andhra Pradesh, Bihar, Gujarat, Haryana, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh and West Bengal affecting a total of 69 districts, according to some estimates. Some other estimates find that 65 per cent of India’s villages are exposed to fluoride risk.

The groundwater in some districts of Andra Pradesh and Karnataka in the south and some districts in Punjab and Haryana in the north has excess quantity of fluoride acquired naturally and not through anthropogenic activity (Siddiqui 1962, Kanwar and Mehta 1968). In Rajastan more than 80% of the districts have high fluoride level in their drinking/groundwaters. (Teoltia and Teoltia 1984, Susheela 1993). The first cases of fluoride toxicosis were reported from Jaipur district (Kasliwar and Solomon 1959). A few reports on endemic flourosis have also been reported from Jhunjhunu (Thergaonkar and Bhargava 1974) and Ajmer. Purohit (1988) observed that well waters of several villages of Nagaur and Churu districts contain 60-100 ppm fluoride.

2.4.1.2 Arsenic

High levels of arsenic above the permissible levels of 50 parts per billion (ppb) are found in the alluvial plains of Ganges covering six districts of West Bengal. An alarmingly large population of India and Bangladesh, 66 million in the Gangetic belt of India 79.9 million in Bangladesh (Bose and Sharma 2002, Ahmed et al. 2004) is exposed to arsenic poisoning due to continuous usage of arsenic contaminated groundwater. Arsenic poisoning reported in West Bengal few years back caused a lot of panic (Muraleedharan 1998, Bhattacharya et al. 2002, Ahmed et al. 2004). It was also reported in 24 Paraganas (south) district close to Culcutta. The reported cause was due to two reasons, first due to dissolved chemical pesticides with arsenic salts which seeped into subsoil level and second due to over drawl of subsurface water to ensure supply to multistoried buildings those sprang up recently in south Culcutta.

2.4.1.3 Nitrate-Nitrogen

Non-point pollution caused by fertilizers and pesticides used in agriculture, often dispersed over large areas, is a great threat to groundwater systems. Intensive use of chemical fertilizers in farms and indiscriminate disposal of human and animal waste on land result in leaching of the residual nitrate causing high nitrate concentrations in groundwater. Excessive occurrence of nitrite-nitrogen in groundwater has been observed in several districts of Punjab, Madhya Pradesh, Rajastan and Tamil Nadu. In Assam and adjoining areas in north east, liquid petroleum crude often comes with water when pumped. Trivendi et al. (1988) observed greater quantities of nitrate in the well waters of Maharashtra. Excessive use nitrogenous fertilizers in agriculture have been one of the primary sources of high nitrate in groundwater. Nitrate level in groundwater for different concentration ranges in few districts of Rajastan show that 74% of groundwater samples in Barmer and 40% in Jaipur district exceeded nitrate concentration of 0.3 mg/l (Gopal et

al. 1983, Gupta 1981). Nitrate in groundwater of Delhi indicate that the shallow groundwater bearing high nitrate concentration were unfit for drinking (Central Ground Water Authority (Times of India16-11-98)).

2.4.1.4 Industrial pollutants

There are several reports of groundwater pollution due to industrial discharges. During 1977-79, CGWB analyses the groundwater in Ludhiana where electroplating and textile (cotton and wool) units are the more common types of industry. It was found that the groundwater in Ludhiana contained 1-2mg/l cyanide concentration due to the cyanide containing effluents discharged from electroplating units (Gosh 2002). Another major threat to the groundwater is the contamination by oil pollution (Aggarwal et al. 1993)

There are a number of areas in the country where serious groundwater pollution problems have been caused due to the seepage of effluents from various sources. Olaniya and Saxena (1977) reported that 25 wells around a refuse dumping site in Jaipur have been found to have high dissolved solids, chlorides, iron salts, COD and hardness. The effect was noticed up to distance of 450 meters. Siva and Ramamoorthi (1977) reported that the well waters were generally high in mineral contents and had harder water in the areas where a subsurface method of sewage disposal is practiced. The chlorides and the total dissolved solids of these wells were very high in these wells. Narayan and Madhyastha (1985) reported that water of well in Mukka village near Mangloor have become polluted as oily effluents seeped continuously from the north-eastern and south-eastern sides of the well at a distance of 10 meters dumping pits of a fish oil extracting small scale industry

Similarly, where the tanneries are concentrated in some pockets of Tamil Nadu, well water has been affected even at a distance of 1Km. Total dissolved solids up to 1200mg/l were reported. In addition cases of pollution of groundwater by fluorides from superphate fertilizer plants and chromates from metal plating industry have been reported (Gosh 2002). Contamination of subsurface waters due to percolation of sewages is also a major

concern. An analysis of India, American and English sewage indicate that Indian sewage is comparatively richer in various parameters than those of American and English.

In Rajasthan the concentration of zinc, cobalt, molybdenum, silver and strontium in the groundwater was found to be in excess of the permissible limit for drinking purpose. Khetri Copper Project was identified as the source for this pollution of groundwater. The effluent of the Hindustan Zinc Ltd, in Debari (Rajastan) was also found to be the cause for the higher concentration of zinc and lead in well water (Gosh 2002).

2.5 Groundwater quality status of Kerala

The state of Kerala has the highest density of dug wells in India. This is a reflection of the high population density and peculiar hydrological conditions of the state. In Kerala 65.5% of the urban and 44% of the rural populations are getting protected water. The rest still depend on groundwater sources for domestic purposes. Generally the groundwater problems in Kerala are due to the presence of excess salinity, iron, fluoride, hardness and coli forms. Seawater intrusion, domestic sewage, mineralogical origin, agricultural and industrial activities are the major causes (Remani and Harikumar 1998). According to the CWRDM reports the quality of the groundwater resources in Kerala can be discussed in terms of coastal, midland and highland areas.

2.5.1 Problems in the costal stretch

The water quality problems in the coastal areas are mainly due to the presence of excess chloride (CWRDM 1997). The study on the interaction of seawater with top unconfined aquifer along the Kozhikode coast revealed that there is definite relation. A study on the water quality problems related to excess fluoride in Alappuzha reported to have fluoride concentrations greater than the permissible limit in all the pumping wells of KWA (CWRDM 1997a).

2.5.2 Problems in the midlands

In the midlands of Thiruvananthapuram, Kottayam, Muvvatupuzha, Kannur and Kasargode, the water quality problems are mainly associated with pH and iron. In Palakkadu the problem is mainly due to fluoride. In Trichur problems are especially due to fluoride, chloride, and coli form bacteria (CWRDM 1997b).

2.5.3 Problems in the highlands

In the highland regions of Idukki, the bore well samples were contaminated mainly due to high concentration of iron and coli forms (Remani and Harikumar 1998).

In addition to the CWRDM reports there are many other studies on groundwater quality in different parts of Kerala. Localized problems of fluoride are reported from Alappuzha and some parts of Palakkad (Antu and Harikumar 2007). Hydrochemical studies of Muthalamad region of Palakkadu was carried out by Antu and Harikumar (2007). They reported that most of the waters are of Na-Ca-Mgf-HCO3-Cl type. By taking 3243 samples from three panchayaths of Chittur block, a mapping of fluoride contaminated area was done by Raveendran and Kadeeja Beevi (2007). The dissolution mechanism of fluoride in the groundwater of Alappuzha was carried out by Noushaja et al. (2008).

The quality of groundwater and pipe water in Fort Cochin area was studied by Shaju et al. (2007). They found that most of the physico-chemical parameters are above the limit for drinking purposes. The pollution of waters in terms of coliform bacteria is also high in these regions. Urbanization has a direct impact on the quality of groundwater. Seasonal changes in the water level and quality of subsurface waters of Neyyattinkara municipal area was carried out by Suvarna Kumari et al. (2002).

Industrial activity is one of the major causes of groundwater contamination in Kerala. Sathyanarayanan (1998) has conducted a study on the effects of industrial activity to the nearby groundwater resources of three major industrial cities namely Kochi, Kozhikkode and Kannur. Apart from the acidity, hardness, excess concentration of fluoride, chloride

and nitrate than the permissible limits, heavy metal concentrations far beyond the permissible limits were found in the water samples. In the Kochi industrial area, around 505 are found to be contaminated with heavy metals or nutrients. Effluents from different industries like textile, refinery and chemical manufacturing are polluting the groundwater. A study on the water quality of groundwater samples in Athani industrial area of Trichur was conducted by Vijayalakshmi Amma et al. (2002).

2.6 Isotope studies on precipitation

Realizing the importance of stable isotopes in hydrology, the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) established a Global Network of Isotopes in Precipitation (GNIP), in which samples are collected regularly to monitor the $\delta^{18}O$ and δD of precipitation. The data produced by this network are essential for environmental isotope hydrology. They are available on the World Wide Web at http://www.isohis.iaea.org. Over the last three decades, the data have been useful in understanding the systematics of isotope hydrology as also in tracing large-scale atmospheric vapor transport systems. Unfortunately, long-term precipitation isotope data are available only for two Indian stations, namely New Delhi (1967–2000) and Mumbai (1960–78)**.** No data on isotopes in precipitation from anywhere along the east coast of India exist (Gupta and Deshpande 2005).

2.6.1 Global precipitation

The variation of $\delta^{18}O$ and δD in global precipitation has been studied by several investigators (Dansagaard 1964, Rozanski et al. 1993). An interesting relationship between $\delta^{18}O$ and δD exists in the precipitation and based on this a Global Meteoric

Water Line (GMWL) has been constructed by Craig (1961). The dependence of the isotope variations on the local temperature (or the closely related parameter of the precipitable water content) appears as the overriding parameter (Fricke and O'Neil 1999). An extreme case of the absence of an inland effect over thousands of kilometers, in spite of strong rainfalls enroute, was reported over the Amazon (Salati et al. 1979). The

continental effect in δD is nicely shown by the iso-δD contours reported by Taylor (1972) for the United States. Siegenthaler and Oeschger (1980) calculated the deviation of δ value due to altitude and temperature effect. The variation of δ^{18}O with altitude in the mountain regions in Czechoslovakia (Dinçer et al. 1970), Nicaragua (Payne and Yurtsever 1974),

Cameroon (Fontes and Olivry 1977) and Switzerland (Siegenthaler and Oeschger 1980) has been studied. Moser and Stichler (1974) observed pseudo-altitude effect in inter-mountain valleys and on the lee side of a mountain range. Dansgaard (1964) observed a relation between the amount of precipitation and $^{18}\delta$.

The regional scale spatial and temporal variation of stable isotope composition of precipitation over Southeast Asia and the western Pacific region, with emphasis on China, has been explained in terms of meteorological and pluviometric regime of climatology and atmospheric circulation pattern (Araguas-Araguas et al. 1998). The variation of stable isotopes in monsoonal rains of Sri Lanka has been studied by Dharmasiri and Atuluwage (1992).

2.6.2 Indian precipitation

The hydrology in India is largely controlled by precipitation during the summer (SW) and winter (NE) monsoons. The SW monsoon operates during the months of June-September and NE monsoon during the months of October–January. The causal mechanism (Das 1985) for these monsoon systems is the seasonal reversal of temperature and pressure gradients and associated wind circulation following the annual northward and southward motion of the sun. These two seasonal circulation systems are part of the larger monsoon circulation of South Asia. Because of the geography of the continental drainage area, the river discharges into Arabian Sea (AS) and Bay of Bengal (BOB) differ by an order of magnitude. As a consequence, the surface waters of the BOB get more diluted by freshwater. In terms of average sea water isotopic composition, the BOB has been shown to be ~1‰ depleted in $\delta^{18}O$ with respect to the AS (Duplessy et al. 1981) due to large influx of monsoon run-off from Himalayan rivers. As a result, the BOB is

expected to have large seasonal changes in isotopic composition of its surface water, similar to large seasonal surface water salinity changes (Rao and Sivakumar 2003).

The annual hydrological cycle begins with the onset of SW monsoon over Lakshadweep, Minicoy and Kerala, which brings copious rain over the Western Ghats. Slowly, the monsoon current advances over the southern peninsular region and crosses over to the east coast (Ghosh et al. 1978). This is the AS branch of the SW monsoon. Over the BOB, the monsoon current turns anti-clockwise and re-enters India across the central and northern parts of the east coast, giving rise to the BOB branch. During winter and spring, winds originating in the east and central Asia and moving towards the southwest direction pass over the BOB before entering the southeast parts of India in the form of NE monsoon (Menon 1995). Roughly around the same period, the northern and northwestern parts of the country receive rains due to western disturbances that originate over the Mediterranean and West Asia.

By the end of the rainy season in September – early October, the inflow of water vapor from the sea surface gradually decreases and the resident moisture within the country in different components continues to redistribute through evapotranspiration to the atmosphere, soil moisture drainage to the groundwater and effluent groundwater discharge to the rivers. Finally, with the beginning of summer in March–April, the evapotranspiration of the surface water and soil moisture becomes the dominant process controlling the hydrological cycle in the country until the end of May, when the yearly cycle begins afresh.

The synoptic hydrology of India, based on the regional maps of amount-weighted monthly distribution of $\delta^{18}O$ and *d*-excess of precipitation, for different seasons over the Indian subcontinent, has been described by Gupta and Deshpande (2003). The differing seasonal distributions of isotopes at Mumbai (Bombay) and New Delhi representing two different regions of the Indian monsoon have been explained by differing mechanism of precipitation and moisture source regions by Bhattacharya et al. (2003). Data et al. (1991) explained the seasonal difference in the isotopic composition of rain water at New Delhi,

which was contributed by evaporation from falling rain drops. Other than New Delhi and Mumbai, precipitation isotope data of shorter length (1-5 years) are available from Kozhikode, Allahabad, Shillong, Hyderbad and a few closely spaced stations in Lower Maner Basin.

2.7 Surface water isotopic studies

The isotopic characteristics of the surface water systems have great importance in hydrological studies (Jong-Sik Ryu et al. 2007). There are few surface-water isotopic measurements in the subcontinent to establish the identity and origin of stream-water in any given part of the year to different parts of the catchments. Available data do indicate that during non-monsoon months most streams derive their base flow from local effluent groundwater discharge, which also indicates signatures of evaporative enrichment in isotopes (Dalai et al. 2002). Additionally, the following observations have also been made.

Data on isotopic composition of the headwaters of the Indus and its tributaries, surface ice in glaciers, saline and freshwater lakes and thermal springs in Himalayan and Kashmir region showed (Pande et al. 2000) high *d*-excess that could be due to precipitation from western disturbances with unique signature of vapor source in the Mediterranean Sea (Raina 1997). All along the path of the western disturbance (Iran, Afghanistan, Pakistan and Kashmir) the precipitation is characterized by high *d*-excess. In this region the ‘altitude effect’ decreases with elevation.

In another study of the Ganges river system, high-altitude tributaries showed $\delta^{18}O$–δD relationship close to GMWL, but streams from the lowland region showed a significant evaporation effect (Ramesh and Sarin 1992).

Seasonal variations in isotopic composition of the Yamuna and its tributaries were explained in terms of amount effect with most depleted values during the monsoon period and from high altitude samples (Dalai et al. 2002). The observed high *d*-excess during

October was ascribed to the inherent signature of a source with a significant component of high *d*-excess vapor, possibly western disturbances.

Temporal variations in isotopic composition of Nainital Lake have been used to estimate subsurface components of the water balance to the lake (Nachiappan et al. 2002), and the dynamics of the lake in terms of seasonal process (Gupta and Deshpande 2004).The variation of δ along the estuaries was also done by different isotope hydrologists. In both Krishna and Godavari estuaries, δD was shown to behave conservatively during mixing between sea water and stream water (Sarin et al. 1985).

2.8 Groundwater isotopic studies

Understanding the effect of evaporation on stable isotopes is an important factor in discussing the relationship between precipitation and groundwater (Boronina et al. 2005, Maki Tsujimura et al. 2007). Compilation of published isotopic data on groundwater samples from across India analyzed over the last three decades is given in a downloadable tabular form at (URL:http://www.prl.res.in/%Ewebprl/web/announce/ind-gw.pdf). Several groundwater measurements for which geographic coordinates could not be ascertained are not included in the table. Observations from those few locations, where multiple measurements are available, suggest that temporal variation are likely to be <1‰ in $\delta^{18}O$ of groundwater's that may not be near (<1Km) a large surface water bodies and/ or not located in areas with thin soil cover or do not have secondary porosity.

A large number of groundwater samples have been analyzed in the country principally by the four active groups, viz. PRL, BARC, NGRI and NRL. These studies, spread almost over a quarter century, indicate the following: Repeat measurements of isotopic composition of groundwater samples (Datta et al. 1996a & 1996b) do not show significant temporal variation in several parts of the country, indicating mixing of soil water of several years before groundwater recharge. However, regions with secondary porosity and/or otherwise fast recharge, particularly during storm events (Shivanna et al. 2004) have shown significant temporal variations in groundwater.

Groundwater's show a significant evaporation-related modification of isotopic signals of precipitation in large parts of the country, particularly in the western and central parts comprising Rajasthan, Gujarat, Haryana, Madhya Pradesh; on the eastern side of the Western Ghats in Maharashtra, Karnataka, parts of Andhra Pradesh and Orissa. In Lower Maner Basin of Andhra Pradesh, the extent of enrichment was found to vary with recharge characteristics of various soils and rock types in the basin.

In these regions, the groundwaters are enriched with respect to the precipitation in $\delta^{18}O$ and show (Dalai et al. 2002, Datta 1999, Krishnamurthy and Bhattacharya 1991) lower values of *d*-excess. This indicates that there is little to significant kinetic evaporation of the precipitated water before groundwater recharge. In a study of groundwater in Pushkar valley a decrease in $\delta^{18}O$ with depth of water table was observed (Datta et al. 1994), which may be due to stratification of groundwater with shallower zones being recharged from relatively modern rainfall.

Several other cases, particularly from Rajasthan and Gujarat in India, and in Bangladesh have indicated that older groundwater's have lower $\delta^{18}O$, suggesting a somewhat different past climatic regime with less aridity and/or increased precipitation (Aggarwal et al. 2000, Nair et al. 1997)

Using the groundwater $\delta^{18}O$ values from the Kolkata–Delhi segment and departure from the expected continental gradient due to rainout (Gupta et al. 2004), it was estimated that atmospheric return back of precipitation by transpiration was as high as ~40%.

In southern India with dual monsoon influence, groundwaters from the regions dominated by NE monsoon showed distinctly depleted stable isotopic compositions compared to those dominated by the SW monsoon. The $\delta^{18}O$–δD regression line slope of ~6 in the east coast region was lower than that expected for local precipitation, suggesting secondary evaporation (Deshpande et al. 2003).

The large difference in $\delta^{18}O$ values in groundwater samples from the west and east coast samples confirms the inferred $\delta^{18}O$ difference in precipitation along the two coasts during principal rainy seasons (Deshpande et al. 2003). It may be recalled that there are no direct precipitation isotope data from any station along the east coast of India and the isotopic signatures of precipitation on this coast have been interpreted from neighboring stations of Hyderabad and Shillong in India and few stations in Sri Lanka, Myanmar and Thailand with data only of few years.

Deshpande et al. (2003) was undertaken oxygen and hydrogen isotopic investigation of groundwater and river water samples from the southern Indian peninsula to characterize the isotopic nature of the near surface water sources. The $\delta^{18}O$ characteristics of the groundwater samples from continental areas of central Asia and oceanic areas of the Bay of Bengal were investigated by Deshpande et al. (2003). Gupta and Deshpande (2005) have done a compilation of studies using tritium tagging of soil moisture for estimating fractional groundwater recharge in the country and found that the highest fractional recharge of groundwater occurs in the region of Eastern Plateau, the Ganga Plains, North and South Central Highlands and Western Plains. There have also been two important studies from India (Gupta et al. 2004) employing radiocarbon dating of groundwater and found that the recharge to the aquifers have occurred at the time around the last glacial maxima about 20 thousand years ago from the present day of recharge.

It is thus seen that with the available isotope data on groundwater, isotopic modifications due to evaporation during rainfall and subsequent percolation through soil zone can also be understood, which may in turn, be useful to correlate the isotopic character of various components of the hydrological cycle. However, to make quantitative estimates, a much larger databank of isotopes in both precipitation and groundwater is required (Gupta and Deshpande 2005).

2.9 Surface water subsurface water interconnection

The most effective in quantifying mixing between groundwater and surface water is $\delta^{18}O$ and δD (Katz et al. 1997). Understanding the effect of evaporation on stable isotopes is an important factor in discussing the relationship between precipitation and groundwater (Boronina et al. 2005, Maki Tsujimura et al. 2007). Repeat measurements of isotopic composition of groundwater samples (Datta et al. 1996a & 1996b) do not show significant temporal variation in several parts of the country, indicating mixing of soil water of several years before groundwater recharge. Due to the enrichment of $\delta^{18}O$ and δD in surface water that undergoes evaporation, the resulting isotopic signature is different than that of groundwater and provides an ideal conservative tracer for evaluating the extent of mixing of surface water and groundwater (Gonfiantini 1986). Differences between the composition of the water isotopes ($\delta^{18}O$ and δD) in rainfall, groundwater, stream runoff to a sinkhole, and lake water are used to quantify mixing of groundwater and surface water. Results are presented for three study areas that represent various types of interactions between groundwater and surface water (Green, 1997). Natural recharge of water from sinking streams to this aquifer can result in water quality contamination, such as high concentrations of iron, hydrogen sulfide, and organic material, and undesirable bacteria, protozoa, and fungi (Krause 1979, McConnell and Hacke 1993). There are few studies on interconnection of surface and subsurface waters in India (Nachiappan and Bhishm Kumar 1999).

2.10 $\delta^{34}S$ of Sulphate

The isotopic composition of sulfate in water reflects the sulfur sources. The isotopic composition of oxygen-18 and sulfur-34 can be used to identify the sources and conversion of sulfates in water (Caron et al. 1986). It is well known that the $\delta^{34}S$ value of marine sulfates remained constant at +20‰ for millions of years (Holster et al. 1986). Shahul hameed (2002) studied the isotopic composition of sulphate in groundwater sources around a clay mining industry in Kannur, Kerala. The data indicate the sulphate contamination is derived from the mine effluents.

2.11 Sedimentation rate using radioisotopes

Inflow of eroded material and other contaminants from the lake catchments has accelerated the rate of sedimentation and eutrophication process (Chakrapani 2002,Kumar et al. 1999). Higher rate of sedimentation has diminished the usefulness of several small lakes and many others are shrinking at an alarming rate. Hence, knowledge of accurate sedimentation rate and its causes are of utmost importance for appropriate management of lakes and future planning. Radiometric dating techniques are reliable tools for estimating sedimentation rates in lakes and are used worldwide. Although several radioisotopes are useful in geochronological studies of lake sediments, lead-210 (^{210}Pb) and caesium-137 (^{137}Cs) isotopes find the largest application (Edgington et al. 1991, Ritchie and McHenry 1985).

The different models connecting the ^{210}Pb specific activity profile of sediment cores with sediment deposition rates or the rate of sedimentation are described in the literature (Carroll and Lerche 2003). The most widely used method for the lakes, coastal zones or estuaries, where sedimentation processes are intensified by anthropogenic actions is the constant rate of supply (CRS) of unsupported ^{210}Pb, proposed by Appleby and Oldfield (1978). An alternative method, based on the Weibull distribution of anthropogenic ^{137}Cs, which originally was proposed for soil samples (Dahm et al. 2002), has been later developed also for dating of the bottom sediments (Lu X 2004). This method has been very recently applied by the authors for preliminary determination of the sediment rates for two bottom sediment cores from the Kuwait Bay (Al-Zamel et al. 2005).

Physico-chemical and biological characteristics of various lakes in the country have been studied in detail, but few studies (Das et al. 1994, Kumar et al. 1999, Sarvana Kumar et al. 1999) have been carried out to estimate the sedimentation rate and deposition pattern in lakes. Kumar et al. (1999) have observed large variation in life-expectancy estimation of Nainital lake using dating techniques (^{137}Cs and ^{210}Pb) and bathymetric data due to errors associated with the lake sounding data. Recent sedimentation rates in Nainital,

Bhimtal, Sattal and Naukuchiatal lakes, Uttarakhand; Mansar and Dal lakes, Jammu and Kashmir, and Sagar and Bhopal lakes, Madhya Pradesh have been determined employing ^{210}Pb and ^{137}Cs dating techniques. (Bhishm Kumar et al. 2007). ^{210}Pb and ^{137}Cs were used to calculate the rate of sedimentation of the floodplain sediments of the Yamuna river basin (tributary of the river Ganges, India).

The work presented in the present study had been carried out covering both the southern and northern part of the wetland. The present study also reports the heavy metal toxicological aspects of the core sediments collected from the lake. The dynamics and sedimentation rate of the lake is reported using isotopes such as ^{18}O, ^{2}H and ^{137}Cs. The surface water groundwater interconnection was studied using isotope. The biomonitoring of heavy metals by macrophytes and speciation of phosphorous in the sediments has been attempted as part of the study. To the best of our knowledge, isotope studies of the Vembanad Lake have not been reported elsewhere.

3.0 Materials and Methods

3.1 Sampling

The objective of the sampling is to collect a portion of material small enough in volume to be conveniently transported to and handled in the laboratory while still accurately representing the material being sampled. This implies, firstly, that the relative portions of the concentrations of all pertinent components must be the same in the sample as in the material being sampled and secondly, that the sample must be handled in such a way that no significant changes in composition occurs before the test are performed. The analysis is generally intended to reveal the composition of the waters at the time or over the period of sampling. Consequently errors are introduced if changes take place between taking of the sample and analysis being carried out. There is in fact a strong likelihood that such changes will occur in most of the waters. The arrangements should be such that these are prevented or at least minimized.

3.1.1 Water sampling

Water is a dynamic system. During sampling the water is removed from its natural environment. Constituents of water sample may interact with the surface wall of the container and consequently their concentration may be altered. These considerations are therefore prerequisite of sampling program.

3.1.2 Site selection for lake water samples

The selection of sampling site was decided by the various uses of water and by their location, relative magnitude and importance. The chance of accidental pollution was also considered for sampling.

Water sampling stations were selected on the upstream Thanneermukkom bund towards the Alappuzha side of Vembanad Lake. Twenty representative stations were selected throughout the lake based on different stresses imposed on the system by different activities (Figure 3.1). The factors which were considered during the site selection included the portion of the lake were it receives urban waste discharge, domestic waste discharge, agricultural waste discharge, pollution due tourism, barrage and fishing activities. The details of the stations are discussed in chapter 4.

3.1.3 Site selection for groundwater samples

The important parameters considered during the selection of groundwater sampling sites include parameters such as location, aquifer type, total yield, the population served, its value to industry and agriculture and the magnitude of threats to its water quality. The sampling stations were fixed in the basin of Vembanad Lake covering the whole southern part of the wetland system (Figure 3.1). Thirteen stations were fixed and the details are discussed in chapter 5.

3.1.4 Sample collection

The sampling was carried manually using a water sampler. Samples form various depth were collected using automatic depth sampler. The collected sample were transferred to transparent polyethylene bottles, which was thoroughly cleaned and rinsed three times with the water which was sampled. Care was exercised to clean the devices inside the bottle for any possible sediment or precipitate. Recorded the complete information regarding the source and the conditions under which the sample was collected. Attached a record tag to the sample container, by noting the sample number, source of sample and sampling location.

While collecting the water sample from a hand pump, care was taken to run at least fifteen minutes so that the sediment, precipitates already formed either on the surface of the well or in the pipelines due to drying of materials, were washed away and were prevented from contaminating the sample. In taking the sample from open well the bucket was lowered at least two to three meters below the surface and collected preferably from the centre of the well.

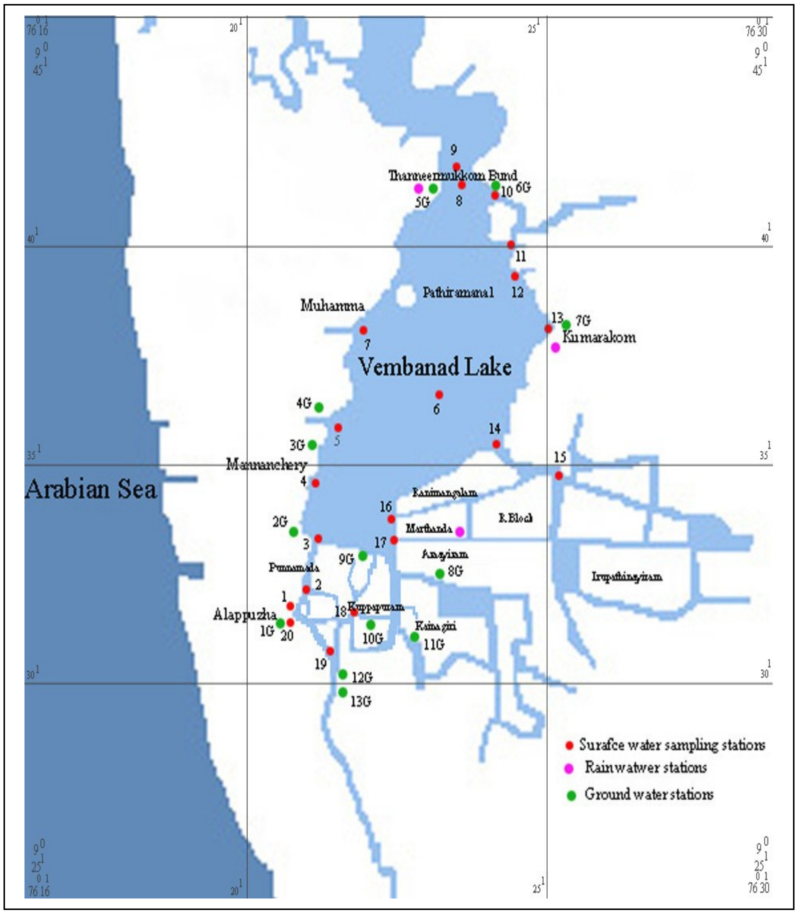


Figure 3.1 Map of the study area showing sampling sites

3.2 Parameters measured in the field

A number of parameters including pH, conductivity, ammonia, temperature and residual chlorine were measured in the sampling site immediately after the collection of water sample. For measuring the dissolved oxygen, the fixing was done in the site itself.

3.3 Preservation and handling of samples

Between the time that the sample is collected in the field and until it is actually analyzed in the laboratory, physical changes, chemical changes and biochemical reactions may take place in the sample container which will change the intrinsic quality of the sample. It is necessary therefore to preserve the sample before shipping and to prevent or minimize their changes. This was done by various procedures such as keeping the sample in the dark, adding chemical preservatives, lowering the temperature to retard the reaction by freezing or by combination of all these methods.

For different parameters, different methods of fixing are required which vary widely in terms of physical conditions, nature and concentration of chemicals. Summary of the sampling protocols is shown in Table below (APHA 2006).

Table 3.1 Summary of sampling protocol

Determinant	Minimum sample size	Method of preservation	Maximum storage Preferable/Regulatory
Alkalinity	200	Refrigerated to ~4°C	24hour/14days
BOD	1000	Refrigerated to ~4°C	6hour/14days
Color	500	Refrigerated to ~4°C	48hour
Order	100	Analyzed as soon as possible	
Turbidity	300	Analyzed the same day, stored in dark up to 24h, refrigerated	24hour/48hour
Fluoride	300	None	28days
Oil&Grease	1000	Added H_2SO_4 to bring pH<2 and refrigerated at ~ 4°C	28days
Hardness	100	Added HNO_3 to pH<2	28days/28days
Metals in general		For dissolved metals, filtered immediately through 0.45 micron filter, added HNO_3 to pH<2	6months/6months
Nitrate	100	Refrigerated to ~4°C	48hours/28days
Nitrite	100	Refrigerated to ~4°C	None/28days
Organic compounds/ pesticides	200	Refrigerated, added 100mg ascorbic acid/l	7days/7days until extraction, 40day after extraction
Oxygen dissolved	300	Fixed from the field	24hours
pH	100	Analyzed immediately	2hours/none
Phosphate	100	Refrigerated to ~4°C	48hours
Sulphate	200	Refrigerate to ~4°C	7days
Conductance	200	Analyzed immediately	24hours

(Source: APHA 2006)

Samples were analyzed as quickly as possible. In case immediate analysis was not possible, the sample was stored at 4°C in dark. Additional sampling precautions were taken depending upon the sample condition at particular location.

3.4 Field quality control

Quality control is an essential element of a field quality assurance program. It requires the submission of blank. ie, bottle blanks, filter blanks, sample blanks, field blanks and duplicate sample to test the purity of chemical preservatives: to check for contamination, sample containers, filter papers, filtering equipments that is used in the sample collection or handling and to detect systematic or random errors occurring from the time of sampling to the time of analysis. Replicate samples were taken to check the reproducibility of the sampling.

3.5 Physico-chemical analysis of water sample

Preservation of samples and estimation of various water quality parameters were done as per standard procedures reported in APHA (APHA 2006).

3.5.1 Temperature

Temperature of the water sample was measured insitu using mercury thermometer having a scale marked for every 0.1°C, checked against a precision thermometer.

3.5.2 pH

pH of the samples was measured using Systronics digital pH meter. The instrument was calibrated using pH 4, 7 and 9.2 buffer solutions.

31.5.3 Color and Turbidity

Color and turbidity were measured using Merck SQ 118 spectrophotometer

3.5.4 Electrical conductivity and Salinity

Electrical conductivity and salinity was measured using ELICO conductivity meter and salinometer. The instrument was standardized against standard conductivity solution of 1413µS/cm. The results are reported in micro-Seimens/cm.

.3.5.5 Total dissolved solids

The TDS of the water sample was determined using gravimetric technique. The sample was filtered through a Whatmann No. 30 filter paper, evaporated the filtered sample, dried the residue and weighed. The increased weight gave the total dissolved solids.

3.5.6 Dissolved oxygen and Biochemical Oxygen Demand (DO&BOD)

Dissolved Oxygen was estimated volumetrically. Oxygen present in the sample was made to react with divalent manganese hydroxide, which gets oxidized to its higher state of valence, and precipitates as brown hydrated oxide after addition of NaOH and KI. Upon modification, manganese reverts to divalent state and liberates iodine from KI equivalent to the original DO content. The liberated iodine was titrated against sodium thiosulphate solution using starch as indicator. To determine the Biochemical Oxygen Demand (BOD) incubation of the sample at a constant temperature (at 20°C) for a time period of 5 days was done so that micro organisms can act upon the bio-degradable matter. After 5 days the DO content was determined. The difference between the initial and final DO gave BOD.

3.5.7 Alkalinity

Using the principle of acid-base titrations total alkalinity of the sample was determined. The water sample was titrated against std. H_2SO_4 (0.02N) using methyl orange as the indicator. The results were expressed as mg/l as $CaCO_3$.

3.5.8 Hardness

Complexometry was the principle used for the determination of total hardness and calcium hardness. Total hardness was estimated using std. EDTA (0.01M) and Eriochrome Black-T indicator in presence of NH_4Cl-NH_4OH buffer of pH 10. For the determination of calcium hardness Murexide indicator in presence of NaOH buffer was used. The difference between the two gave the magnesium hardness.

3.5.9 Calcium and Magnesium

Calcium and Magnesium concentrations in the water samples were estimated from their corresponding hardness using the equations.

Calcium in mg/l = Calcium hardness x 0.4

Magnesium in mg/l = Magnesium hardness x 0.243

Magnesium hardness = Total hardness-Calcium hardness

3.5.10 Sodium and Potassium

Alkali metals like Sodium and Potassium were estimated using Flame Emission Photometry. Followed the instructions of flame photometer manufacture for selecting proper photocell, wavelength, slit width adjustments, fuel gas and air pressure, steps for warm up, correcting for interference and flame background, rinsing of burner, sample ignition and emission intensity measurements. Prepared a blank solution and sodium calibration standards of 25, 50, 75 and 100 mg sodium per liter. The instrument was set at zero containing no sodium (blank solution). Measured emission at 589 nm and prepared the calibration curve. Determined the sodium concentration of the sample, or diluted sample, from the curve. For potassium the calibration graph was plotted using the standards 2, 4, 8 and 10 mg potassium per liter and measured the emission at 766.5 nm.

3.5.11 Chloride

Argentometric titration was adopted for the estimation of chloride in the water sample. The sample after the addition of potassium chromate indicator was titrated against std. $AgNO_3$ solution (0.0282N).

3.5.12 Sulphate

Sulphate concentrations of the samples were determined using Nephelometric technique. Sulphate ion was precipitated in an acid medium with barium chloride in such a manner as to form barium sulphate crystals of uniform size. Nephelo turbidity meter measured the absorbance of barium sulphate suspension and the sulphate ion concentration was determined by comparison of the reading with a standard curve.

3.5.13 Phosphate-phosphorous

Ammonium molybdate–spectrophotometry was the method used for the estimation of Phosphate-P. Ammonium molybdate was made to react with Phosphate-P in the water sample to form molybdophosphoric acid, which was then reduced to a blue colored complex ' *Molybdenum blue'* by the addition of stannous chloride. The estimation of the blue colored complex was made at 690nm. A standard curve was plotted using known standards of 0.2, 0.4, 0.8 and 1.0 mg per liter of phosphorous. The instrument directly calculates the concentration in the sample and reported as mg/l of phosphate-P.

3.5.14 Nitrate-nitrogen

Cadmium reduction technique-Spectrophotometry was used for the estimation of nitrate-N. By passing the water sample through a column containing amalgamated cadmium fillings nitrate was reduced to nitrite. The nitrite–N thus produced was determined by diazotizing with sulphanilamide and coupling with N (1-Naphthy1) ethyl diamine to form a highly colored azo dye which was measured colorimetrically. The amounts of azo dye formed will proportional to the initial concentration of Nitrate-N over a wide range of concentration. The estimation of dye was made at 543nm using UV-Visible spectrophotometer (Hitachi, U-2800).

3.5.15 Fluoride

Colorimetric technique using SPADNS reagent was used for the estimation of fluoride. Under acid condition fluoride react with zirconium SPADNS solution and the ‘lake’ (color of SPADNS) gets bleached due to the formation of ZrF_6. The concentration was estimated using the UV-Visible spectrophotometer.

3.6 Microbial analysis-Total coliform and Faecal coliform

The major microbial estimation conducted was the coliform estimations. The method used for their estimation was the Multiple Tube Dilution (MTD) technique. In this technique the results were reported in terms of Most Probable Number (MPN) of bacteria in 100ml of the sample. MPN value for a given sample was obtained by the use of MPN table. Mac Conkey broth, Brilliant Green Lactose Broth (BGLB) and peptone water were used as the media for the determination of total coliforms, faecal coliforms and E coli respectively. For total coliform estimation, 10,1 and 0.1ml of the samples were inoculated in to the Mac Conkey media and incubated at 37.5^0C for 48 hours. Tubes having both gas and growth were taken as the positive tubes and counted the number of positive tubes. The positive tubes were gently shaken re-suspend the growth and with a sterile loop, transferred three loopful to a fermentation tube containing BGLB. This was then incubated at 44.5^0C for 24 hours. In a similar manner the number of positive tubes were noted. In both the above cases the count was determined using MPN index. The previous positive tubes were gently shaken to re-suspend the growth and with a sterile loop, transferred three loopful to a fermentation tube containing peptone water. The inoculated tubes were incubated at 44.5^oC for 24 hours. After the incubation added 2-3 drops of Kovac’s reagent. Formation of a violet ring indicated the presence of Escherichia coli.

3.7 Biological analysis-Chlorophyll

The Chlorophyll pigments, *a,b* and *c* were extracted from the plankton, concentrated using aqueous acetone 90% (v/v) and the estimation was done spectrophotometrically. The extract was kept overnight at 4°C in the dark. The tube was centrifuged for 20 minutes at 2000rpm. Decanted the extract, measured the volume and read the absorbance at 663, 645 and 630nm. Using the respective equations the concentrations of the three pigments were calculated. The algal biomass was estimated by multiplying the chlorophyll *a* content by a factor of 67 (here the assumption is that chlorophyll *a* constitutes, on the average, 1.5 % of the dry weight organic matter of the algae) (APHA 1995).

3.8 Sediment sampling and analyses

The core samples of sediments were collected using gravity type sediment corer of 50cm length. The sampling stations were selected based on the criteria that they were near the urban and domestic effluent discharge points, agricultural dewatering areas, places of tourism activities, industrial discharge points and estuarine region. A total of eight sediment cores, including five from southern region and three from northern part, were collected for the present study. The details of the sampling stations are further discussed in chapter 6.

3.8.1 Preservation of sediment sample

The collected sediment cores were cut into slices of approximately 2-4cm length from the field itself and properly labeled. The samples were brought to the laboratory using ice bags and stored in a deep freezer unit until the drying procedure (UNEP 1985).

3.8.2 Methodology of Sediment Analyses

The various physicochemical parameters like pH, electrical conductivity, total alkalinity, chloride and sulphate were estimated following soil analysis procedures (Jackson 1973) and APHA (APHA 2006).

3.8.2.1 Mechanical analysis

Using the hydrometer method the weight percentages of sand, silt and clay in the sediments were calculated and classified the sediments into various textural classes using the ternary model. For this a known weight (40g) of the sediment was taken, washed with acid to remove the carbonates, then washed with water to remove the soluble impurities and treated with Hydrogen peroxide to oxidize the organic matter completely. The sediment was then dispersed in a dispersing medium (3.6% Sodium hexametaphosphate +0.8% Sodium carbonate), transferred in to the sedimentation cylinder, made up to a volume of 1000ml with distilled water and shaken well .After 4 minutes and 120 minutes the hydrometer was dipped into the cylinder and noted the scale reading. From these readings and that of the blank percentages of sand, silt and clay were calculated. Classification into various textural classes were done using the ternary model.

3.8.2.2 pH

The pH of the sediment was determined using 1:10 soil water (w/v) suspension. 10g of air-dried sediment was mixed with 100ml of distilled water in a beaker. The solution was stirred at least 5 times over a 30 minutes period and allowed the sediment and water to reach equilibrium. The sediment suspension was shaken and inserted the electrodes into it. The pH meter was standardized with known buffer solutions.

3.8.2.3 Electrical conductivity

Electrical Conductivity of the sediment was determined using 1:10 sediment water (w/v) suspension. The sample was put overnight and inserted the conductivity meter into it.

3.8.2.4 Alkalinity, Sulphate and Chloride

The sediment water suspension was used for the estimation of the total alkalinity, sulphate and chloride content in the sediments. The sample was filtered through 0.45 micron filter paper and the filtrate was analyzed using the procedures explained for water samples.

3.8.2.5 Organic carbon

A portion of the sediment was oven dried, ground and sieved. 0.25g of the material was taken for the estimation of organic carbon using the Walkley Black's method. In this method the nascent oxygen formed by the reaction between potassium dichromate and concentrated sulfuric acid oxidizes the organic carbon in the sediment. The organic carbon content in the sediment was then estimated by titrating the rest of potassium dichromate with ferrous ammonium sulphate. The organic matter was computed by multiplying with a factor of 1.723.

3.8.2.6 Exchangeable cations

Ammonium acetate was used to extract the exchangeable sodium, potassium, calcium, and magnesium. The extract was filtered through 0.45 micron filter paper and the filtrate was used for the estimation. Estimation of exchangeable sodium and potassium was done by flame photometry using Flame Photometer. Exchangeable calcium and magnesium was estimated by complexometric titration using EDTA.

3.8.2.7 Phosphorous

Inorganic Phosphate-P was extracted using 1N HCl and determined colorimetric ally using Spectrophotometer. The sediment samples were digested using $HClO_4$-HNO_3 acid mixture was used for total phosphorous measurement. For the determination of hydrolysable form, the sample was extracted using 0.01N sulfuric acid. Organic form was determined as the difference between total and sum of inorganic and hydrolysable form.

3.8.2.8 Kjeldahal Nitrogen

The total nitrogen content of the sediment was determined using digestion with sulfuric acid followed by distillation and titration with hydrochloric acid. The distillate was collected in 4% boric acid. Titration value of a blank solution of boric acid and mixed indicator has determined. From the titral value the percentage of nitrogen was calculated.

3.8.2.9 Heavy metals

The concentration of different heavy metals in the sediment sample was estimated using digestion technique followed by analysis using AAS. One gram of dry sediment was taken in a 250 ml beaker added 6 ml con. HNO_3 and 2 ml of perchloric acid ($HC1O_4$), the beaker was closed and kept at room temperature for about 2 hours. The above mixture was heated in an oven at 100°C for one hour and evaporated the sample over a hotplate. The residue was diluted with 20 ml of 6% 1:1 mixture of HNO_3 and $HClO_4$ and heated the mixture on a hot plate for about 10 mints. The sample was filtered the sample through Whatmann No.41 filter paper, into a 50 ml. standard flask and adjust the volume with the same acid mixture. A blank was prepared by the same procedure. The amount of heavy metals were determined from the filtrate with the help of atomic absorption spectrophotometer (AAS, Thermo Scientific M-Series).

3.9 Methodology for Isotopic analysis

3.9.1 Collection of water samples

The precipitation samples were collected from three sampling stations which are marked in the area map. Samples were collected daily as and when there was rain. A composite sample was prepared after the end of each month by pooling the samples collected at daily/weekly /whenever rain during the month. Care was taken to prevent air entry into the collecting vessel to avoid exchange tritium from air into the sample. Water samples were collected during 2007 to 2008, daily basis, during the summer, southwest monsoon and northeast monsoon periods. Surface water samples from 20 representative stations of Vembanad Lake were collected for ^{2}H and ^{18}O measurement in three seasons, pre-monsoon, monsoon and post-monsoon. Samples from the depth were also collected in two seasons. The sampling stations were marked in the area map. Thirteen groundwater samples including samples from shallow open well, deep bore well and a small pond were also collected from the basins of the Vembanad Lake, which is marked in Figure 5.3. Large volumes, around 20 litters of surface water samples were collected in the pre-monsoon season for the determination of $\delta^{34}S$. A total of 56 samples including surface and bottom water, from different stations of Cochin estuary were collected during different time intervals in pre-rinsed Tarson bottles. . A core sediment sample was collected from the middle of the lake (C/V) to find out the sedimentation rate of the lake by finding the cesium-137 activity.

3.9.2 Preservation of the sample

The samples were collected in clean polythene bottles of 60 ml capacity. The bottles were filled with water samples to the maximum, leaving only a little space to account for the expansion during the transport. While filling the bottles, only a little space was left in order to prevent air, which may introduce error due to the exchange of the ^{18}O present in the air with water. The analysis was made using the instrument Isotope Ratio Mass Spectrophotometer.

3.9.3 Analysis of the water samples for the stable isotope, ^{18}O

200µl water sample was taken in a special glass vial fitted with a screw cap provided with septum, which allows the injection needle to pass through. The sample was then equilibrated with a slow stream of carbon dioxide–Helium mixture, which was passed at a rate of 50ml/min so that the ^{18}O of water is exchanged with the ^{16}O of carbon dioxide through isotope exchange. This is achieved by keeping the water sample agitated for a period of 18 hours.

$$H^{16}O^{18}O+C^{16}O_2= H^{16}O^{16}O+C^{16}O^{18}O$$

The equilibrated oxygen gas was then introduced in to the mass spectrometer for analyses. Helium was passed at the rate of 5ml/min, to flush out the gasses. Since the international standard was also subjected to the same equilibration, the δ value was not expected to vary. The results were analyzed using the software, Isodat NT, provided along with the system by the manufacturer.

3.9.4 Analysis of water samples for deuterium

200μl of water sample was taken in a special glass vial fitted with a screw cap provided with septum, which allows the injection needle to pass through. A platinum rode was added as a catalyst. The sample was then equilibrated with a low stream of hydrogen and helium mixture, passed at a rate of 50ml/min so that the hydrogen is exchanged, with deuterium of water samples through isotope exchange.

$$^{2}H^{1}HO + {}^{1}H \rightarrow {}^{1}HO + {}^{2}H^{1}H$$

The equilibrated hydrogen gas was then introduced to the mass spectrometer for analysis.

3.9.5 Analysis of water for ^{34}S

For the analysis of $\delta^{34}S$ of sulfates, it was precipitated as BaSO4 by adding a saturated $BaCl_2$ solution to the filtered water sample. SO_2 gas was then prepared from this and the composition of $\delta^{34}S$ was analyzed using mass spectrometer.

Stable isotopic compositions are expressed in usual d notation relative to the V-SMOW for oxygen and hydrogen isotopes, and CDT for sulfur isotopes. D (‰) = (Rsample/Rstandard-1)*1000, where R represents$^{18}O/^{16}O$, D/H, $^{34}S/^{32}S$. The analytical reproducibility for each standard were ±0.1‰ for $d^{18}O$, ±1‰ for dD and ±0.2 for $d^{34}S$

3.9.6 Sedimentation rate from ^{137}Cs activity

The sediment core was sliced at every 2 cm intervals and analyzed for ^{137}Cs activities. The ^{137}Cs activity in each oven-dried section of sample was determined by gamma-ray counting using Hyper Pure Germanium detector coupled with a 4096 multi-channel analyzer system. The detection limit for ^{137}Cs measurement was 0.25mBq/g and the standard counting error was less than 10% in the core sections. The analysis was carried out with the help of the facility available at Bhabha Atomic Research Centre Mumbai.

4.0 Surface Water Quality of Vembanad Wetland System

4.1 Introduction

Water is the most essential and prime necessities of life. It is the most indispensable resources and the elixir of life. Water one of the fundamental resources, is at once one of the most common substances and also one of the most unusual. Our life depends upon water and man needs water for his drinking and other domestic and industrial processes. Water has other unusual physical and chemical characteristics that play a large but often recognizable role in our daily lives. The Worlds human population depends for the daily requirement only on a tiny fraction of about 0.03% of the total water resources. These sources include groundwater up to 800meters depth and surface water such as river, ponds and lakes.

Growing population and human activities results in greater water demand, while global water resources are limited. The distribution of water among different users is severely competitive. Of all natural resources, water is amongst the most challenging ones to manage (Walling ford 2000). Thus water plays a major role in virtually every aspect of human life. Water bodies and their aquatic system play a key role in ecological balance and sustainable development. Nevertheless, they suffer from mismanagement. Regrettably, too few persons understand the physical and chemical properties of water well enough to effectively solve urgent and nearly universal problems relating to its cost, availability, distribution, and contamination. Water problems of any type came largely from lack of knowledge and, therefore, from mismanagement of the natural system. These problems are intensified by the technological impact of man on that system.

4.1.1 Water and Wetlands

Water is the most critical feature that defines a wetland. Wetlands are land-water ecotones or transitional zones that occupy an intermediate position between dry land and open water. The water regime in a wetland is usually referred to as hydroperiod. Hydroperiod is defined as the periodic or regular occurrence of flooding and/or saturated soil conditions; it encompasses depth, frequency, duration, and seasonal pattern of inundation. Different hydroperiods will usually create different types of wetlands (tidal, non-tidal, semi-permanently flooded, permanently flooded) and will require that certain water quality characteristics be evaluated differently. In fact, most wetland water quality functions are tied directly or indirectly to the hydroperiod, and many impacts to wetlands directly or indirectly affect the hydroperiod of the wetland (Nelson and Randall 1990). This makes all aspects of wetland hydrology extremely important for the purposes of the water quality standards.

4.1.2 Role of wetlands in water quality protection

Wetlands play an important role in the landscape through their ability to improve water quality and thereby protect the water supply in adjacent rivers, lakes, streams and marine waters. One of the most important, but usually non-marketed, services provided by coastal wetlands is water quality control, and in particular the retention, removal, and transformation of nutrients. Numerous studies have shown that natural and constructed wetlands can be effective tertiary processors of wastewater effluent (Reed 1991, Kadlec and Knight 1996). Efficient at removing excess nutrients and pollutants, wetlands and their environmental services are especially critical in coastal wetlands (Doering et al. 1999). The value of this service comes in the form of reduced costs of water purification, where the water is used in production and consumption, or reduced contamination where the water continues to reside in the environment. As with most types of pollution, however, the economic damages associated with water quality impairment, and thus the value of the purification services performed by wetlands, are difficult to measure. Thus, the key economic issue is to establish the value to water quality of an acre of coastal wetland preserved, restored, enhanced or created.

Water clarity, nutrients and chemical content, physical and biological content, dissolved gas levels, pH, and temperature contribute to a wetland's life-sustaining capabilities. Changes in the clarity, color, odor, and taste of water through the addition of contaminants such as suspended particulates and dissolved materials can reduce or eliminate the suitability of a wetland for direct or indirect maintenance of water supply.

4.1.3 Water quality deterioration in wetlands

In spite of the valuable roles played in terms of water quality maintenance, wetlands in today are experiencing serious ecological problems which kill the capability of wetland in many aspects. The kidney of wetlands, water, is getting contaminated by different sources of natural and anthropogenic origin. Loading rates of incoming water should not exceed the wetland's ability to assimilate sediments, nutrients or toxicants. The introduction of nutrients or organic material to a wetland can lead to a high biochemical oxygen demand (BOD), which in turn can lead to reduced dissolved oxygen. Increases in nutrients can favor one group of organisms such as algae to the detriment of other types such as submerged aquatic vegetation, potentially causing adverse health effects, objectionable tastes and odors, detrimental impacts to aquatic organisms and wildlife, and other problems.

Changes in hydroperiod can significantly affect a wetland's ability to provide water quality and water quantity support to the beneficial use of water supply. Severe water fluctuations will limit denitrification and phosphorus retention. Changes in pH to more acidic conditions can reduce the wetland's ability to process nitrogen and phosphorus. Increases in water volume and/or velocity will increase loading and decrease sedimentation rates in the wetland, thereby decreasing the effectiveness of the wetland's ability to remove and retain nutrients and sediments. Increased velocities can also cause decreased water storage time in the wetland which will reduce the opportunity for the wetland to serve as a groundwater recharge source. Drawdown of wetland water levels often concentrates and mobilizes nutrients locked up in the exposed substrate

The sediment load of the incoming water is an important factor to consider. If incoming sediment loads are high, the wetland's assimilation and storage capacity may be compromised over time, ultimately affecting the wetland's ability to function. If a wetland is unable to assimilate the nutrients or toxicants it is receiving, there could be an increased threat to the ecosystem and other wetland functions. If the wetland is functioning as a groundwater recharge site, the sediment could seal the bottom of the wetland and create an impervious surface, preventing the wetland from providing a beneficial use.

Wetlands are integral to the functioning of both surface and groundwater systems. Their position in the watershed allows for storm water detention and desynchronization; water quality improvement through biofiltration of sediment and pollutants; maintenance of hydraulic interactions between uplands, other wetlands, surface and groundwater within the watershed; low flow augmentation; shoreline stabilization and erosion abatement; and critical food chain support and habitat for both terrestrial and aquatic ecosystems. Wetland water quality, like other surface waters, is protected by clean water act.

Since Vembanad wetland is an important water body which was declared as a Ramsar site in November 2002, an investigation was carried out on the environmental status with respect to the surface water quality. Thus this chapter provides an insight into the present surface water quality status of Vembanad wetland system and the causes responsible for the water quality deterioration.

4.2 Methodology

Surface water sampling stations were fixed along the Vembanad Lake. A total number of 20 representative sampling sites were selected depending on different stresses observed in the wetland system. The water quality analyses were conducted in three seasons, pre-monsoon (March 2007), monsoon (July 2008) and post-monsoon (January 2009). Water samples were collected using a water sampler and stored in pre-rinsed poly ethylene bottles. For microbial analysis, samples were taken in pre-sterilized bottles and were refrigerated. The details of the sampling stations were given in Table 4.1 and marked in the area map (Figure 4.1). Water quality parameters such as temperature, pH and DO were measured insitu. Preservation of samples and estimation of various water quality parameters were done as per standard procedures reported in APHA (APHA 2006). The major microbial estimation conducted was the coli form estimation using Multiple Tube Dilution technique and the results were expressed in terms of Most Probable Number of Bacteria (MPN) in 100ml of sample. The different analytical procedures for the determination of different parameters were discussed in chapter 3.

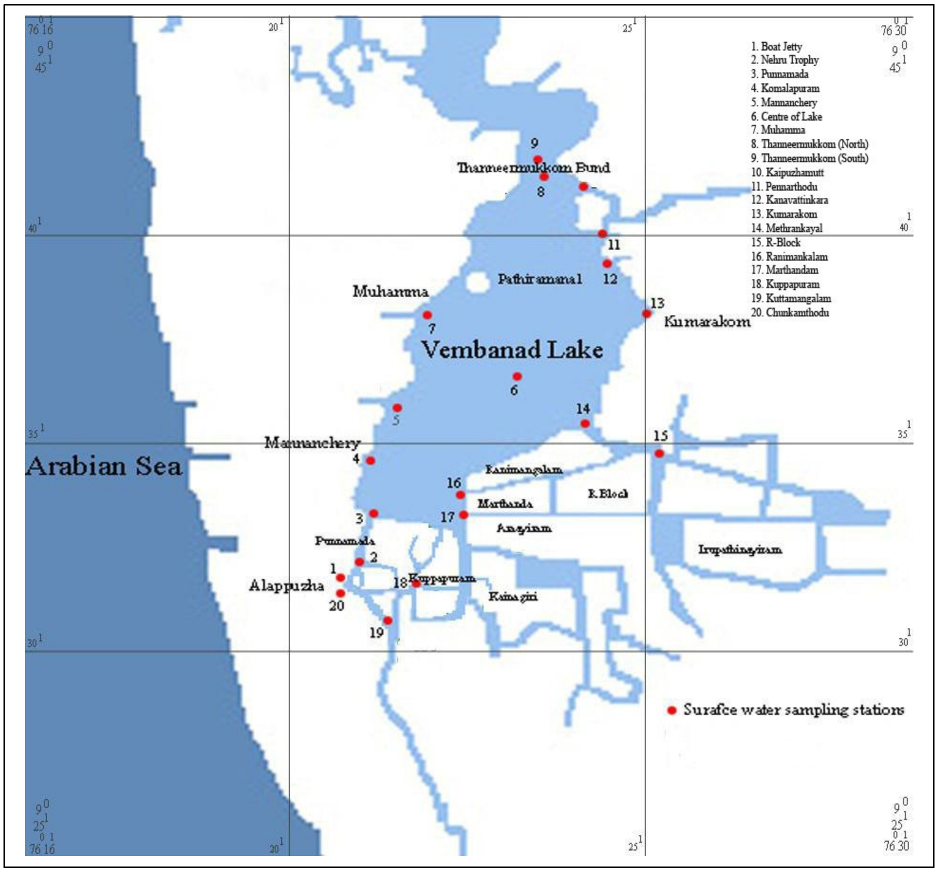


Figure 4.1 The map of Vembanad Lake showing surface water sampling stations

4.3 Results and discussion

4.3.1 Hydrochemistry of major ions

The chemistry of surface water samples in different season were plotted as trilinear piper diagrams (Figure 4.2) and is explained in Table 4.2. The cation and anion concentrations are dominated respectively by sodium and chloride. The relative proportion of the alkali and alkaline earth elements showed that, 100% of the sample showed alkali group in pre-monsoon season followed by 15% in monsoon and 85% in post-monsoon. For anion concentration in the pre-monsoon season, 100% of the samples were of strong acids followed by 90% in monsoon and 100% in post-monsoon season.

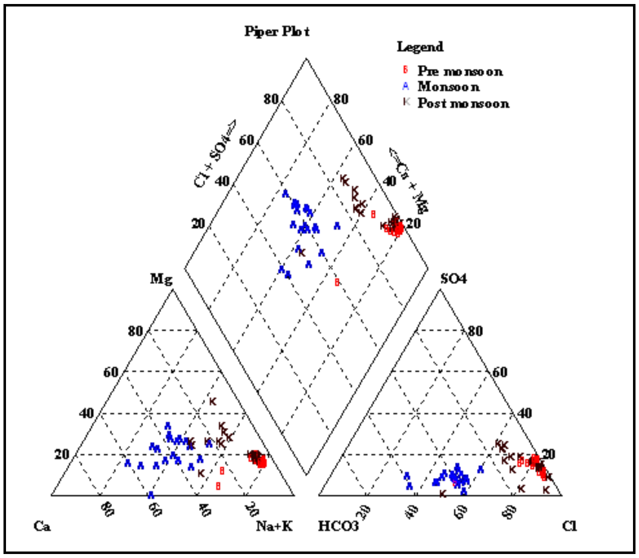


Figure 4.2 Piper plot for surface water samples in differet seasons

Seasonal variation of solute concentration in the Vembanad Lake showed high ionic concentration in pre-monsoon primarily due to saline water intrusion from Cochin estuary and low solute concentration in the monsoon season due to high flow regime. A plot of Ca+Mg versus HCO_3 (Figure 4.3) showed that in both pre-monsoon and post-monsoon season Ca+Mg is very much higher than carbonate suggesting the cations are balanced by SO_4+Cl. In monsoon season Ca+Mg is exactly balanced by carbonate anions. The variation of weight ratio of (Na+K)/(Na+K+Ca) as a function of total dissolved solids has been plotted to decipher the mechanism controlling water chemistry. This plot (Figure 4.4) places the Vembanad Lake in the region of precipitation and rock dominance in the monsoon season. In pre-monsoon and post-monsoon the field is in the saline water dominance. The sodium to chloride ratio of the lake water in different seasons such as pre-monsoon, monsoon and post-monsoon ranged between 1.28 to 0.76, 0.98 to 0.19 and 1.1 to 0.48 respectively. The close relation in Na/Cl ratio of pre-monsoon with that of sea water (0.85) confirmed the role of sea water in determining the ionic concentration of Vembanad Lake. Scatter diagram for sodium and chloride in different seasons are shown in the Figure 4.5. The different ionic ratios such as SO_4/Cl, Ca/Mg and Ca/SO_4 have also established the above results. The abundant sodium in the pre-monsoon and post-monsoon season promoted cation exchange with positive values for the chloro-alkaline indices. The negative value of the indices in monsoon indicated no cation exchange in the lake water.

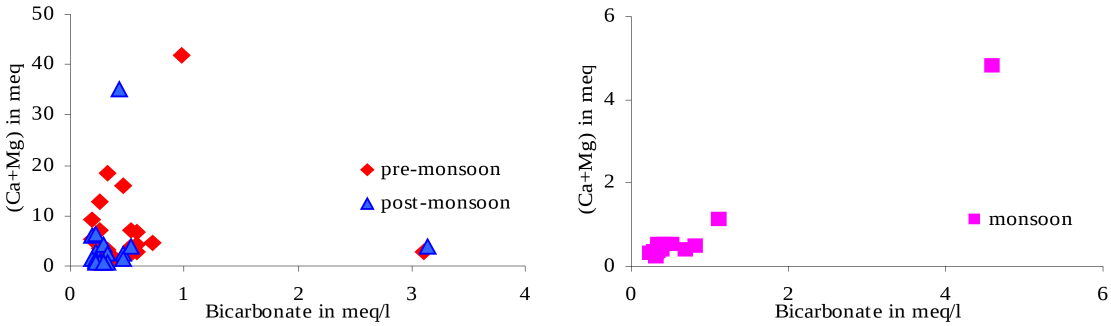


Figure 4.3 A plot of Ca+Mg versus bicarbonate for Vembanad Lake

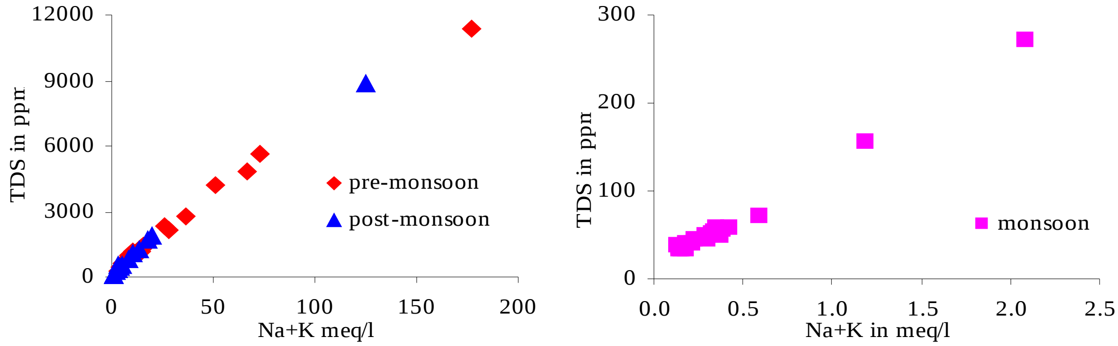


Figure 4.4 Mechanism controlling the water chemistry of Vembanad Lake

The plots of water chemistry of the lake samples in the USSL diagram are shown in Figure 4.6. Nearly 100% of the samples in the monsoon season are grouped within C1S1. In post-monsoon season 30% of samples are in C1S1, 35% in C2S1, 15% in C3S1, 10% in C3S2 and 10% in C4S2 group. But the 75% of samples in the pre-monsoon season are above C2 and S1. The USSL diagram best explains the combined effect of sodium hazard and salinity hazard. Accordingly all the samples in the monsoon season fall in C1S1 type and hence is suitable for irrigation. In post-mosoon season the 50% of the samples were below the salinity hazard. The pre-monsoon season is characterized by samples in the region of C3S2, C4S3 and C4S4, which shows very high hazard for irrigation.

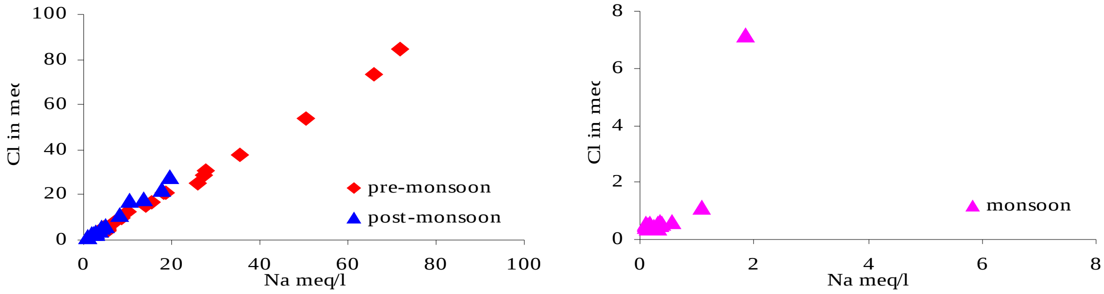


Figure 4.5 Sodium versus chloride plots for the Lake water samples of Vembanad

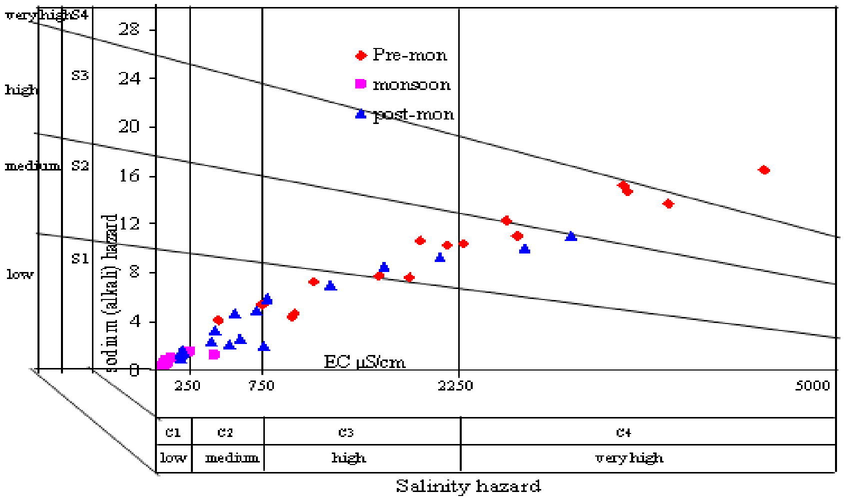


Figure 4.6 USSL classification of surface water samples from Vembanad lake in different seasons

The chemical classification of water samples based on Wilcox diagram is given in Figure 4.7. It is observed that 100% of samples in the monsoon season were excellent to good for irrigation. In post-monsoon season 40% of the samples belongs to excellent to good category, 5% in good to permissible, 40% in permissible to doubtful and 15% in doubtful to unsuitable for irrigation purposes. Pre-monsoon season have 40% of the samples in the category of unsuitable for irrigation. No samples in this season are excellent to good class.

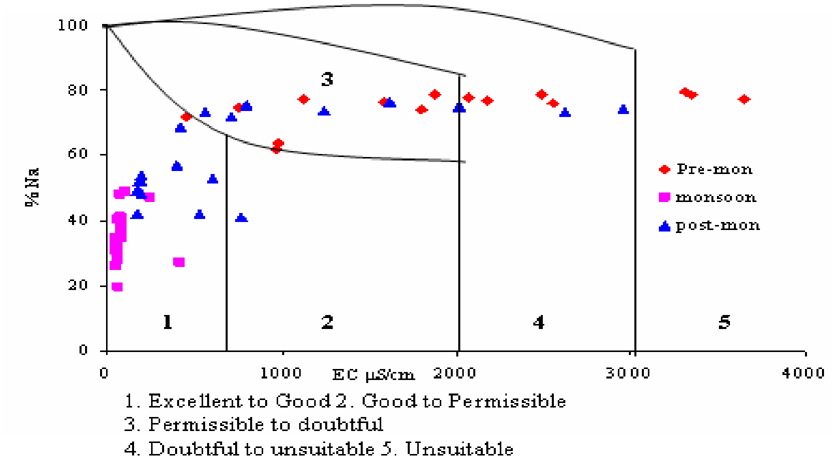


Figure 4.7 Wilcox diagram for lake water samples from Vembanad Lake in different seasons

The soil permeability is affected by long-term use of irrigation water. Doneen (1964) evolved a criterion for assessing the suitability of water for irrigation based on a permeability index (P.I) where

P.I. = (Na+√HCO3×100)/(Ca+Mg+Na)

Based on permeability index (PI) the water can be grouped and can be classified as class I, class II and class III orders. Class I&II waters are categorized as good for irrigation with 75% or more of maximum permeability. Class III waters are unsuitable with 25% of maximum permeability. The present study shows class I category in all the three seasons. The highest residual sodium carbonate value reported was 0.3. According to the US department of agriculture, water having more than 2.5epm of RSC is not suitable for irrigation purposes. The present study indicated no threat to the agriculture due to residual sodium carbonate.

The chemical classification of the lake water in pre-monsoon, monsoon and post-monsoon seasons were done. The different chemical characteristics such as sodium absorption ratio, sodium percentage, soluble sodium percentage, Kelly's ratio, magnesium hazard ratio, residual sodium carbonate, chloro-alkaline index and Permeability index of the water samples were calculated and are listed in Table 4.3.

4.3.2 General water quality

The result of the physico-chemical and bacteriological analysis of the water samples in different seasons of Vembanad Lake are given in Table 4.4 to 4.6. Basic statistics including maximum, minimum, mean and standard deviations reported for the hydrochemical variables are given in Table 4.7. The analytical results are discussed in the following sections.

4.3.2.1 pH

pH maintenance is one of the most attribute of any aquatic system since all the biochemical activities depend on pH of the surrounding. By measuring the pH of lake water, it can help us to understand the conditions that organisms in the lake are experiencing, and like any other long term water quality measurement. In the case of lake water with full of chemicals, small or localized changes in pH are quickly modified by various chemical reactions, so little or no change may be measured. This ability to resist change in pH is called buffering capacity.

Most of the stations showed acidic pH in all the seasons, which is a contribution from total organic carbon through organic acids (Eshleman and Hemond, 1985; Kerekes et al. 1986). Temporal variation of the pH was from 5.85 to 8.91 and it varied seasonally in the order monsoon> pre-monsoon> post monsoon (Figure 4.8). When pollution results in higher algal and plant growth (e.g., from increased temperature or excess nutrients), pH levels may increase (Wetzel 2001), which is reflected in the observed pH at Chunkam thodu (8.91), a eutrophic area. The high acidic pH, 5.85 reported at the station Pennarthodu (11/V) was the contribution from coir retting activities found in that area.

The spatial variation in the pH was due to the variation in the water temperature (Singhai 1997).

Although these small changes in pH are not likely to have a direct impact on aquatic life, they greatly influence the availability and solubility of all chemical forms in the lake and may aggravate nutrient problems. For example, a change in pH may increase the solubility of phosphorus, making it more available for plant growth and resulting in a greater long-term demand for dissolved oxygen.

4.3.2.2 Turbidity and Color

Turbidity is the striking characteristic to know the physical status of a water body. Turbidity of water is mainly caused by suspended particles such as clay, silts, finely divided organic and inorganic matters, plankton and other microscopic organisms.

Seasonal variation of turbidity follows monsoon>pre-monsoon>post-monsoon (Figure 4.9). Inflow of eroded materials due to high rain causes the water to be highly turbid in monsoon. Temporal variation of turbidity shows highest value at the station Boat jetty, where flushing of water due to boating was utmost. Most of the stations in the lake were colorless and clear during the observation period except Boat jetty and Chungam thodu.

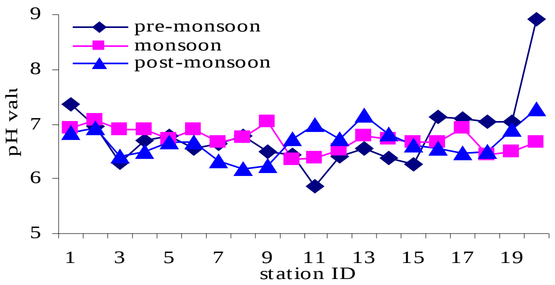


Figure 4.8 Variation of pH in Vembnad lake

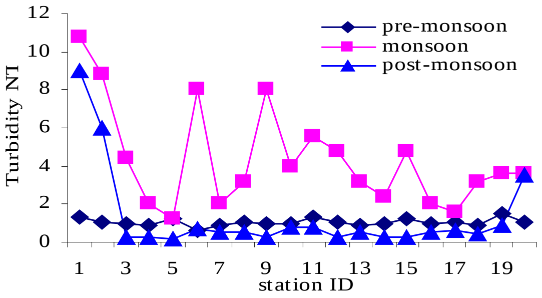


Figure 4.9 Turbidity in different seasons

4.3.2.3 Salinity

The fresh water source for the lake is from the monsoon and the rivers draining into the Lake. During monsoon season the tidal influence is restricted and its influence decreases as it moves southwards. The surface salinity progressively diminishes from near the estuary mouth. It is due to incursion of fresh river water, which is in agreement with some earlier reports at different estuaries (Padmavathy and Satyanarayana 1999). The pre-monsoon samples reported highest salinity and was spatially varying with highest concentration at Thanneermukkom, which confirmed the salinity intrusion through the bund.

4.3.2.4 Electrical conductivity and Total dissolve solids

Electrical conductivity is a measure of ionic concentration. The high electrical conductivity values indicate high ionic concentration (Young et al. 1972). During the study period conductivity ranged from 17800µS/cm to 449µS/cm, 422µS/cm to 51µS/cm and 13890µS/cm to 175µS/cm in pre-monsoon, monsoon and post-monsoon seasons respectively (Figure 4.10). A gradual decrease in conductivity values from the Thanneermukkom bund towards upstream remained in unison with the findings of Harikumar et al. (2007). There were great differences in the values of conductivity and TDS in different seasons. The minimum value (51.4µS/cm) was reported in the monsoon season which is due to the dilution caused by much inflow from rivers.

4.3.2.5 Dissolved Oxygen

Dissolve oxygen (DO) is a very important indicator of a water body's ability to support aquatic life. Organisms living in the water breathe the oxygen dissolved in the water. Oxygen enters the water by absorption directly from the atmosphere or by aquatic plant and algae photosynthesis. Oxygen is removed from the water by respiration and decomposition of organic matter. Too little oxygen can severely affect aquatic communities, often reducing diversity and population sizes. Low oxygen can directly kill or stress organisms such that they are not being able to successfully reproduce or grow. Therefore, the amount of DO in the water is very important to aquatic life in a lake (Kalff and Jacob 2002). Dissolved oxygen is necessary to sustain aquatic biota and provides a self purification capacity for water. Biodegradation of dissolved, suspended and deposited organic materials depend on oxygen as does of course respiration of aquatic biota.

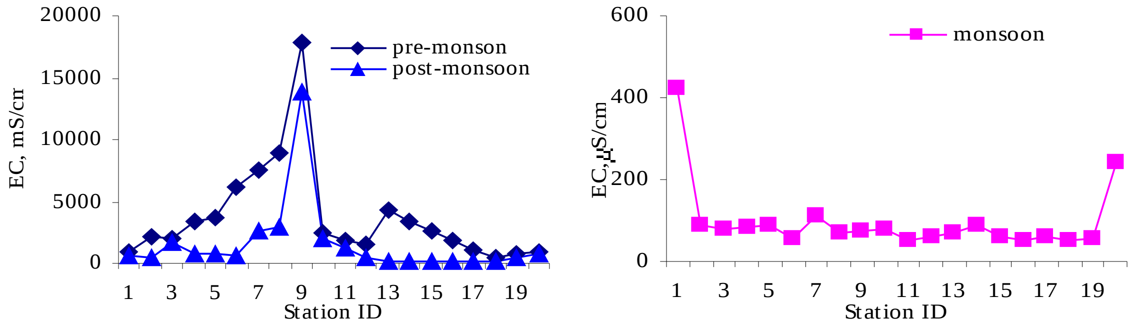


Figure 4.10 Spatial and temporal variation electrical conductivity in Vembanad lake

The spatial and temporal variation of dissolved oxygen in Vembanad Lake is shown in Figure 4.11. Average value of DO in pre-monsoon, monsoon and post-monsoon are 5.54mg/l, 5.38mg/l and 6.46 mg/l respectively. Boat jetty and Chunkam thodu reported lowest concentration of dissolved oxygen. It was likely that the increase in sewage input from the town of Alappuzha influenced the concentration of oxygen at these sites (Harikumar et al. 2007). Coir retting activities at station Pennarthodu depleted the dissolved oxygen to a level of 0.7mg/l. Maximum concentration of dissolved oxygen was reported at Kuttamangalam which was probably due to the process of photosynthesis (Catarina da Silva Pedrozo and Odete Rocha, 2007). When nutrients such as nitrate and phosphate are released into the water, growth of aquatic plants is stimulated. Eventually the increase in plant growth leads to an increase in plant decay and a greater "swing" in the diurnal dissolved oxygen level. The result is an increase in microbial populations and increased oxygen demand from the photosynthetic organisms during the dark hours, which was reflected in the station Chunkamthodu.

Monsoonal variation has uniform and higher distribution of dissolved oxygen in the lake. During rainy seasons, oxygen concentrations tend to be higher because the rain interacts with oxygen in the air as it falls. Everything else being equal, cold water contains more oxygen than warm water. As temperature increases, dissolved oxygen decreases. Summer season recorded comparatively less dissolved oxygen. During dry seasons, water levels decrease and the flow rate of a river slows down. As the water moves slower, it mixes less with the air, and the DO concentration decreases. There is no accountable variation in dissolved oxygen concentration of surface and bottom samples because of high flow and shallow depth. The solubility of dissolved oxygen decreases when salinity increases, if other factors are kept constant, which is reflected at the regions of Thanneermukkom.

4.3.2.6 Biochemical Oxygen Demand

Biochemical Oxygen Demand, or BOD, is a measure of the quantity of oxygen consumed by microorganisms during the decomposition of organic matter and is a most useful technique to assess the level of organic pollution in surface water. BOD is the most commonly used parameter for determining the oxygen demand on the receiving water of a municipal or industrial discharge. BOD can also be used to evaluate the efficiency of treatment processes, and is an indirect measure of biodegradable organic compounds in water (Kalff Jacob 2002).

Water from an exceptionally clear lake might show a BOD of less than 2 mg/L of water. The values of BOD observed in pre-monsoon, monsoon and post-monsoon seasons at the station Boat jetty are 15mg/l, 20mg/l and 19mg/l respectively. The high amount of domestic sewage discharged to the area near by station Boat jetty increased the level of organic pollution of the lake. The biological oxygen demand at Methran Kayal was the lowest (0.07mg/l).

Spatial and temporal variation in BOD is shown in Figure 4.12. If elevated levels of BOD lower the concentration of dissolved oxygen in a water body, there is a potential for profound effects on the water body itself, and the resident aquatic life. When the dissolved oxygen concentration falls below 5 milligrams per liter, species intolerant of low oxygen levels become stressed. The lower the oxygen concentration, the greater is the stress. Eventually, species sensitive to low dissolved oxygen levels are replaced by species that are more tolerant of adverse conditions, significantly reducing the diversity of aquatic life in a given body of water. If dissolved oxygen levels fall below 2 mg/l for more than even a few hours, fish kills can result. At levels below 1 mg/l, anaerobic bacteria (which live in habitats devoid of oxygen) replace the aerobic bacteria. As the anaerobic bacteria break down organic matter, foul smelling hydrogen sulfide can be produced (Bronmark et al. 1998). The BODs of all the stations except Boat jetty and Chungam thodu was below 4mg/l and hence safe for aquatic life.

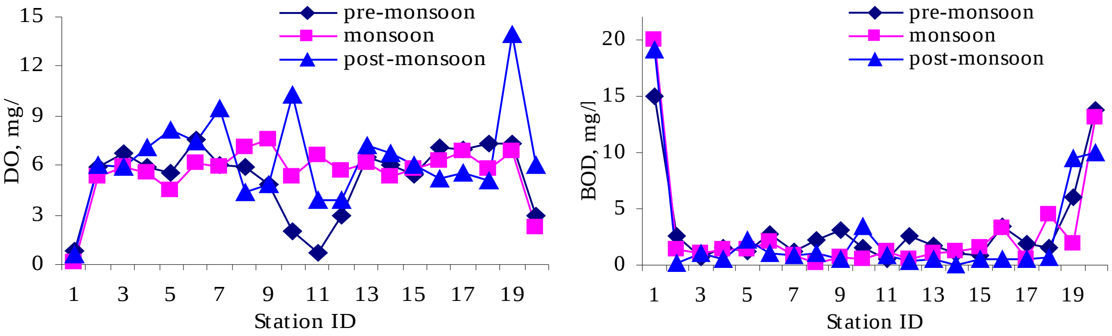


Figure 4.11& 4.12 Variation of Dissolved Oxygen and Biological Oxygen Demand

4.3.2.7 Total Alkalinity

Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. Alkalinity does not refer to pH, but instead refers to the ability of water to resist change in pH. The presence of buffering materials helps neutralize acids as they are added to the water. These buffering materials are primarily the bases bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and occasionally hydroxide (OH^-), borates, silicates, phosphates, ammonium, sulfides, and organic ligands.

The alkalinity of lake water is mostly determined by the geology of the soils and marine sediments deposited in the lake. Marine sediments contain carbonate, bicarbonate and hydroxide compounds, which may contribute to alkalinity. Also, borates, silicates and phosphates may add to the buffering capacity of water. Limestone is an example of a rock that is rich in carbonates, and has contributes to alkalinity in lake water. Granite is the opposite in that it does not contain any minerals that contribute to alkalinity, so lakes with granite geology have low alkalinity, and poor buffering capacity.

Alkalinity results revealed a clear gradient, higher values being found at the sites located closer to the sewage outlet from the town of Alappuzha (Boat jetty and Chungam thodu), and lower uniform values at the other sites (Figure 4.13). The wastewater from cities, shops and houses contains carbonate and bicarbonate from the cleaning agents and food residues (Schafer 1990). The high concentration of sewage was the cause of high alkalinity at these stations (Robert 1997).

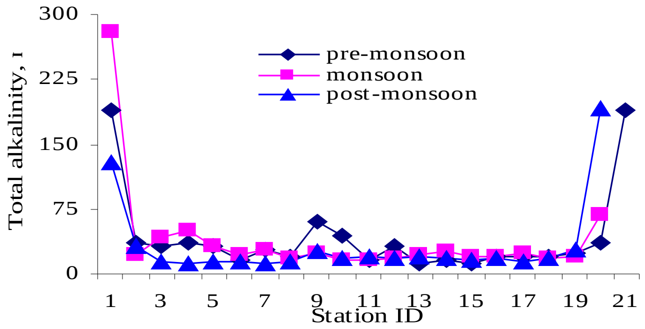


Figure 4.13 Spatial and temporal variation of total alkalinity in Vembanad Lake

4.3.2.8 Total Hardness

Hardness is a measure of polyvalent cations in water. It generally represents the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, because these are the most common polyvalent cations. Other ions, such as iron (Fe^{2+}) and manganese (Mn^{2+}), may also contribute to the hardness of water, but are generally present in much lower concentrations. Waters with high hardness values are referred to as "hard," while those with low hardness values are "soft". Hardness of the water is very important in industrial uses, because it forms scale in heat exchange equipment, boilers, and pipe lines. Some hardness is needed in plumbing systems to prevent corrosion of pipes.

The hardness varied seasonally in the pattern pre-monsoon> post-monsoon> monsoon (Figure 4.14). Spatial variation has higher values at Thanneermukkom and lower values in the southern region. Salinity intrusion through the bund is the cause for this type of spatial variation. Comparative high value was also recorded at stations like, Boat jetty, Chunkam thodu, and Kumarakom, were municipal sewage is the main cause. The spatial variation in the figure clearly explains the pattern of salinity mixing in the lake.

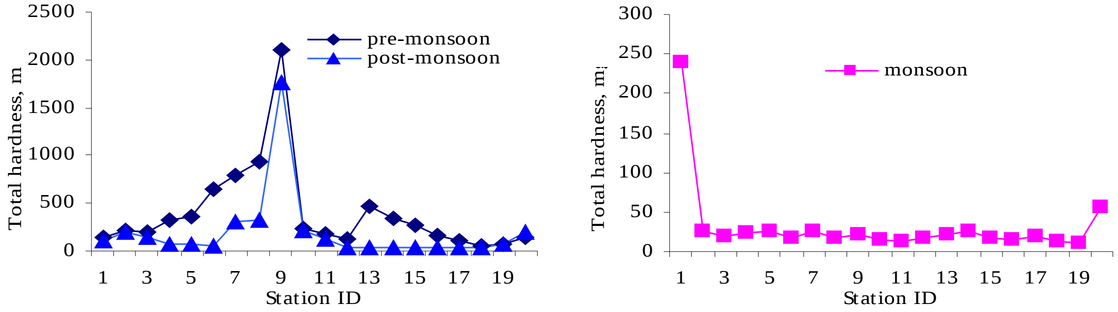
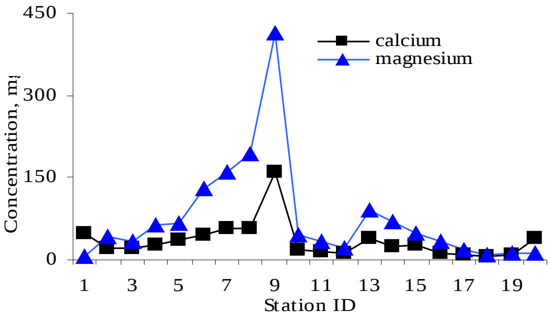


Figure 4.14 Spatial and temporal variation of total hardness in Vembanad Lake

4.3.2.9 Cations

The cations estimated in the water samples include alkali and alkaline earth metals like sodium, potassium, calcium and magnesium and iron, the heavy metal. Correlation analysis indicated that except iron, all the other cations are very well positively correlated with salinity. The correlation coefficient, r between the cations and salinity is sodium 0.66, potassium 0.79, calcium 0.96 and magnesium 0.91. Among the cations sodium is highest in all the three seasons. In pre-monsoon and post-monsoon season the concentration of magnesium is higher than calcium. But in monsoon calcium dominates over magnesium. The spatial and temporal variation of calcium and magnesium is in the same order as that of hardness. The concentration of iron was found to be very low. Spatial variation of cations in the monsoon showed highest distribution at Boat jetty which is the contribution from sewage. The relatively higher amount of magnesium than calcium in most of the stations (pre-monsoon, post-monsoon) indicated a direct impact of sea water (Boyd 2000) (Figure 4.15). The higher proportion of magnesium in monsoon with highest at Boat jetty indicated sewage contribution (Figure 4.16).



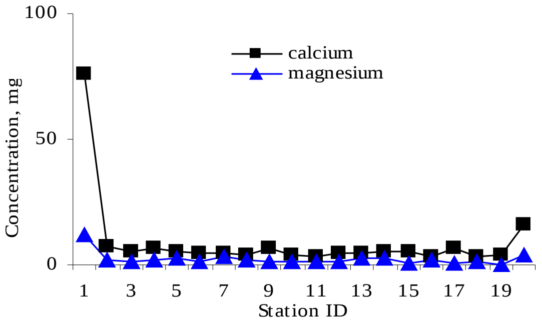


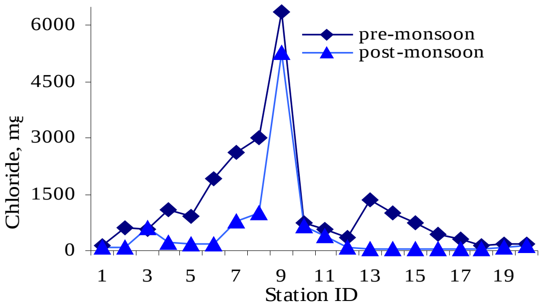
Figure4.15 Variation of **c**alcium and magnesium during pre-monsoon season

Figure 4.16 Monsoonal variation of calcium and magnesium in the lake

4.3.2.10 Chloride

Chloride is one of the most important inorganic ions, being highly soluble and present in virtually all water bodies. Chloride in water influences salinity balance and ion exchange and is contributed by dissolution of salt deposits, sewage discharges, effluents from chemical industries, intrusion from sea, and irrigation drainage to natural waters.

Chloride is distributed seasonally in the pattern pre-monsoon > post-monsoon > monsoon in most of the stations. Monsoonal decrease is due to the dilution and the flushing. The observed chloride concentration in the Vembanad Lake is showing a positive correlation with salinity, with a coefficient of 0.94. So the main source of chloride in the lake is the near by Arabian Sea. The spatial variation showed a decreasing trend towards the southern side (Figure 4.17).



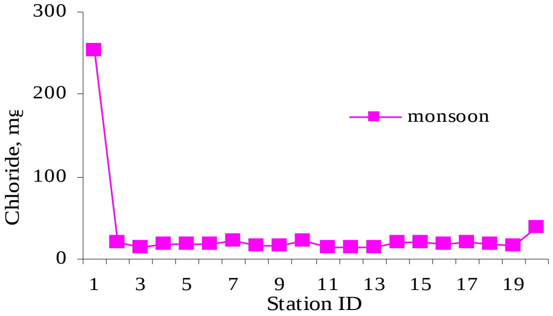


Figure 4.17 Spatial and temporal variation of chloride in Vembanad Lake

4.3.2.11 Sulfate

Sulfate in lake water is primarily related to the types of minerals found in the watershed and to acid rain. Industries that burn coal, releases sulfur compounds into the atmosphere that are carried into lakes by rainfall. According to Esteves (1988), sulphate content in the water is strongly influenced by the geological nature of the underlying rocks. Distance from the sea and the evolutionary stage of the system can also determine the concentration of this element.

The average concentration of sulphate in pre-monsoon, monsoon and post-monsoon seasons are respectively 357mg/l, 5mg/l and 117mg/l. Temporal and spatial variations are given in Figure 4.18. As like chloride, the highest concentration was found at Thanneermukkom. A gradient of sulphate was observed, mainly between summer and winter. A seasonal pattern was found among the sampling stations. This probably indicated that sulphate entered the system from saline mixing. But in monsoon highest concentration at Boat jetty indicated sewage as the main source.

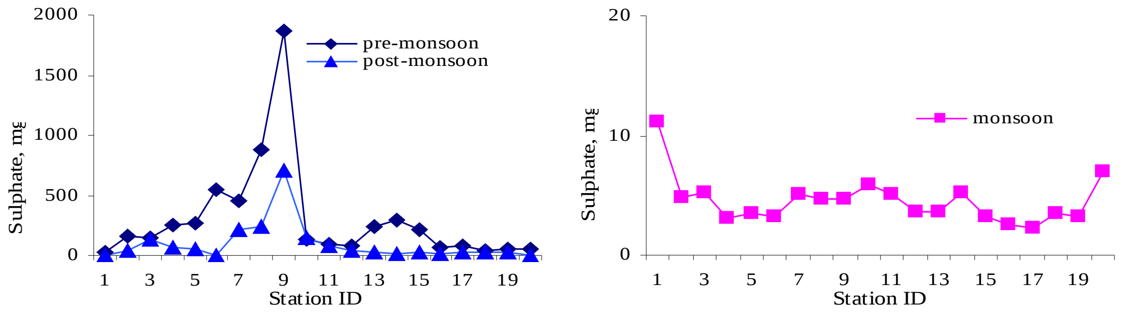


Figure 4.18 Spatial and temporal variation of sulfate in Vembanad Lake

4.3.2.12 Nitrate-N

Nitrogen is the second most important nutrient for plant and algae growth in surface water with only phosphorus being more important (Shaw et al. 2000). Nitrogen is very significant in determining primary production of aquatic systems, and microbial cycling of organic matter. It is added to the lakes by way of precipitation, surface or groundwater drainage and from the fixing of nitrogen from the atmosphere. Nitrogen levels in lakes vary greatly depending on the amount of human activity on the land surrounding the lake.

Generally the concentration of nitrogen in Vembanad Lake is uniform and varied between 0 to 0.4 mg/l in most stations. High concentration of nitrate nitrogen (3.8 mg/l) observed at station Muhamma was contributed from large amount of food residue thrown to the lake at this region. Boat jetty showed a concentration of 3.7mg/l nitrogen which was added from the sewage. Decomposing of organic (plant and animal) matter releases ammonium (NH_4^+); at high pH, this is converted to ammonia (NH_3) which is finally converted to nitrate by bacterial oxidation, which was observed at station Chunkam thodu with 8.2 mg/l of nitrate-nitrogen.

Seasonal variation of nitrogen signified highest distribution in pre-monsoon followed by approximately equal distribution in monsoon and post-monsoon season (Figure 4.19). In some situations nitrogen can limit algae growth. This occurs when the ratio of nitrate plus ammonia to soluble reactive phosphorus is less than 10:1 (at or below this ratio, adding nitrogen will stimulate algae growth). Values between 10:1 and 15:1 are considered transitional, and values greater than 15:1 are considered phosphorus limited (at this or higher ratios, adding phosphorus will stimulate algae growth). The ratio for the present study was greater than 15:1 and hence is phosphorous limited.

4.3.2.13 Phosphate-P

Phosphorus levels in a lake can tell us how productive a lake is in plant growth, and can tell us how human activities on the land surrounding the lake are affecting the lake system. Phosphorus is almost always a limiting nutrient to plant growth in a lake, meaning that plant growth increases at the same rate as phosphorus is added to the system. Phosphorus can enter a lake from the land surrounding the water body by way of sediments, agricultural fertilizer, by septic waste washing into the lake or by way of streams that carry and deposit pollutants in the lake.

A high PO4-P concentration of 1025µg/l was observed at Boat jetty. It shows a similar pattern of distribution as like NO_3-N. Increased phosphorus delivery to lakes occurs in areas where large amounts of sediment are suspended, where human and animal waste are carried in runoff, and where soil fertilizer is delivered to water bodies (Garn 2002), which are observed in the present system. According to Robert G. Wetzel (Robert G. Wetzel 2001) a lake with a total phosphorous content of >100ppb is hypereutrophic, 30-100ppb is eutrophic, 10-30ppb is mesotrophic, 5-10ppb is oligotrophic and <5ppb is ultra-oligotrophic in their level of productivity. Referring to this and to the observed Phosphate-P concentrations the lake is classified into different zones based on their productivity.

Seasonal variation of the phosphorous showed highest concentration in monsoon followed by pre-monsoon and post-monsoon season (Figure 4.20). The concentration of phosphorous in the monsoon season is below detectable limit in most of the stations. Phosphorus does not stay dissolved in water because phosphorus forms insoluble precipitates with calcium, iron, and aluminum, in addition to being taken up by plants. Phosphorus can adsorb to soil particles; however if the soil’s capacity to hold phosphorus is exceeded, the phosphorus will be more likely to leach to the groundwater or be lost to runoff. In the lake, phosphorus can be adsorbed by marl (calcium carbonate) that forms in the lake. When the marl settles to the lake bottom, it can take phosphorus with it. Phosphorus settling in the sediment can remove phosphorus from the water, but this phosphorus can become available again for plant use when rooted macrophytes withdraw phosphorus from the sediment. Also, disturbance and mixing of lake sediments can cause phosphorus to be redistributed throughout the water column

The problem with too much algal growth in a lake is that the blooms can form green scum on the top of the water, which may have a foul odor. More importantly, too much algal growth can disrupt the balance between natural systems in a lake. For example, one consequence of increased algal production is that as the algae die, they fall to the bottom of the lake as dead organic matter. The process of decomposition by bacteria of this organic matter at the bottom of the lake uses valuable oxygen in the deeper, colder waters of lakes. Many lakes with phosphorus and algal population problems become anoxic in the summer, meaning that there is no oxygen in the deep waters of the lake. This can put many cold-water species at risk of death, or extinction as conditions may not be adequate for reproduction or survival to adult stage.

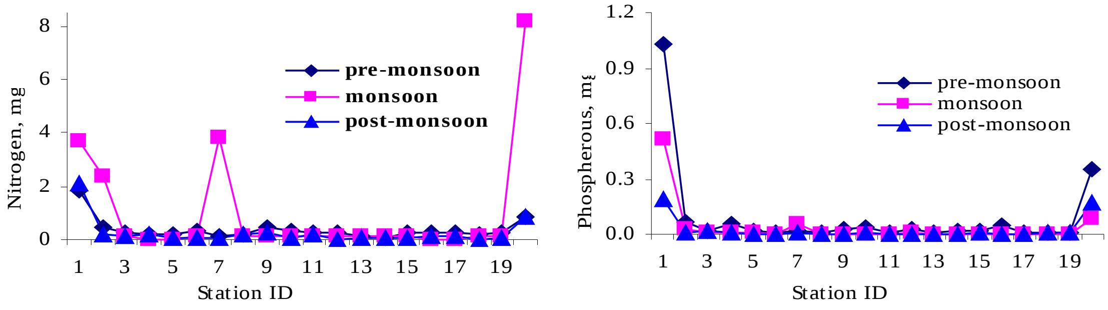


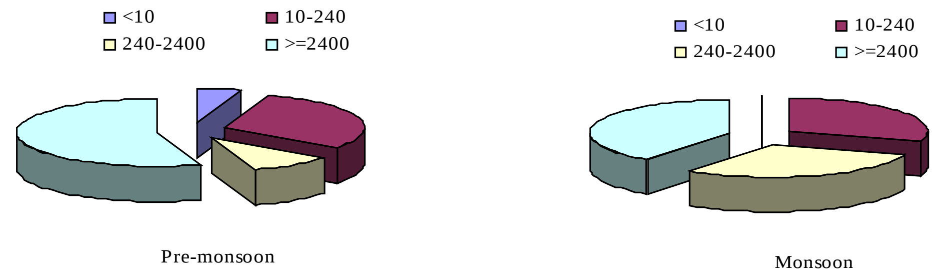
Figure 4.19&4.20 Variation of nutrients (nitrogen and phosphorous) in Vembanad lake

Other lake chemistry may affect phosphorus conditions in a lake. For example, the pH of water affects the transport of phosphorus between the sediments and water in a lake. As the pH of water rises, it promotes the release of phosphorus from sediments. This is called internal loading. Primary production from plants such as algae increases the pH of water, therefore increasing the amount of phosphorus released from sediments. The increase of phosphorus increases the amount of algal growth, making the situation worse, which is a serious problem of concern to the Vembanad wetland system. In order to prevent nuisance algal blooms Shaw et al. (2000) recommend total phosphorus concentrations below 0.030 mg/L in lake water.

4.3.2.14 Microbiological characteristics

Water quality parameters of utmost importance are the Coliform bacteria. Pathogenic organism can cause water born diseases. All the stations were found to be microbially contaminated. While the use of bacterial indicators to measure water quality is wide spread, there is not universal agreement on which indicator organism(s) is most useful, nor are there federal regulations mandating a single standards for bacterial indicators. Thus different indicators and different indicator levels identified as standards are used by water quality programs in different states, countries and regions. Today the most commonly used bacterial indicators are total coliforms, fecal coliforms and Escherichia coli.

The coliform contamination of Vembanad Lake is severe in all seasons. The degree of contamination is found to be more during pre-monsoon season. Seasonal variation of total coliform was in the pattern post-monsoon<monsoon<pre-monsoon (Figure 4.21). The degree of fecal pollution was shown in Figure 4.22. No stations in the monsoon season were free of coliform bacteria (Figure 4.23). The causative factors include tourism activities, discharge of untreated municipal and domestic sewage and poor sanitation in the catchments of Vembanad Lake (Babu et al. 2006).



Pre-monsoon

Monsoon

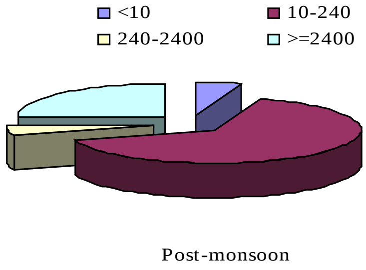
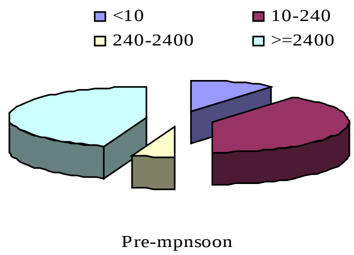


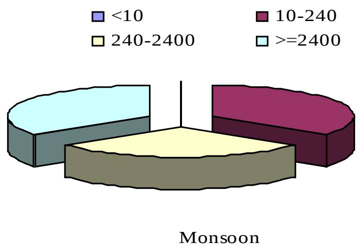
Figure 4.21 Percentage of samples contaminated with Total coliforms

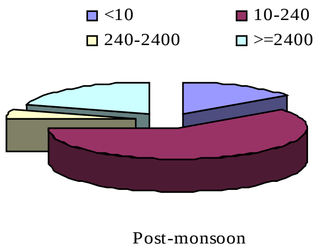
4.3.2.15 Oil and Grease

The problem of oil pollution may be thought in terms of short-term and long-term effects. The short-term effects have been immediately obvious and have been the ones that have received the most publicity. The problems of oil and grease include the reduction in light transmission, depletion in dissolved oxygen, which cases considerable damage for the aquatic life.

The level of oil and grease in the study area was very high and is varied from 0.19mg/l to 0.81mg/l (Figure 4.24). The highest concentration (0.81 mg/l) was found at the station Punnamada were most of the houseboats were playing. Similar concentration was also observed in Chungamthodu. Concentration in the range of 100-1000ppb causes effect on growth and reproduction of aquatic organisms. Stations towards the north showed lower concentration with least at Muhamma.







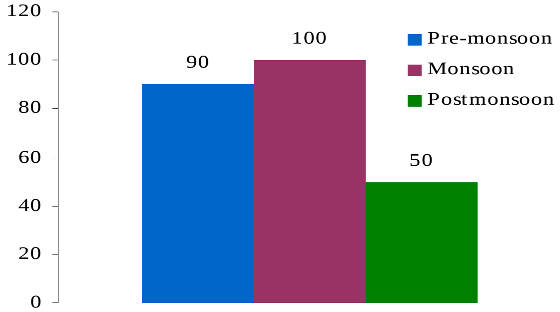


Figure 4.22 Percentage of samples contaminated with fecal coliforms

Figure 4.23 Percentage of samples containing E-coli

4.3.2.16 Biological characteristics-Chlorophyll and Biomass

To get an estimate of the total amount of algae growing in the lake Chlorophyll was estimated. Chlorophyll is the green pigment that is found in all plants which allows them to photosynthesize. The three chlorophylls commonly found in planktonic algae are chlorophylls a, b and c.

The concentration of different chlorophyll pigment for different stations and the variation in bottom of the lake was determined. Concentration of Chlorophyll-*a*, ranged between 2.35mg/m^3 to 19.4 mg/m^3 (Figure 4.25). Chlorophyll-*b* varied between 0.94 mg/m^3 to 11.36 mg/m^3 (Figure 4.26) and chlorophyll-*c* was in the range of 4.93 mg/m^3 to 29.57 mg/m^3 (Figure 4.27). Comparatively higher values of chlorophyll were observed in the samples collected from the bottom of the lake.

Chlorophyll-*a* is a plant pigment whose concentration in water is used to estimate the amount of phytoplankton or algae. Quantitative national standards are not currently established for algae populations and eutrophication. Abnormally high chlorophyll-*a* concentration suggest that excessive nutrients possibly from anthropogenic sources are present in the water. This biological phenomenon of excess nutrient load, heightened vegetative growth, and subsequent low dissolved oxygen which is called eutrophication. The uptake and utilization of nutrients by algae can result in dissolved nutrient levels appearing more moderate than what is actually discharged into the water. The areas in the south especially Chungamthodu was facing such a situation.

Chlorophyll-*a* concentrations in water are used as an estimate of the spatial distribution and frequency of phytoplankton biomass. On an average, 1.5% of algal organic matter is chlorophyll-a. A value of 10 μg/L of chlorophyll-a will translate into 667 μg/L of algal organic matter. An algal organic matter of 1.23 mg/l was observed in the Chungamthodu. The biomass distribution showed a general decreasing trend towards the northern side of the lake.

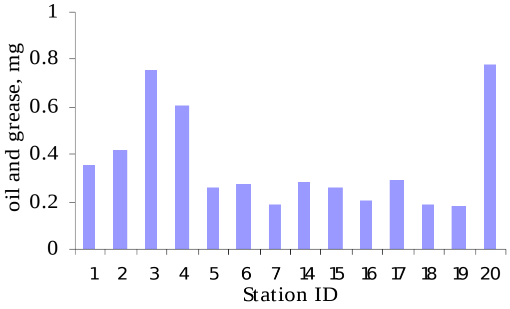


Figure 4.24 Variation of oil and grease

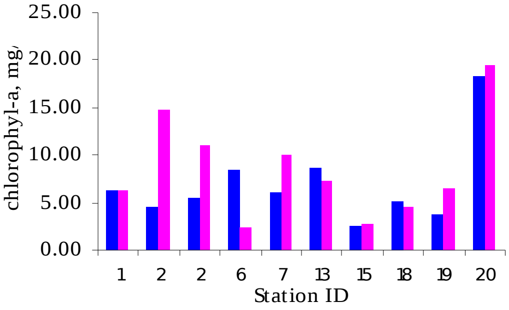


Figure 4.25 Chlorophyll-*a* variation

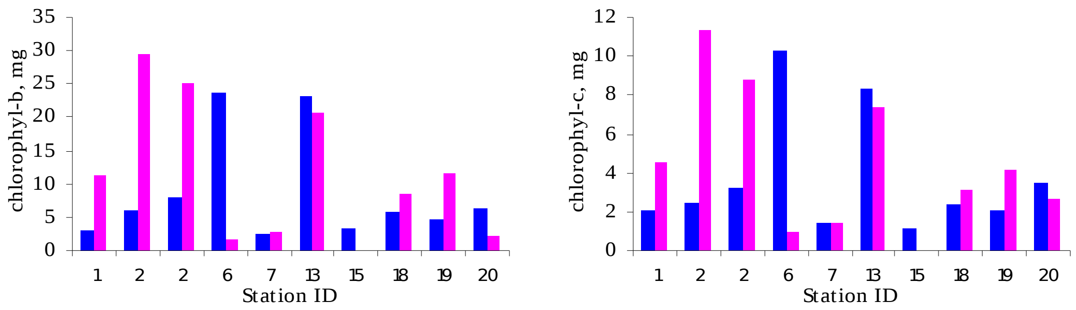


Figure 4.26&4.27 Variation of Chlorophyll-*b*, Chlorophyll-*c* in Vembanad Lake

4.3.3 Irrigational quality status

The suitability of water for irrigation is dependent upon factors such as soil texture and composition, crop grown and irrigation practice, in addition to the chemical characteristics of water. The quality of irrigation water is judged not by the total amount of salts but by the kind of salt it contains. Classification of irrigation waters is an expression of quality of water in terms of one or more variables. It presents the criteria for evaluating the suitability of irrigation water.

Kuttanad is a low lying land around Vembanad Lake having an area of 304sq.km of garden lands and 524sq.km of low lying rice fields, the rest being water bodies. Flooding is a common phenomenon during monsoon due to the discharge of water from rivers in the southern part of the lake. During post-monsoon, the salinity intrusion from Arabian sea through Cochin bar mouth stretch makes the Vembanad Lake more saline. Irrigation parameters of the water samples were determined and classified based on sodium absorption ratio, sodium percentage, soluble sodium percentage, Kelly’s ratio, magnesium hazard ratio, residual sodium carbonate. These parameters and their specifications are given in Table 4.8. The respective values for lake water are given in Table 4.3, and suitability of water for agricultural purpose, based on these parameters is given in Table 4.9&4.10.

The water quality assessment based on irrigation quality thus revealed that during pre-monsoon season, lake water is not suitable for irrigation. But in monsoon water quality is excellent for irrigation. The study strongly recommends the proper operation of Thanneermukkom bund to prevent salinity to the upper reaches of Kuttanad.

4.3.4 Water quality near agricultural areas

Fourteen water samples from the agricultural areas were collected and subjected to physico-chemical and bacteriological analysis. The details of the sampling stations are tabulated in Table 4.11. The results of the analysis were given in Table 4.12 and are discussed below.

The water quality of agricultural areas was good for agriculture in the pre-monsoon season. The pH of the samples varied from 5.88 to 6.85. Abnormal value of color (39 Hazen) was observed at R-block, which is the sample dewatered from the agricultural area. Dewatering causes movements of sediments to the lake which increases the rate of sedimentation of the lake. The electrical conductivity showed a deviation from 56.7µS/cm to 683µS/cm. Highest conductivity was observed at the station Marthandam, which is directly bordering with the lake. Chloride is the dominant anion. In the case of cations sodium dominates over calcium and magnesium. In the alkaline earths present in the sample calcium dominate over magnesium in most stations. Iron concentration varied from 0.04 mg/l to 0.56 mg/l. Chloride has a good correlation with the conductivity, whereas bicarbonate and sulfate have less correlation with salinity. Dissolved oxygen and biological oxygen demand was with in the permissible limit. Bacterial contamination was severe and no stations selected for the present study were free of E-coli.

4.3.5 Tidal study in Vembanad Lake

A study has been conducted to find out the role of tidal movements in the distribution of water quality parameters, salinity in particular along the Vembanad Lake. Starting from 8 am and ending at 8 pm, 56 water samples, at 2 hours interval were collected from the four fixed sites in Vembanad wetland system. The stations include, Pathalam, Ernakulam Boat jetty, Aroorkutty and Thanneermukkom, which are marked in the area map (Figure 4.28). The samples from the bottom of each station were also collected. The results of the analysis were given in Tables 4.13 to 4.16.

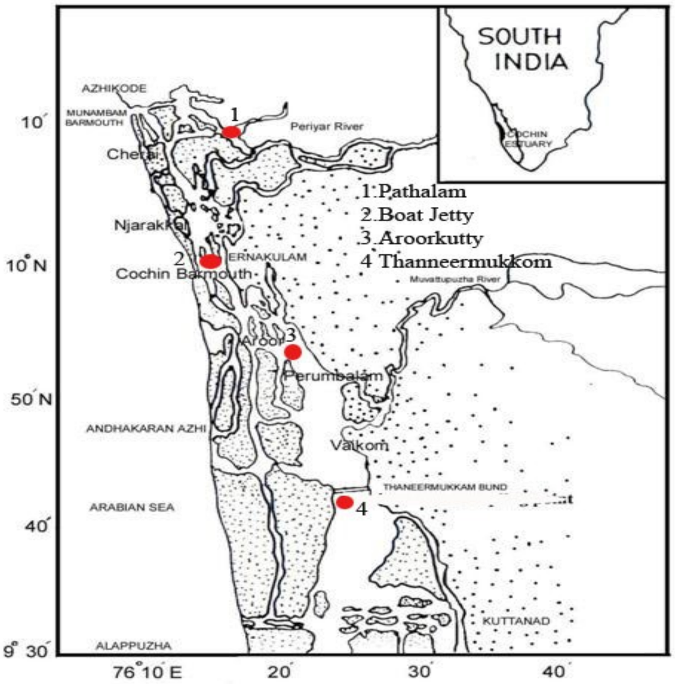


Figure 4.28 Sampling stations for tidal study in Vembanad wetland system

The pH of different stations varied differently in each station based on time and space (Figure 4.29). It has no correlation with the change in salinity. The boat jetty has alkaline pH and has good variation over the time with higher values in the surface samples.

Bottom samples have continuous increase in pH from staring to the ending. Surface samples have small increase in pH till 10 am followed by a continuous decrease till 8pm. All other stations have acidic pH with little change over the time period.

The present study mainly focused on variation of salinity. The temporal variation of salinity at the station boat jetty was directly in accordance with the tidal change. In the morning from 8am, salinity increases till 4pm. After that it decreases corresponding to the low tide. The bottom simples have higher salinity indicating more influence of tide in the bottom. Aroorkutty also have an impact of tide, but it is comparatively less. The low tide influenced the salinity at this station only after 6pm. Spatial variation of salinity has no influence in other stations namely Pathalam and Thanneermukkom (Figure 4.30, 4.31, 4.33). It is greatly due to unexpected rain which flooded the system, even though the sampling was done during pre-monsoon season (in April 2008).

The piper plot for the samples indicated two major groups. One cluster belongs to Pathalam and the other is includes Boat jetty, Aroorkutty and Thanneermukkom (Figure 4.33). It shows that salinity have greater impact towards the southern region (towards Alappuzha). The correlation analysis indicated high correlation of salinity with major cations (Ca, Mg, Na& K) and anions (Cl, SO4). The different ionic ratios such as Ca/Mg, Ca/SO4 and Na/Cl were calculated and compared with sea water. A scatter diagram for sodium and chloride were drawn to understand the mixing of saline water with the fresh water (Figure 4.34). It is confirmed that as it goes away from the estuary the ratios changes greatly.

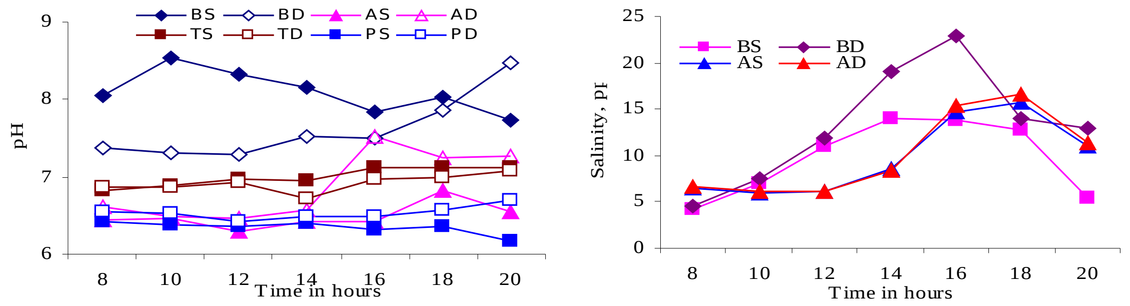
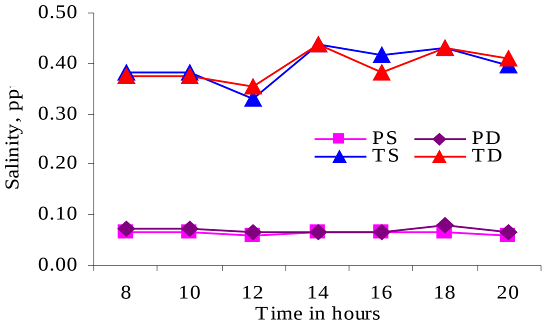


Figure 4.29&4.30 Spatial and temporal variation of pH and salinity



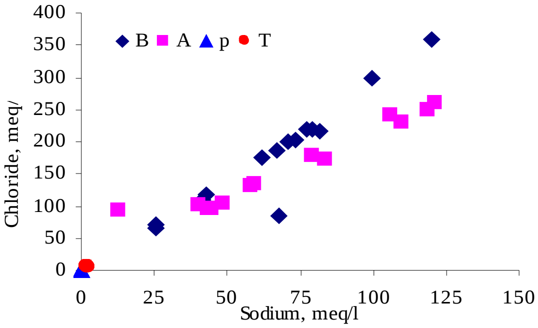


Figure 4.31 Variation of salinity

Figure 4.32 Scatter plot for Na and Cl

Dissolved oxygen was good for aquatic life throughout the study time. It decreases continually at station Aroorkuttty whereas in other stations it increases gradually. Heavy metals were found in Boat jetty and Aroorkutty. Highest concentration of iron, manganese, copper and cadmium detected were 6.6mg/l, 0.2mg/l, 0.045mg/l and 0.059mg/l respectively

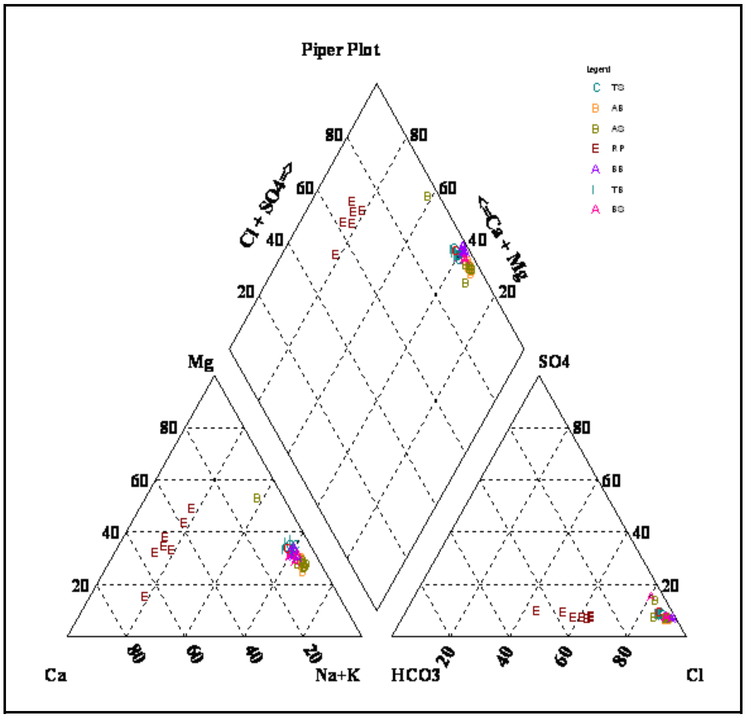


Figure 4.33 Piper plot for the tidal study of Vembanad Lake

4.4 Summary

The study on the spatial and temporal variation in water quality of Vembanad Lake thus gave an insight into the major stresses exposed to the system. Physico-chemical and microbiological analysis of the water sample from the Lake indicated that water quality of the Vembanad Lake is severely threatened by various pollutant sources. Seasonal variation of water quality indicated more problems in the pre-monsoon season. Areas in and around Alappuzha town was found to be hot spot area with reference to water quality. Absence of dissolved oxygen in the southern side may cause serious problems to the aquatic organisms. Biological oxygen demand was very high in these parts. Coir retting is also a reason for the decrease of dissolved oxygen in some regions. Nutrient level in water is as high to cause eutrophication in the system, which is reflected by hypereutrophic status in many parts of the water body. The sewage running through the open canals of Alappuzha is contributing high amount of inorganic and organic components to the water body. The dewatering from the agricultural areas also causes damage to physical and chemical quality of water. The improper management of Thanneermukkom bund flushes high concentrations of ions to the fresh water region where by threatening the ecosystem. Domestic sewage, tourist boats and other anthropogenic activities is the cause of microbiological contamination of the water body. The discharge of organic wastes from the house boats caused high amount of oil and grease in the lake water. High chlorophyll-*a* concentration indicated excessive nutrients in the water body possibly from anthropogenic sources. The water quality assessment based on irrigation quality revealed unsuitable condition for irrigation during pre-monsoon season. The tidal study conducted indicates direct input of ions from the Cochin estuary to the southern side of the wetland system.

Table 4.1 Details of surface water sampling stations of Vembanad wetland system

STATION ID	**STATION NAME**	**North**	**East**
01/V	Boat Jetty	09°29.577'	76°20.523'
02/V	Nehru Trophy	09°30.119'	76°21.197'
03/V	Punnamada	09°31.548'	76°21. 447'
04/V	Komalapuram	09°32.264'	76°21.225'
05/V	Mannancheri	09°33.003'	76°21. 399'
06/V	Centre of lake	09°34.366'	76°23.086'
07/V	Muhamma	09°36.305'	76°21.936'
08/V	Thanneermukkom (North)	09°40.414'	76°23.958'
09/V	Thanneermukkom (South)	09°40.414'	76°23.958'
10/V	Kaipuzhamuttu	09°38.890'	76°25.835'
11/V	Pennarthodu	09°38.316'	76°25.798'
12/V	Kanavattinkara	09°37.706'	76°25.754'
13/V	Kumarakam	09°35.917'	76°25.407'
14/V	Methran kayal	09°33.888'	76°24.903'
15/V	Between Methran,Maran,R-block&H-block	09°33.210'	76°25.986'
16/V	Between Rani&Marthanda	09°32.081'	76°23.019'
17/V	Between Marthanda and Six thousand	09°31.630'	76°23.004'
18/V	Kuppapuram	09°30.997'	76°22.890'
19/V	Kuttamangalam	09°29.375'	76°21.946'
20/V	Chunkam thodu	09°29.629'	76°20.872'

Table 4.2 Characterization of surface water of Vembanad Lake in different seasons on the basis of Piper tri-linear diagram

Subdivisions of the diamond	Characteristics of corresponding subdivisions of diamond shaped field	Percentage of samples		
1	Alkaline earths (Ca+Mg) exceeded alkalies (Na+K)	0	85	15
2	Alkalies exceeded alkaline earths	100	15	85
3	Weak acids (CO3+HCO3) exceeded strongacids (SO4+Cl+F)	0	10	0
4	Strong acids exceed weak acids	100	90	100
5	Cabonate hardness (secondary alkalinity) exceeds 50% (chemical properties are dominated by alkaline earths and weakacids)	0	10	0
7	Carbonate alkali (primary salinity) exceeds 50%(chemical properties are dominated by alkalies and weak acids)	100	15	85

Table 4.3 Chemical characteristics of surface water samples collected temporarily from Vembanad Lake

Stations/ Indices	01/V	02/V	03/V	04/V	05/V	06/V	07/V	08/V	09/V	10/V
SP	63.79	76.8	78.03	79.82	77.21	78.88	79.71	78.61	79.7	78.86
	27.09	40.57	41.18	36.75	38.24	26.18	48.68	40.28	34.37	47.94
	53.01	42.24	76.25	75.52	72.12	73.41	73.11	74.24	76.42	74.99
SAR	4.59	10.42	10.35	15.18	13.65	20.0	23.38	23.63	38.11	12.26
	1.2	0.75	0.67	0.61	0.68	0.32	1.07	0.63	0.53	0.83
	2.65	2.09	8.48	5.94	4.94	4.59	10.06	11.0	29.17	9.32
RSC	0.32	-3.81	-3.27	-6.01	-6.67	-12.53	-15.53	-18.26	-40.99	-3.92
	-0.2	-0.16	0.29	0.34	0.01	0.0	-0.06	-0.06	-0.05	-0.06
	-1.86	-3.31	-2.73	-1.32	-1.29	-0.89	-5.88	-6.16	-34.75	-3.86
MHR	14.31	77.3	73.71	78.81	75.03	82.84	82.52	84.97	80.98	81.06
	20.86	30.8	30.03	33.37	46.19	33.37	53.89	44.48	27.3	37.54
	24.17	81.27	73.0	78.97	78.97	78.6	73.71	70.03	81.84	76.95
SSP	66.01	77.85	78.97	80.69	78.25	79.81	80.53	79.49	80.62	80.1
	28	42.3	42.83	38.44	40.15	27.53	51.14	42.58	36.28	50.95
	55.16	43.05	77.71	77.31	73.93	75.43	74.26	75.46	77.66	76.38
KR	1.94	3.51	3.76	4.18	3.6	3.95	4.14	3.88	4.16	4.03
	0.39	0.73	0.75	0.62	0.67	0.38	1.05	0.74	0.57	1.04
	1.23	0.76	3.49	3.41	2.84	3.07	2.89	3.07	3.48	3.23
PI	87.47	81.72	82.98	82.94	80.44	80.62	81.35	80.12	81.08	83.75
	60.19	109.03	161.59	154.71	123.61	148.59	114.86	129.32	127.25	129.56
	68.27	53.8	81.32	83.94	82.15	85.95	76.14	77.3	78.08	79.47
CAI 1	2.88	16.0	14.58	30.13	24.35	52.64	72.43	83.77	178.15	19.96
	6.87	-0.21	-0.46	-0.18	-0.29	0.17	-0.38	-0.25	-0.21	-0.01
	1.42	1.59	16.75	5.09	4.53	3.72	21.48	27.5	148.68	17.59
CAI 2	-4.69	12.94	11.13	26.4	21.28	49.38	66.81	80.99	175.57	14.5
	2.73	-3.28	-1.95	-3.91	-4.33	-1.52	-4.54	-2.37	-2.13	-2.18
	-27.6	-0.02	13.71	1.99	1.54	-21.99	18.34	24.4	141.43	14.12
Pre-monsoon, Monsoon, Post-monsoon										

Contd…

Stations/ Indices	11/V	12/V	13/V	14/V	15/V	16/V	17/V	18/V	19/V	20/V
SP	78.89	76.66	78.17	78.94	76.12	74.2	77.4	72.06	74.7	62.1
	30.92	28.26	29.92	34.51	32.35	25.66	19.56	32.98	34.77	47
	73.65	68.79	49.5	52.25	53.64	52.13	48.41	41.94	57.08	41
SAR	10.61	7.84	16.38	14.7	11.04	7.71	7.32	4.09	5.38	4.35
	0.37	0.36	0.43	0.59	0.44	0.3	0.23	0.41	0.38	1.45
	6.97	3.28	1.42	1.52	1.62	1.51	1.34	1.03	2.35	2.06
RSC	-3.26	-1.87	-9.2	-6.73	-5.2	-2.95	-1.67	-0.75	-1.05	-2.37
	-0.02	-0.06	-0.08	-0.09	-0.03	0.01	-0.01	0.02	0.13	0
	-2.31	-0.58	-0.55	-0.5	-0.54	-0.5	-0.65	-0.58	-0.9	-0.69
MHR	79.57	73.36	78.75	82.88	74.1	80.51	76.03	70.4	72.25	35.18
	42.9	33.37	45.49	46.19	22.25	50.04	20.03	42.9	0	28.6
	78.81	72.76	72.76	60.04	60.04	70.03	54.58	45.49	70.62	47.96
SSP	80	78.17	79.08	79.72	77.07	75.06	78.56	73.56	76.04	64.19
	32.82	29.81	31.47	36.56	34.02	27.31	20.66	35.32	37.56	49.16
	75.21	71.21	51.66	54.6	56.12	54.49	50.24	43.73	58.81	42.7
KR	4	3.58	3.78	3.93	3.36	3.01	3.66	2.78	3.17	1.79
	0.49	0.42	0.46	0.58	0.52	0.38	0.26	0.55	0.6	0.97
	3.03	2.47	1.07	1.2	1.28	1.2	1.01	0.78	1.43	0.75
PI	82.91	84.76	80.07	81.2	78.96	79.42	84.7	87.59	86.49	73.49
	155.85	135.87	125.11	116.3	139.13	157.53	145.27	160.96	216.67	97.16
	80.59	89	83.14	85.46	84.24	85.42	77.36	78.5	79.34	69.2
CAI 1	14.65	9.1	36.85	27.52	20.29	12.14	7.39	2.76	4.49	4.05
	-0.04	-0.08	-0.22	-0.08	0.16	0.2	0.31	0.13	0.11	0.03
	10.55	2.16	1.09	0.67	1.04	0.68	0.73	0.88	1.74	2.46
CAI 2	8.02	5.44	30.96	24.26	17.21	5.29	4.1	0.14	1.32	0.48
	-0.87	-1.71	-2.43	-2.21	-2.25	-1.91	-1.79	-1.77	-1.36	-5.91
	6.88	0.11	0.37	-1.29	-0.45	-1.22	-0.14	0.39	-1.85	-61.9
Pre-monsoon, Monsoon, Post-monsoon										

Table 4.4 Physico-chemical characteristics of water sample collected from Vembanad Lake during pre-monsoon season

Parameters	01/V	02/V	03/V	04/V	05/V	06/V	07/V	08/V	09/V	10/V
pH	7.35	6.96	6.3	6.69	6.79	6.56	6.63	6.77	6.49	6.43
EC, µ S/cm	976	2180	2070	3310	3640	6110	7600	8880	17800	2490
Salinity, ppt	0.3	0.9	0.8	1.3	1.4	2.4	2.9	3.4	6.8	1.0
Turbidity, NTU	1.3	1.1	1.0	0.9	1.2	0.6	0.9	1.1	1.0	1.0
TDS, mg/l	624.6	1395.2	1324.8	2118.4	2329.6	4198.4	4864	5683.2	11392	1593.6
TA, mg/l	190	36	32	36	32	16	28	20	60	44
TH, mg/l	140	220	190	330	360	640	800	930	2100	232
Ca, mg/l	48	20	20	28	36	44	56	56	160	17.6
Mg mg/l	4.9	41.3	34	63.2	65.6	128.8	160.4	192	413.1	45.7
Na, mg/l	124.8	355.2	327.8	633.6	595	1162.8	1520	1656	4013.2	429.2
K, mg/l	11.2	10.6	8.5	14.5	17.3	29.3	33	39.6	97.8	14.4
Fe, mg/l	0.07	0.05	0.02	0.06	0.03	0.06	0.13	0.06	0.03	0.07
Cl, mg/l	150	600	550	1100	900	1900	2600	3000	6350	740
SO4, mg/l	22.8	165.1	141.7	257	273	550.2	460	883.2	1869.4	128.8
NO3-N	1.86	0.46	0.25	0.22	0.19	0.3	0.16	0.2	0.44	0.32
NO2-N, mg/l	0.019	0.008	0.004	0.002	0.004	ND	0.004	0.004	0.008	0.008
PO4-P, mg/l	1.025	0.063	0.015	0.055	0.022	0.012	0.021	0.012	0.027	0.036
DO, mg/l	0.87	5.93	6.73	5.93	5.53	7.53	6.07	5.93	4.87	2.07
BOD, mg/l	15	2.53	0.67	1.53	1.27	2.73	1.13	2.2	3.13	1.53
Total coliform, MPN/100 ml	≥2400	≥2400	≥2400	1100	150	9	240	≥2400	≥2400	≥2400
Fecal coliform, MPN/100 ml	≥2400	≥2400	≥2400	28	28	9	240	≥2400	≥2400	43
Escherichia coli	P	P	P	P	A	P	P	P	P	P
BDL – Below Detected Level, P- Present, A-Absent										

Contd…

Parameters	11/V	12/V	13/V	14/V	15/V	16/V	17/V	18/V	19/V	20/V
pH	5.85	6.4	6.54	6.37	6.26	7.13	7.1	7.03	7.04	8.91
EC, μ S/cm	1880	1580	4310	3340	2560	1800	1117	449	758	968
Salinity, ppt	0.8	0.5	1.6	1.3	1	0.7	0.4	0.2	0.3	0.4
Turbidity, NTU	1.3	1.1	0.9	1	1.2	1	1.1	0.9	1.5	1.1
TDS, mg/l	1203.2	1011.2	2758.4	2137.6	1638.4	1152	714.9	287.4	485.1	619.5
TA, mg/l	16	32	12	16	12	20	20	20	24	36
TH, mg/l	176	120	470	350	270	164	100	54	72	148
Ca, mg/l	14.4	12.8	40	24	28	12.8	9.6	6.4	8	38.4
Mg mg/l	34	21.4	89.9	70.5	48.6	32.1	18.5	9.2	12.6	12.6
Na, mg/l	323.4	197.4	816.2	632	417	226.8	168.3	69	105	121.8
K, mg/l	9.7	8.5	20.4	13.2	11.6	5.9	5.4	3.3	4.2	10.4
Fe, mg/l	0.11	0.11	0.02	0.05	0.04	0.04	0.03	0.08	0.04	0.04
Cl, mg/l	552	354	1340	1010	750	458	294	128	190	182
SO4, mg/l	88	83.4	245.9	297.6	213.6	60.5	79.2	39	50.7	51
NO3-N	0.26	0.29	0.15	0.04	0.28	0.26	0.26	0.23	0.28	0.84
NO2-N, mg/l	0.008	0.012	0.004	0.004	ND	0.004	0.008	0.004	0.019	0.012
PO4-P, mg/l	0.013	0.025	0.01	0.015	0.015	0.051	0.01	0.011	0.006	0.355
DO, mg/l	0.73	3	6.47	6	5.47	7.07	7	7.33	7.33	3
BOD, mg/l	0.53	2.6	1.8	1	0.8	3.47	1.87	1.47	6	13.67
Total coliform, MPN/100 ml	≥2400	≥2400	240	21	15	150	≥2400	1100	≥2400	≥2400
Fecal coliform, MPN/100 ml	≥2400	460	93	7	15	21	≥2400	210	≥2400	≥2400
Escherichia coli	P	P	P	P	A	P	P	P	P	P
BDL – Below Detected Level, P- Present, A-Absent										

Table 4.5 Physico-chemical characteristics of water sample collected from Vembanad Lake during monsoon season

Parameters	01/V	02/V	03/V	04/V	05/V	06/V	07/V	08/V	09/V	10/V
pH	6.92	7.08	6.89	6.91	6.72	6.89	6.68	6.76	7.03	6.34
EC, µS/cm	422	90	80.1	82.4	88.5	55.8	110.2	69.6	76.7	77.1
Salinity, ppt	0.2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Turbidity, NTU	10.8	8.8	4.4	2	1.2	8	2	3.2	8	4
TDS, mg/l	270.1	57.6	51.3	52.7	56.6	35.7	70.5	44.5	49.1	49.3
TA, mg/l	280	22	42	50	32	22	28	18	24	16
TH, mg/l	240	26	20	24	26	18	26	18	22	16
Ca, mg/l	76	7.2	5.6	6.4	5.6	4.8	4.8	4	6.4	4
Mg, mg/l	12.2	1.9	1.5	1.9	2.9	1.5	3.4	1.9	1.5	1.5
Na, mg/l	42.85	8.75	6.88	6.88	8.01	3.14	12.5	6.13	5.75	7.63
K, mg/l	8.8	1.5	1.1	1.4	1.7	1	2.1	1.4	1.5	1.6
Fe, mg/l	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cl, mg/l	253.8	19.5	13.7	17.6	17.6	17.6	21.5	15.6	15.6	21.5
SO4, mg/l	11.1	4.8	5.2	3.1	3.5	3.3	5.1	4.7	4.7	5.9
NO3-N	3.7	2.4	0.1	ND	ND	0.16	3.84	0.11	0.1	0.1
PO4-P, mg/l	0.51	0.03	0.011	0.012	0.012	BDL	0.059	0.002	BDL	BDL
DO, mg/l	0.07	5.33	5.87	5.53	4.47	6.2	5.87	7.13	7.53	5.27
BOD, mg/l	20	1.3	1.1	1.3	1.4	2.1	0.9	0.2	0.7	0.5
Total coliform, MPN/100 ml	≥2400	460	≥2400	≥2400	240	460	150	93	240	460
Fecal coliform, MPN/100 ml	≥2400	460	≥2400	≥2400	93	150	150	93	240	460
Escherichia coli	P	P	P	P	p	P	P	P	P	P
BDL – Below Detected Level, P- Present, A-Absent										

Contd…

Parameters	11/V	12/V	13/V	14/V	15/V7	16/V7	17/V7	18/V7	19/V7	20/V7
pH	6.39	6.52	6.77	6.73	6.67	6.68	6.94	6.43	6.51	6.67
EC, µS/cm	52.2	61.2	69.9	89.4	62.2	51.1	59.8	51.6	55	244
Salinity, ppt	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.1
Turbidity, NTU	5.6	4.8	3.2	2.4	4.8	2	1.6	3.2	3.6	3.6
TDS, mg/l	33.4	39.2	44.7	57.2	39.8	32.7	38.3	33	35.2	156.2
TA, mg/l	16	18	22	26	20	20	24	18	20	68
TH, mg/l	14	18	22	26	18	16	20	14	10	56
Ca, mg/l	3.2	4.8	4.8	5.6	5.6	3.2	6.4	3.2	4	16
Mg, mg/l	1.5	1.5	2.4	2.9	1	1.9	1	1.5	0	3.9
Na, mg/l	3.14	3.51	4.64	6.88	4.26	2.76	2.39	3.51	2.76	24.86
K, mg/l	1	1.1	1.3	1.9	1.1	1.1	1.1	1.2	1	4
Fe, mg/l	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cl, mg/l	13.7	13.7	13.7	19.5	19.5	17.6	19.5	17.6	15.6	39.1
SO4, mg/l	5.1	3.6	3.6	5.2	3.3	2.6	2.3	3.4	3.3	7
NO3-N	0.11	0.12	0.13	0.11	0.13	BDL	BDL	0.14	0.12	8.2
PO4-P, mg/l	0.001	0.011	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.087
DO, mg/l	6.67	5.67	6.2	5.27	5.73	6.27	6.8	5.8	6.8	2.2
BOD, mg/l	1.2	0.5	1.1	1.3	1.5	3.3	0.5	4.4	1.9	13
Total coliform, MPN/100 ml	≥2400	1100	93	1100	93	≥2400	460	≥2400	≥2400	≥2400
Fecal coliform, MPN/100 ml	1100	1100	93	1100	93	≥2400	460	≥2400	≥2400	≥2400
Escherichia coli	P	P	P	P	p	P	P	P	P	P
BDL – Below Detected Level, P- Present, A-Absent										

Table 4.6 Physico-chemical characteristics of water sample collected from Vembanad Lake during post-monsoon season

PARAMETERS	01/V	02/V	03/V	04/V	05/V	06/V	07/V	08/V	09/V	10/V
pH	6.83	6.92	6.42	6.5	6.67	6.68	6.33	6.17	6.23	6.74
EC, µS/cm	602	525	1616	796	716	561	2620	2950	13890	2020
Salinity, ppt	0.09	0.1	0.62	0.21	0.19	0.16	0.79	1.0	5.3	0.65
Turbidity, NTU	9.0	6.0	0.3	0.3	0.2	0.7	0.5	0.5	0.3	0.8
TDS, mg/l	385	336	1034	509	458	359	1677	1888	8890	1293
TA, mg/l	128	32	14	12	14	14	12	14	26	18
TH, mg/l	116	192	148	76	76	56	304	320	1760	208
Ca, mg/l	35.2	14.4	16	6.4	6.4	4.8	32	38.4	128	19.2
Mg, mg/l	6.8	37.9	26.2	14.6	14.6	10.7	54.4	54.4	349.9	38.9
Na, mg/l	65.5	66.7	237	119	99	79	403	452	2812	309
K, mg/l	8.2	5.1	9.9	6.2	5.7	4.9	14.6	16.7	100	12.7
Cl, mg/l	92	96	615.4	212	190	160	790	1000	5300	650
SO4, mg/l	4.8	44.8	130.6	61.2	52.8	6.4	207.6	238.8	705	146.4
NO3-N	2.11	0.22	0.117	0.185	0.061	0.055	0.067	0.193	0.236	0.062
PO4-P, mg/l	0.194	0.006	0.017	0.008	ND	0.002	0.008	0.003	ND	0.006
DO, mg/l	0.53	6.07	5.87	7.07	8.13	7.4	9.47	4.33	4.87	10.33
BOD, mg/l	19	0.2	1.0	0.53	2.2	1.0	0.8	1.0	0.5	3.47
Total coliform, MPN/100 ml	≥2400	240	23	15	150	15	43	150	240	240
Faecal coliform, MPN/100 ml	≥2400	240	23	15	93	9	43	21	150	240
Escherichia coli	P	A	A	A	A	A	P	P	P	P
BDL – Below Detected Level, P- Present, A-Absent										

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pH	11/V	12/V	13/V	14/V	15/V	16/V	17/V	18/V	19/V	20/V
EC, µS/cm	6.99	6.73	7.17	6.8	6.62	6.55	6.46	6.49	6.89	7.26
Salinity, ppt	1237	417	176.7	183.9	192.6	193.7	193.7	175.4	396	770
Turbidity, NTU	0.4	0.1	0.06	0.05	0.06	0.05	0.05	0.05	0.09	0.12
TDS, mg/l	0.8	0.3	0.5	0.3	0.3	0.5	0.6	0.4	0.9	3.5
TA, mg/l	792	267	113	118	123	124	124	112	253	493
TH, mg/l	20	18	20	18	16	18	14	18	28	192
Ca, mg/l	132	44	44	40	40	40	44	44	68	192
Mg, mg/l	11.2	4.8	4.8	6.4	6.4	4.8	8	9.6	8	40
Na, mg/l	25.3	7.8	7.8	5.8	5.8	6.8	5.8	4.9	11.7	22.4
K, mg/l	184	50	21.6	22.1	23.5	22	20.4	15.7	44.6	65.7
Cl, mg/l	8.8	4.2	3.1	3.1	3.3	3.1	2.6	2.6	3.9	10.8
SO4, mg/l	400	104	60	50	60	50	50	50	90	120
NO3-N	83.6	35.2	29.6	16.7	22.1	17	25.7	27.3	20.2	2.2
PO4-P, mg/l	0.19	BDL	0.048	0.04	0.039	0.102	0.142	0.009	0.044	0.86
DO, mg/l	0.002	0.003	0.002	0.002	0.006	0.004	0.003	0.013	0.007	0.168
BOD, mg/l	3.93	3.87	7.2	6.73	6	5.2	5.6	5.07	13.93	6
Total coliform, MPN/100 ml	0.8	0.27	0.53	0.07	0.47	0.6	0.58	0.63	9.4	10
Faecal coliform, MPN/100 ml	≥2400	≥2400	21	9	21	93	150	1100	≥2400	≥2400
Escherichia coli	1100	≥2400	21	9	7	23	150	210	≥2400	≥2400
	A	P	P	A	A	A	A	P	P	P
BDL – Below Detected Level, P- Present, A-Absent										

Table 4.7 Statistical analysis of surface water quality data of Vembanad Lake

Seasons	Pre-monsoon				Monsoon				Post-monsoon			
Parameters	Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD
pH	8.91	5.85	6.83	0.62	7.08	6.34	6.73	0.21	7.26	6.17	6.68	0.29
EC, m S/cm	17800	449	4185	4021.2	422	51.1	110	87.02	13890	175.4	2013.5	3028.4
Salinity, ppt	6.8	0.2	1.61	1.54	0.2	0.1	0.15	0.07	0	0	0	1.16
Turbidity,	1.5	0.6	1.06	0.19	10.8	1.2	4.51	2.65	9	0.2	1.6	2.27
TDS, mg/l	11392	287.4	2691.4	2583.5	270.08	32.7	70.46	55.69	8890	112	1289	1938.1
TA, mg/l	190	12	41.1	38.37	280	16	49.18	58.12	192	12	34	45.2
TH, mg/l	2100	54	455.5	467.68	240	10	40.91	49.71	1760	40	261	378.1
Ca, mg/l	160	6.4	38.5	33.52	76	3.2	11.85	15.98	128	4.8	24.4	28.06
Mg mg/l	413.1	4.9	87.1	94.49	12.15	0	2.72	2.47	349.9	4.9	48.5	75.67
Na, mg/l	4013.2	69	817.1	904.38	42.85	2.39	9.66	9.54	2812	15.7	360.9	615.73
K, mg/l	97.8	3.3	21.4	21.02	8.8	1	2.12	1.77	100	2.6	15.1	21.26
Cl, mg/l	6350	128	1346.6	1457.17	253.83	13.67	39.58	52.93	705	2.2	117.5	158.92
SO4, mg/l	1869.4	22.8	356.9	425.75	11.12	2.32	4.74	1.95	5300	50	704.1	1163.25
NO3-N	1.86	0.04	0.418	0.39	8.2	0.1	1.55	2.28	2.11	0.009	0.329	0.49
PO4-P, mg/l	1.025	0.006	0.129	0.23	0.51	0	0.1	0.16	0.194	0.002	0.032	0.06
DO, mg/l	16.2	0.73	5.54	2.14	7.53	0.07	5.38	1.7	13.93	0.53	6.46	2.76
BOD, mg/l	15	0.53	3.66	3.99	20	0.2	3.55	4.89	19	0.07	3.28	4.77

Table 4.8 Water quality parameters and their suitability for irrigation

Parameter	Calculation, meq/l	Range	classification
Sodium Percentage	(Na*100) / (Na+Ca+Mg+K)	<20	Excellent
		20-40	Good
		40-60	Permissible
		60-80	Doubtful
		>80	Unsuitable
Sodium Absorption Ratio	(Na) / ((Ca+Mg)/2)$^{1/2}$	<10	Excellent
		10--18	Good
		18-26	Fair
		>26	Poor
Magnesium Hazardous Ratio	(Mg*100) / (Ca+Mg)	<50	Suitable
		>50	Unsuitable
Residual Sodium Carbonate	(HCO3)-(Ca+Mg)	<10	Excellent
		10-18	Good
		18-26	Fair
		>26	Poor
Soluble Sodium Percentage	(Na*100) / (Ca+Mg+Na)	<20	Excellent
		20-40	Good
		40-60	Permissible
		60-80	Doubtful
		>80	Unsuitable
Kelly's Ratio	(Na) / (Ca+Mg)	<1	Suitable
		1--2	Marginal
		>2	Unsuitable

5.0 Groundwater Quality status of Vembanad Wetland System

5.1 Introduction

Groundwater is a sustainable source of freshwater and its popularity is growing day by day. It is the largest source of freshwater on the planet excluding the polar ice and glaciers. Groundwater acts as a reservoir by virtue of large pour space in earth material as conduit, which can transport water over long distances and act as a mechanical filter, which improves water quality by removing suspended solids and bacterial contaminations (Sharma 1997).

Groundwater constitutes an important component of many water resources systems, supplying water for domestic use, for industry, and for agriculture. At present, nearly one-fifth of all water used in the world is obtained from groundwater resources. Agriculture is the greatest user of water, accounting for 80% of all consumption. Approximately 15% of world’s crop land is irrigated by groundwater. The present irrigated area in India is 60 million hectares of which about 40% is from groundwater (Raghunath 1987).

5.1.1 Groundwater and wetlands

Groundwater is one of the most important components of wetland hydrology, both for quantitative and qualitative purposes, but probably is also one of the most difficult to quantify (Carter 1986). Groundwater can be the dominant component of the water budget of a wetland (Winter 1999, Bendjoudi et al. 2002) or only a small part of it (Brinson 1993, Mitsch and Gosselink 1993, Gilman 1994, Fustec and Lefeuvre 2000) but, whatever its quantitative contribution, groundwater input is important for the physical and chemical quality of wetlands (Hill 1990, Devito and Dillon 1993, Hayashi and Rosenberry 2002). Although groundwater behavior is considered to be less variable than that of other hydrological systems, it may be difficult to collect all the data necessary for the calculation of groundwater inflow to and outflow from wetlands (hydraulic gradients, 3D geometry of the wetland and its surroundings, hydraulic conductivity of the soil).

Combining field studies and hydrological modeling generally helps to test hypotheses about the functioning of a wetland as well as quantifying the importance of groundwater in the ecosystem (Tchamen and Kahawita 1998, Morrison et al. 1999, Gasca-Tucker and Acreman 2000, Su et al. 2000, Weng 2000). Improving the understanding of how wetlands function and describing and quantifying their buffer role (during floods or in nitrate retention and elimination for example), will help authorities to manage such ecosystems in a sustainable development manner. Wetlands serve to maintain water supplies by functioning as groundwater recharge sites and augmenting low flows in adjacent streams and lakes.

5.1.2 Geochemistry of groundwater

The subsurface of earth can be thought of as dynamic geochemical systems. In the natural geochemical system, fresh recharge water with few dissolved constituents and low concentration contacts with the subsurface material and interacts with the other phases of the system.

The dissolved solutes in the groundwater are derived from the dissolution or leaching of the solid phase and from the dissolution of gases from the air or production of gases by chemical reaction. These reactions continue as long as disequilibrium exists between the phases. Solution concentration may stabilize if the dissolved concentration of its components of the solids and/or gases achieves chemical equilibrium. This types of geochemical process are aqueous complexation, oxidation/reduction process, pH dependent redox reactions, gas exchange processes etc.

The water/rock interaction are the geochemical process that soil scientists have studied for decades to optimize plant growth and the groundwater scientists/engineers are now using to understand the chemical facet of subsurface conditions. Along with the physical and biological processes active in the subsurface, geochemistry plays a major role in controlling groundwater composition and the movement of dissolved constituents.

Thirty years ago the main use of geochemistry to groundwater was an aid in differentiating water types in aquifers to help identify and quantify water resources. Today geochemistry plays a much larger role in groundwater studies because of its importance of in characterizing the natural system, understanding contaminant migration and designing remediation programme (William J. Deutsch 1997).

5.1.3 Groundwater pollution

As vital source for drinking and irrigation, groundwater has to meet all physical and chemical parameters for safe use. Though generally considered as safe, groundwater is often liable to contamination through anthropogenic and other sources as alien substances get dissolved in the recharging water. Groundwater contamination is a socio-economic problem that receives considerable attention in modern industrialized societies.

Untreated industrial effluents or municipal wastewaters, leachates from chemical fertilizers and pesticides in the agricultural fields or from land fills and industrial dumpsites are some of the potential sources of contamination (Satake et al. 1997). Adverse water quality may also be due to natural geological sources like high fluoride content from fluorites minerals, iron and manganese from laterites, hexavalent chromium from chrome ores, and arsenic from arsenic containing minerals. In the coastal areas high salinity is a common contaminant originating from seawater ingress or saline water entrapped in older sediments. Apart from point and non-point source of pollution, the principal mechanisms that affect the quality of groundwater can be classified into hydrogeological factors and management factors (Mehran 1997).

5.1.4 Impacts of groundwater pollution

Some 45 million people the world over are affected by water pollution marked by excess fluoride, arsenic, iron, or the ingress of salt water. It is important to realize that groundwater is not a resource that could be utilized unmindfully simply because it is available in abundant quantities.

Groundwater pollution causes irreversible damages to soil, lands, and animals including man. Polluted groundwater is the major cause for the spread of epidemic and chronic diseases in men. It may cause typhoid, jaundice, dysenty, diarrehoe, tuberculosis etc. Groundwaters always causes suffer from being out of sight and hence out of mind and still a matter of wide range of ignorance. Routine monitoring of either groundwater level or quality is rare and non-existed for many centuries. Problems and issues such as water logging, salinity, agricultural toxins, and industrial effluents, all ends up to groundwater pollution.

5.2 Methodology

Groundwater sampling points were fixed around the Vembanad Lake. Thirteen groundwater samples were collected from shallow dug wells, (depth up to 4m) bore wells, (depth up to 800m) and from a small pond (depth 3.5m). The details of the sampling stations are given in Table 5.1 and are marked in the area map (Figure 5.1). Different physico-chemical parameters were determined based on the procedure discussed in APHA (1995). Total coliform, Fecal coliform, E-coli were analyzed using the most probable number method. The analytical procedures for the determination of different parameters were discussed in chapter 3.

5.3 Results and discussion

5.3.1 Hydrochemistry of major ions

Generally the characteristic hydrochemical classification in the study area based on chemical composition of the water sample is different in major aquifers. However most of them showed sodium-calcium-chloride-bicarbonate type. The ionic composition of the groundwater is dominated by major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and anions (Cl^{-}, HCO_3^{-}, and SO_4^{2-}).

Chemical data of the study areas are presented by plotting them on a piper tri-linear diagram (Figure 5.2). These diagrams reveal the analogies, dissimilarities and different types of waters in the study area, which are identified and listed in Table 5.2. Different hydrochemical facies observed in the diagram clearly explains the variations or domination of cation and anion concentrations. The relative proportion of the alkali and alkaline earth elements showed that, 47% of the sample exceeded alkali group compared to alkaline earths. For anion concentration, 70% of the samples predominated for strong acids such as chloride and sulphate.

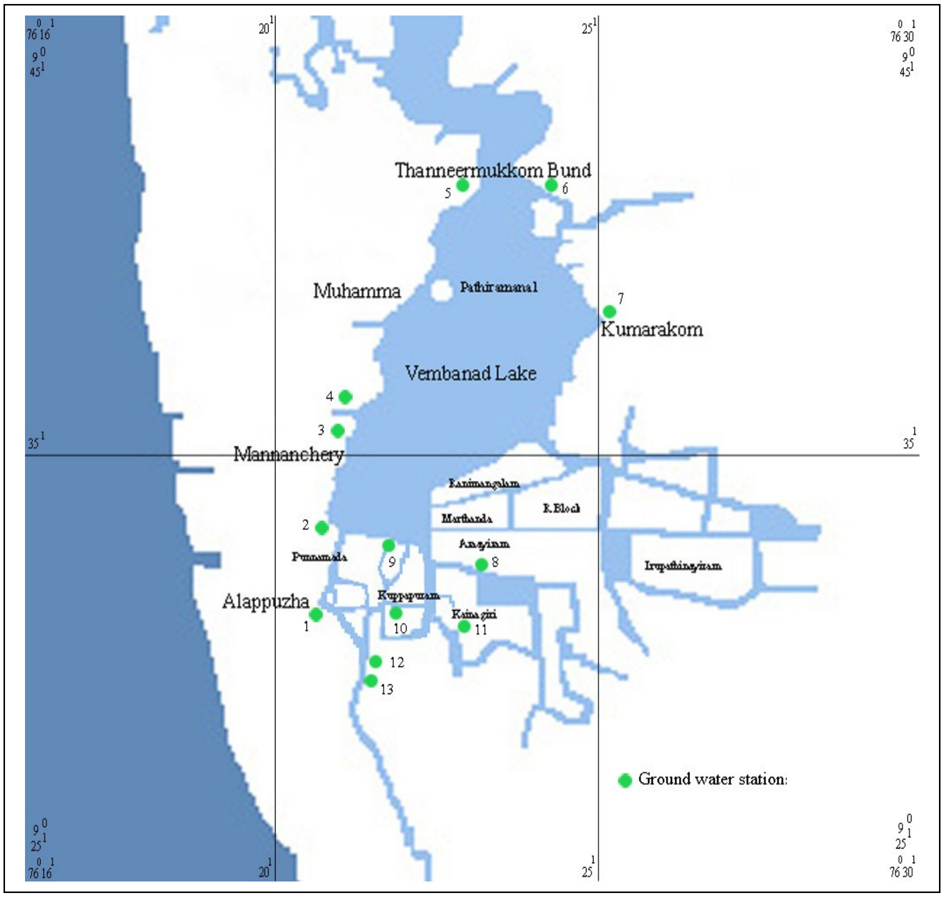


Figure 5.1 Map of Vembanad lake showing groundwater sampling stations

It is generally difficult to find any significant criterion in the chemical classification of groundwater for distinction of the different aquifer types. However based on the major cations four groups of samples were identified, which include 1). $Na^+>Ca^{2+}>Mg^{2+}>K^+$ 2). $Na^+>Ca^{2+}>K^+>Mg^{2+}$ 3). $Na^+>K^+>Ca^{2+}>Mg^{2+}$ 4). $Ca^{2+}>Na^+>K^+>Mg^{2+}$ 5). $Ca^{2+}>Na^+>Mg^{2+}>K^+$. Similarly based on the major anions three groups of samples were identified in the aquifer system, which are 1). $HCO_3^- > Cl^- > SO_4^{2-}$ 2). $Cl^- > HCO_3^- > SO_4^{2-}$ 3). $Cl^- > SO_4^{2-} > HCO_3^-$. Numerous chemical and physical reactions and interactions of the percolating rain water with underlying rocks have been interpreted as producing the groups.

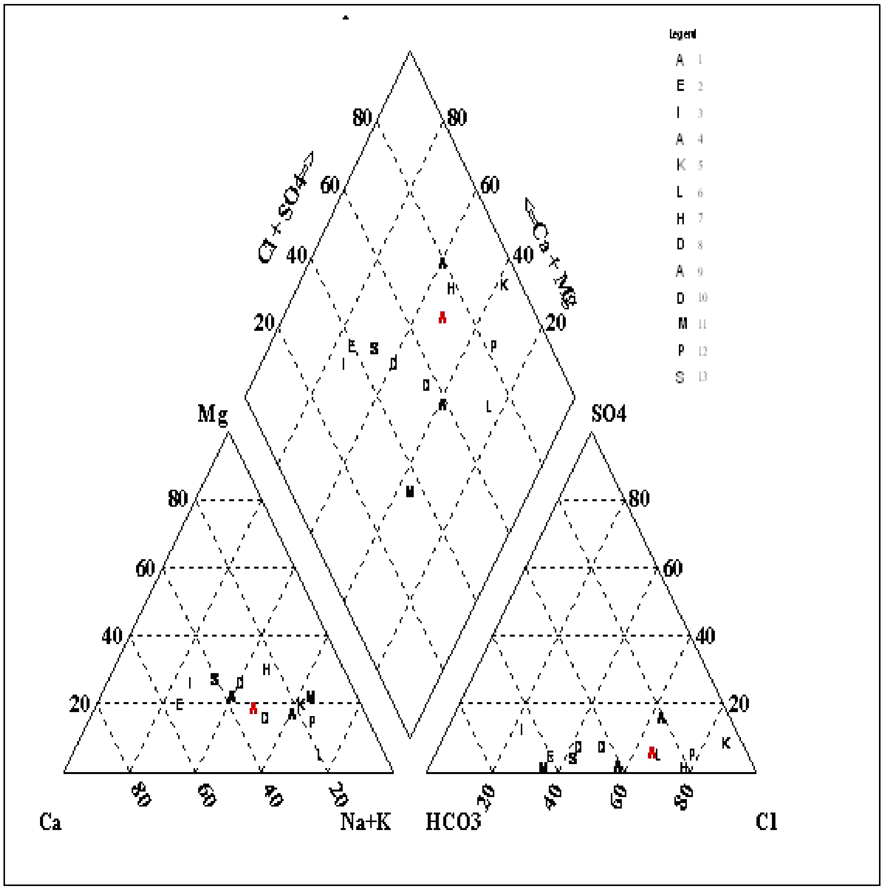


Figure 5.2 Piper classification for groundwater samples

The plot of Na^+ versus Cl^- can be used as a first order indicator of water-rock interaction. Although sodium and chloride exhibit a good correlation (Figure 5.3), halite dissolution may exert a control on the Na^+ and Cl^- chemistry. The highest Na/Cl ratio was observed for the sample collected from a bore well at Pallathuruthi (1.32) whereas all the other samples showed low Na/Cl ratio. The existence of the abundant Na^+ may promote cation exchange. This is confirmed by two indices of base exchanges (IBE), namely chloro-alkaline indices. When there is an exchange between sodium or potassium in groundwater with calcium or magnesium in the aquifer material, both of the indices are positive, indicating ion exchange of sodium in groundwater with calcium or magnesium in the alluvial or weathered materials. In the present study 38% of the samples showed the presence of ion exchange reactions in the aquifer.

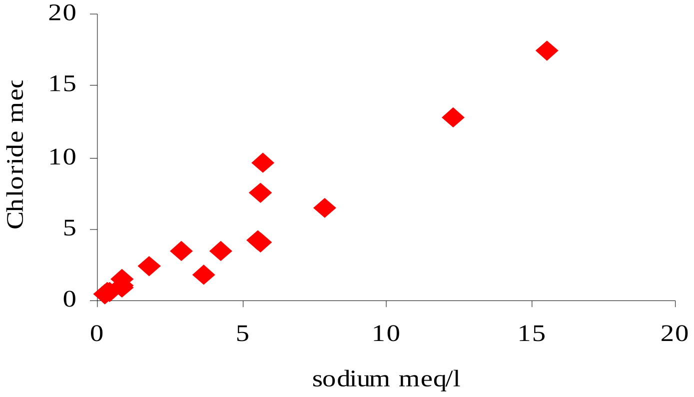


Figure 5.3 Sodium versus chloride plots for the groundwater sample

The different chemical characteristics such as sodium absorption ratio, sodium percentage, soluble sodium percentage, Kelly's ratio, magnesium hazard ratio, residual sodium carbonate, chloro-alkaline index and Gibb's ratio of the groundwater samples were calculated and their values are given in Table 5.3.

Chemical classification of the groundwater samples based on irrigation use can be done by plotting the SAR value against their specific conductance in the USSL diagram, (Figure 5.4). Most of the samples belongs C1S1, C2S1 and C3S1 group, with higher salinity hazard compared to sodium hazard. Accordingly all the shallow groundwater samples in the basins of Vembanad Lake except at Kumarakam are good for agriculture. The deep bore wells and shallow open well at Kumarakom showed higher salinity hazard which decreased the suitability of water for irrigational use.

Wilcox classification of water samples for irrigation purposes based on percent sodium and EC were applied for the groundwater samples (Figure 5.5). The percentage of samples based on irrigational use was calculated. It is observed that about 54% of samples were excellent to good for irrigation. The shallow open well in Kumarakom and the two bore well samples from Pandicheri and Mangalacheri were doubtful to unsuitable for irrigation based on Wilcox classification.

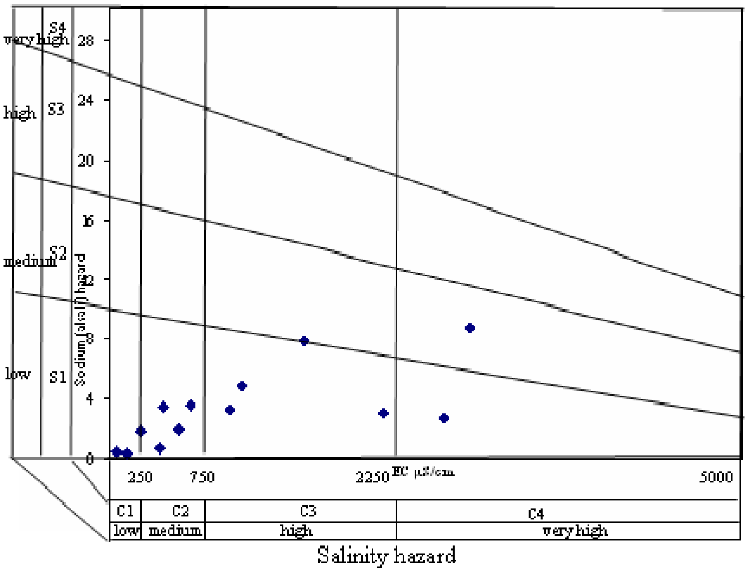


Figure 5.4 USSL Classification of groundwater samples around Vembanad Lake

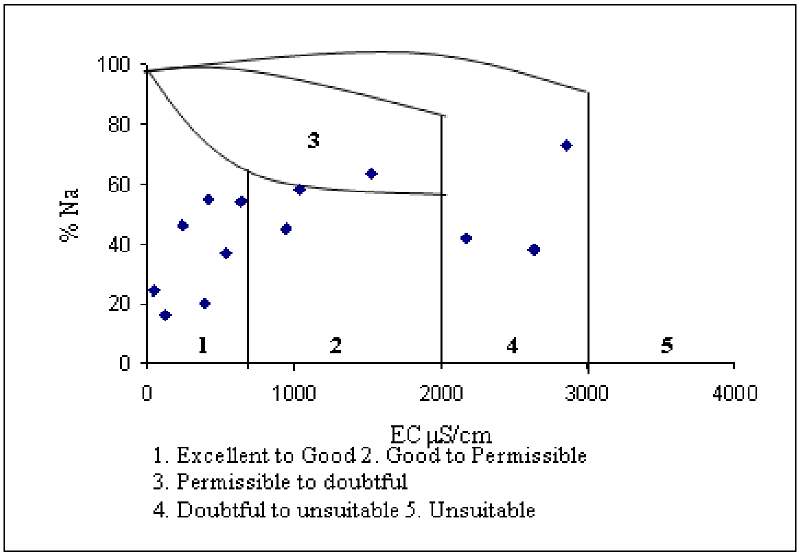


Figure 5.5 Wilcox diagram of groundwater samples around Vembanad Lake

The respective ionic ratios (anions = Cl/(Cl+HCO$_3$), cations = (Na+K)/ (Na+K+Ca) proposed by Gibbs(1970) to understand the relationship of the chemical component of waters from their respective aquifer lithologies have been used in the present study. Gibbs ratios for the study area samples are plotted against their respective total dissolved solids (Figure 5.6) to know whether groundwater chemistry is due to rock dominance, evaporation dominance or precipitation dominance. The results indicated 77% samples of rock dominance and 13% of evaporative enrichment.

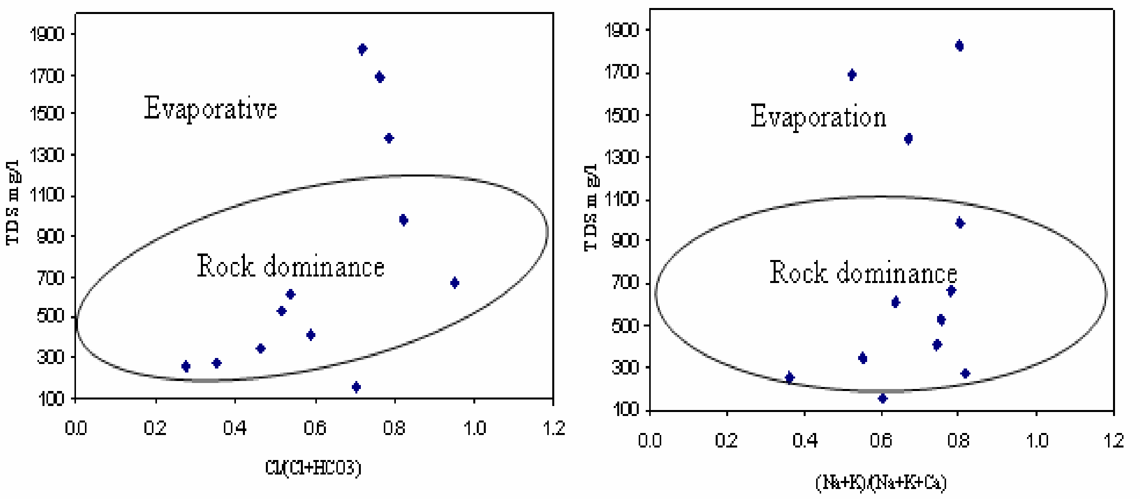


Figure 5.6 Mechanism controlling the chemistry of groundwater

5.3.2 Groundwater quality

The increased popularity and use of groundwater as the main source of potable water supply world wide, is probably due to its readily availability, cool temperatures, ability to undergo natural purification, etc which make it attractive (USGS 1999). The primary purpose of a water analysis is to determine the suitability of water for a proposed use. The three main classes of use are domestic (house hold), agricultural, and industrial. A supply intended for municipal use may include all three classes and accordingly require a standard of quality that is generally higher than that needs for any one class. On the other hand, water for use in a particular industry may require a quality that is substantially higher than the one considered acceptable for a municipal supply.

The result of the physico-chemical and bacteriological analysis of the water samples are summarized in Table 5.4 and correlation coefficient for each variable was given in Table 5.5. The results of the analysis were compared with the drinking water standards reported by Bureau of Indian Standards (BIS). Basic statistics including maximum, minimum, mean and standard deviations reported for the hydrochemical variables are given in Table 5.6. The results of the analytical data are discussed in the following sections.

5.3.2.1 pH

The pH of groundwater responds to variations in dissolved carbon dioxide concentrations, alkalinity, hydrogen ion concentrations and in a small way to temperature. In the study area pH values were in between 6.17 to 7.34 with an average value of 6.87. Accordingly all the samples are in desirable limit of pH proposed by BIS. The highest pH observed in the deep bore well samples of Pallathuruthi might have contributed from long term agricultural practices. The high pH observed in the shallow groundwater is a direct consequence of sewage running through the near by canal. If the water body contains humic acid and fulvic acid components from the organic matter of sediments the pH of the water can be low, which is reflected in the present study. The variation of pH in different stations is given graphically in Figure 5.7.

5.3.2.2 Color

In majority of the samples, color was found to be beyond the desirable limit set by BIS (5 Hazen). In the sample collected from Pandichery, the value recorded was only 2.3 Hazen. The color has good correlation with turbidity (0.95) and iron (0.95). The sample from Kuppapuram has the highest value (69 Hazen), which is in the paddy field adjacent to the lake. The shallow well at Thanneermukkom had also high color and foul smell.

5.3.2.3 Turbidity

Turbidity is a measure of water clarity. It is an optical property that expresses the degree to which light is scattered and absorbed by molecules and particles. Turbidity results from soluble colored organic compounds and suspended particulate matter in the groundwater column. In the study area the turbidity values are below 5 NTU in majority of the sampling points except for the samples collected from the station Kuppapuram (17 NTU).

5.3.2.4 Electrical Conductivity

Electrical Conductivity of the groundwater samples varied from 50µS/cm to 2850µS/cm. The shallow well at Kumarakom and the deep bore wells had comparatively high conductivity. This indicated presence of mineralized substances in water. The sample from Kainagiri reported the lowest value.

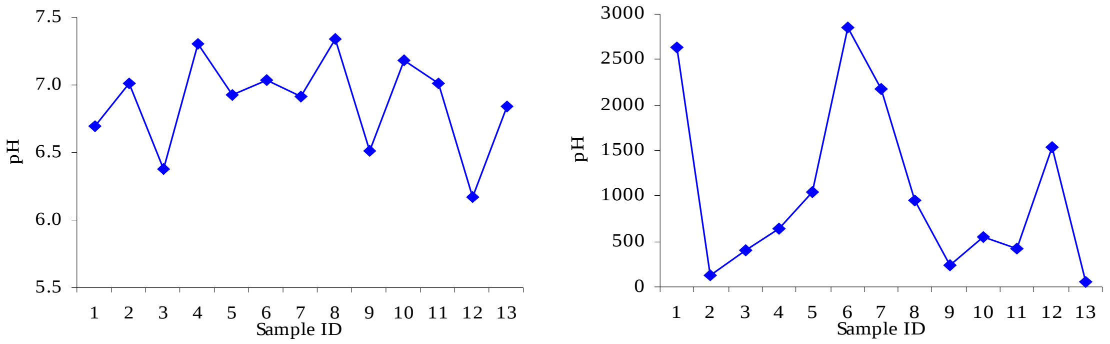


Figure 5.7 & 5.8 Spatial variation of pH and EC in groundwater samples

5.3.2.5 Total Alkalinity

Carbonates and bicarbonates are added to a water system when the water passes through soil and rock that contain carbonate minerals, such as calcite. Where limestone and sedimentary rocks and carbonate-rich soils are predominant, waters will often have high alkalinity. Where igneous rocks (such as granite) and carbonate-poor soils are predominant waters will have low alkalinity

The highest alkalinity of 304 mg/l was observed for the deep bore well sample at Pandicheri indicating the presence of carbonate rocks in the particular region. Minimum concentration of 20 mg/l was seen at Kainagiri. Levels of 20-200 mg/l are typical of fresh water. Below the pH of 8.3, alkalinity is present mostly as bicarbonate (HCO_3^-) and hence the present study confirmed the fact that, alkalinity was mainly due to bicarbonate.

5.3.2.6 Total Hardness

As groundwater moves through soil and rock, it dissolves very small amounts of minerals and holds them in solution. Calcium and magnesium dissolved in water are the two most common minerals that make water "hard". The degree of hardness becomes greater as the calcium and magnesium content increases and is related to the concentration of multivalent cations dissolved in the water.

Analytical results showed that 77% of the samples are hard (150 to 300 mg/l $CaCO_3$). The samples from the deep bore wells are very hard (>300mg/l $CaCO_3$). Hardness has good correlation with the conductivity. Hardness is mainly associated with aesthetic problems especially related to scale formation, difficulty in getting leather to soap etc.

5.3.2.7 Calcium and Magnesium

The range of calcium in the sample was from 9mg/l to 112mg/l. Similarly the value of magnesium ranged between 3.89mg/l to 48.60mg/l. In all the samples concentration of calcium exceeds magnesium. Calcium has more correlation with hardness than magnesium.

5.3.2.8 Sodium and Potassium

The mean value of sodium and potassium in groundwater samples were 118.2 mg/l and 21mg/l respectively. The spatial variation of sodium is given in Figure 5.9. 77% of the samples were found to cross the drinking water standard of 20mg/l set by WHO regarding sodium concentration on health consideration. The excess sodium is problematic for irrigation.

5.3.2.9 Chloride

Chlorides are widely distributed in the groundwater as salts of sodium (NaCl), potassium (KCl) and calcium ($CaCl_2$). In addition to these sources chlorides are leached from various rocks into soil and water by weathering. The chloride ion is highly mobile and is transported to closed basins or oceans. Chloride in surface and groundwater mainly comes from both natural and anthropogenic sources, such as dissolution of mineral salts, use of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation drainage, and seawater intrusion in coastal areas.

The chloride content of the groundwater samples ranged from 15.09mg/l to 618.16 mg/l. The spatial variation of chloride is given in Figure 5.10. High correlation coefficient of chloride with sodium (0.97) indicated weathering of sodium chloride rocks. Chloride in drinking water is generally not harmful to human beings.

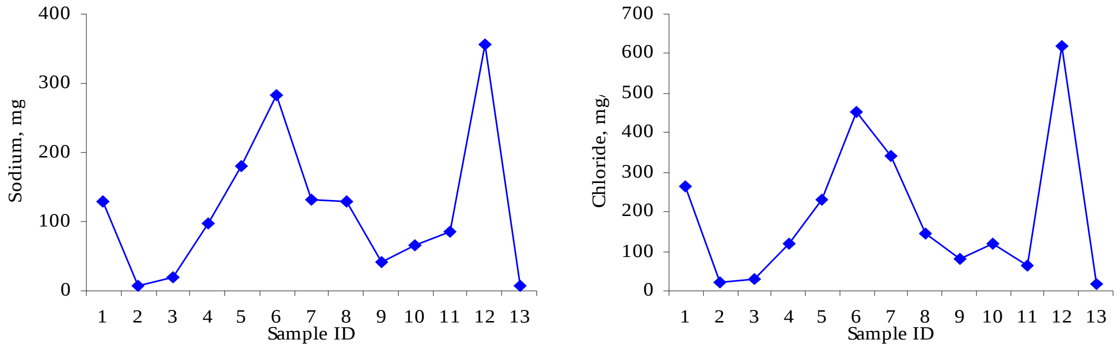


Figure 5.9 & 5.10 Spatial variation of sodium and chloride in groundwater samples

5.3.2.10 Sulfate

Sulfate in groundwater is derived principally from the evaporation minerals gypsum such as (hydrous calcium sulfate, $CaSO_4$ $2H_2O$) and anhydrite (calcium sulfate, $CaSO_4$); it may also come from the oxidation of pyrite, which is an iron sulfide mineral.

Groundwater may have much higher sulfate content near evaporate deposits in sedimentary rocks.

Of the major anions, sulphate concentration was comparatively less. It ranged between 1.6mg/l to 86.4 mg/l. The high correlation of sulphate with calcium indicated more contribution from gypsum. Highest value was observed at station Kumarakom, which may be due to anthropogenic activities.

5.3.2.11 Fluoride

Fluoride, derived from fluorite (the principal fluoride mineral in igneous rocks) and the mineral apatite and mica, is generally present in only low concentration in groundwater. Fluoride occurs in almost all natural water supplies. In amounts of less than 1mg/l, it is an effective preventive of dental caries. Above this limit fluoride may cause dental fluorosis and skeletal fluorosis (Manivasakam 1996).

Out of thirteen samples, four samples had concentration above the permissible limit. The sample from a deep bore well at Pandichery had high fluoride contamination (3.39 mg/l). In high doses fluoride is acutely toxic to man. Only the sample collected from Kumarakom is free of fluoride. Fluoride has high correlation with the temperature and conductivity. It also has good correlation with major cations and anions, which indicated the dependence of these factors on the dissolution of fluoride from minerals present in subsurface.

5.3.2.12 Nitrate-nitrogen

Unlike most other elements in groundwater, nitrate is not derived primarily from the minerals in rocks that make up the groundwater reservoir. Instead, nitrate enters groundwater from another part of the nitrogen cycle in the earth's hydrosphere and biosphere.

Nitrate-nitrogen has a permissible limit of 10mg/l in drinking water. No samples from the study area exceeded the limit. Domestic sewage and agricultural runoff are the chief sources of allochthonous nitrogenous organic matter. Comparative high concentration of nitrate was observed at Chunkamthodu confirmed the above fact.

5.3.2.13 Phosphate-phosphorous

Domestic, industrial and agricultural sewage are very important sources of phosphorus to natural water. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body waste and food residues. Phosphorus is essential in metabolism so is always present in animal waste. Orthophosphates and polyphosphates can be contributed by detergents.

Concentration of phosphorous ranged between 0.038 mg/l to 1.75 mg/l. The highest concentration of phosphorous was found at station Thanneermukkom.

5.3.2.14 Iron

Most water supplies contain some iron, because iron is common in many igneous rocks and is found in trace amounts in practically all sediments and sedimentary rocks. The iron content of water is important because small amounts seriously affect water’s usefulness for some domestic and industrial purposes. The normal concentration of iron in drinking water is 0.3 mg/l.

Among the sampled wells, 54% of the samples exceeded the permissible limit. Shallow groundwater at Kuppapuram has showed high iron concentration (3.79mg/l), which is far from the limit. Organic iron is picked up as groundwater passes through decaying or decayed vegetation. Such water is usually found in shallow wells or surface waters. Iron may be wholly or partially combined with the organic matter. It can be considered as a reason for the occurrence of high iron content in Kuppapuram. The shallow pond at Mannanchery has a concentration of 1.14mg/l.

5.3.2.15 Manganese

Manganese resemble iron in its chemical behaviour and occurrence in groundwater but less abundant than iron (Kemmer 1977). Stains caused by manganese are more objectionable and difficult to remove than those from iron. Therefore, drinking water regulation limits manganese concentration to 0.05mg/l to avoid manganese staining by USEPA.

Shallow groundwater at Kumarakom recorded the highest value of manganese (0.563mg/l). 77% of the samples had concentration limit within the permissible value.

5.3.2.16 Zinc

Zinc is commonly found in small quantities in domestic water supplies and industrial waters and is due to the corrosion of galvanized iron and brass. Zinc may also enter into the water through the discharge of industrial effluents such as galvanizing wastes, zinc plating waters, viscous rayon wastes and rubber factory wastes.

Zinc has no known physiological effects to man. However, high concentration above 5mg/l of zinc in domestic waters is undesirable as they cause a stringent taste. The concentration of zinc varied from 0.099mg/l to 0.407mg/l with an average value of 0.189mg/l.

5.3.2.17 Coliform bacteria

Most pathogens that can contaminate water supplies come from the fecas of humans or animals. There are three different groups of coliform bacteria; each has a different level of risk. Total coliform, fecal coliform, and E.coli are all indicators of drinking water quality. The total coliform group is a large collection of different kinds of bacteria. The fecal coliform group is a sub-group of total coliform and has fewer kinds of bacteria. E. coli is a sub-group of fecal coliform. Drinking water is adequate safe without coliforms (WHO 1997).

Confirmation of fecal coliform bacteria or E. coli in a water system indicates recent fecal contamination, which may pose an immediate health risk to anyone consuming the water. Coliform bacteria may not cause disease, but can be indicators of pathogenic organisms that cause diseases. The present study confirmed 100% contamination of wells by total coliforms (Figure 5.11) and 70% of samples contain E.coli (Figure 5.12). Generally the use of rusted and unhygienic receptacles to draw water due to lack of windlass on the wells, development of fissures etc, sitting of pit latrines and drainage system closer to wells, constitute points of direct microbial contamination of groundwater under heavy rainfall. A minimum distance between the well and the source had been suggested to be 50 feet, while the distance between the well and the source is less than 50 feet in most stations.

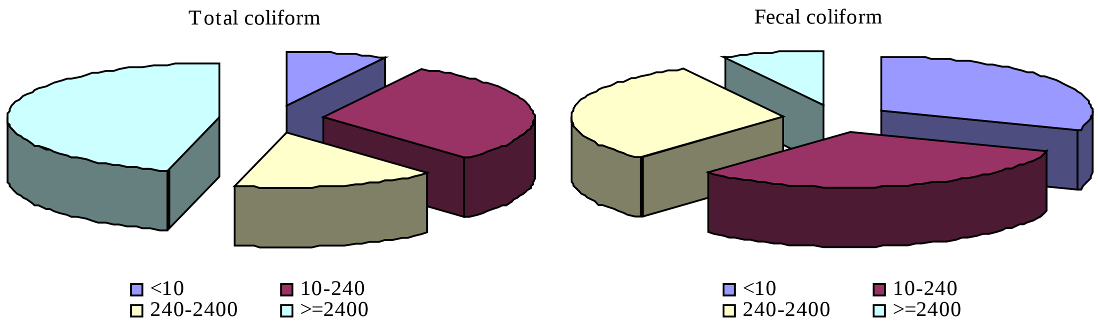


Figure 5.11 Percentage of samples contaminated with Coliforms

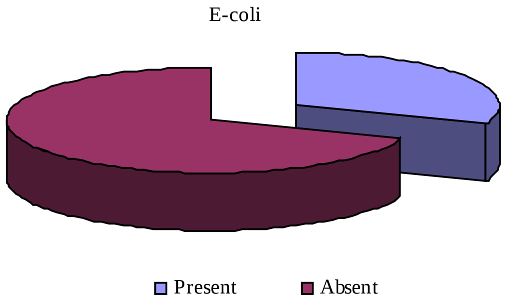


Figure 5.12 Percentage of samples contaminated with E-coli

5.4 Summary

The geochemical analysis of groundwater samples around Vembanad Lake showed sodium-calcium-chloride-bicarbonate type. The ionic composition of the groundwater is dominated by major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and anions (Cl^{-}, HCO_3^{-}, and SO_4^{2-}). Indices of Base Exchange indicated cation exchange in groundwater samples. The deep bore wells and shallow open well at Kumarakom showed higher salinity hazard which decreased the suitability of water for irrigational use. The respective ionic ratios indicated 77% samples of rock dominance and 13% of evaporative enrichment. As a general water quality parameter, 77% of the water samples were hard. High correlation coefficient of chloride with sodium indicated weathering of sodium chloride rocks. The high correlation of sulphate with calcium indicated more contribution from gypsum. A few water samples had problems due to fluoride contamination. More than 50% of the samples are contaminated with iron. All the samples were contaminated with Coliform bacteria.

Table 5.1 Details of groundwater sampling stations

Sample ID	Sampling Stations	Source	Location	Location
1	Alappuzha	OW	9°29.629'	76°20.872'
2	Punnamada	OW	9°31.325'	76°21.397'
3	Mannancheri	Pond	9°34.296'	76°21.501'
4	Ponnad Mannancheri	OW	9°35.328'	76°21.806'
5	Thanneermukkom	OW	9°40.656'	76°23.514'
6	Ambika market	OW	9°40.299'	76°24.472'
7	Kumarakom	OW	9°35.806'	76°25.64'
8	Pandicheri	BW	9°31.125'	76°23.327'
9	Mangalassery	BW	9°31.235'	76°22.800'
10	Kuppapuram	OW	9°30.997'	76°22.890'
11	Kainagiri	OW	9°28.756'	76°23.202'
12	Pallathuruthi Bridge	BW	9°27.787'	76°21.832'
13	Pallathuruthi Bridge	BW	9°27.788'	76°21.833'

OW, Open well: BW, Bore well

Table 5.2 Characterization of groundwater on the basis of Piper tri-linear diagram

Subdivisions of diamond	Characteristics of corresponding subdivisions of diamond shaped field	Percentage of sample
1	Alkaline earths(Ca+Mg) exceeded alkalies(Na+K)	53
2	Alkalies exceeded alkaline earths	47
3	Weak acids (CO_3+HCO_3) exceeded strong acids(SO_4+Cl+F)	30
4	Strong acids exceed weak acids	70
5	Carbonate hardness (secondary alkalinity) exceeds50% (chemical properties are dominated by alkaline earths and weak acids)	23
6	Non-carbonate hardness (secondary salinity) exceeds 50% (chemical properties are dominated by alkaline earths and strong acids)	0
7	Non-carbonate alkali (primary salinity) exceeds 50% (chemical properties are dominated by alkalies and weak acids)	53
8	Carbonate alkali (primary alkalinity exceeds 50% (chemical properties are dominated by alkalies and weak acids	0
9	No cation–anion pair exceeds 50%	38

Table 5.3 Chemical characteristics of groundwater samples collected from the areas around Vembanad Lake

Sample ID	SAR	Sodium %	SSP	Kelly's ratio	MHR	RSC	CAI 1	CAI 2	Gibbs ratio Anion	Gibbs ratio Cation
1	2.70	37.88	39.19	0.64	36.40	-6.49	6.62	6.34	0.76	0.52
2	0.39	16.41	18.18	0.22	26.35	-0.47	-0.20	-5.54	0.38	0.32
3	0.69	19.93	21.40	0.27	35.04	-0.97	-0.52	0.27	0.28	0.36
4	3.49	54.46	58.95	1.44	43.28	-0.60	1.98	-66.80	0.59	0.74
5	4.94	57.85	60.88	1.56	52.42	-4.71	5.18	-7.31	0.95	0.78
6	8.73	73.25	75.54	3.09	20.03	0.99	11.76	2.45	0.72	0.80
7	3.03	42.14	44.39	0.80	55.59	-4.57	8.91	-52.14	0.79	0.67
8	3.32	45.28	49.49	0.98	33.37	-2.28	2.39	-3.99	0.54	0.64
9	1.84	46.50	47.87	0.92	36.04	-1.01	1.51	-7.11	0.70	0.60
10	1.90	36.60	38.30	0.62	43.63	-0.74	2.45	1.56	0.46	0.55
11	3.37	54.93	60.58	1.54	60.04	0.88	-0.57	-105.1	0.36	0.82
12	7.92	63.47	66.92	2.02	45.87	-3.93	16.49	4.18	0.82	0.80
13	0.45	24.11	26.43	0.36	40.04	-0.27	-0.50	-10.79	0.45	0.45

Table 5.4 Water quality characteristics groundwater samples collected from the areas around Vembanad Lake

Sample ID	1	2	3	4	5	6	7	8	9	10	11	12	13
pH	6.70	7.01	6.38	7.30	6.93	7.04	6.91	7.34	6.51	7.18	7.01	6.17	6.84
EC	2640	133	398	642	1046	2850	2170	957	244	546	423	1534	51
Temp, ºC	26.70	28.90	28.10	28.00	26.60	31.50	30.00	27.60	28.60	27.10	30.70	31.70	27.20
Color, Hazen	8.80	3.80	30.10	11.10	69.00	2.30	4.00	9.80	33.00	5.60	15.80	2.60	7.90
Turbidity, NTU	1.00	1.00	4.00	3.00	17.00	1.00	1.00	2.00	5.00	1.00	5.00	1.00	3.00
Na, mg/l	130.2	7.8	20.0	97.6	180.1	283.6	132.0	129.5	42.2	66.7	84.7	356.7	6.6
K, mg/l	19.5	7.8	11.7	23.2	26.4	20.0	27.0	41.4	4.4	13.7	24.5	49.2	4.1
Ca, mg/l	112.0	22.4	41.6	33.6	48.0	64.0	64.0	76.8	25.6	52.8	19.2	83.2	9.6
Mg, mg/l	38.9	4.9	13.6	15.6	32.1	9.7	48.6	23.3	8.7	24.8	17.5	42.8	3.9
F, mg/l	ND	0.17	0.33	0.35	0.41	3.39	1.54	0.55	0.18	0.37	1.70	2.81	0.04
Cl, mg/l	264.1	22.6	30.2	120.7	230.1	452.7	339.5	143.4	83.0	120.7	64.1	618.6	15.1
HCO3, mg/l	140.0	64.0	136.0	144.0	20.0	304.0	160.0	212.0	60.0	240.0	200.0	228.0	32.0
SO4, mg/l	86.4	3.6	20.0	3.2	28.9	40.3	4.8	27.6	9.0	27.0	1.9	47.4	1.6
NO3-N, mg/l	0.288	0.104	0.072	0.884	0.160	0.076	0.392	2.012	0.040	0.005	0.056	0.020	0.336
PO4-P, mg/l	0.095	0.357	1.750	0.905	0.830	0.198	0.127	0.182	0.157	0.273	0.039	0.053	0.038
Fe, mg/l	0.484	0.141	1.076	0.168	3.791	0.609	0.447	0.250	1.142	0.154	0.622	0.056	0.288
Mn, mg/l	0.563	0.000	0.109	0.000	0.071	0.024	0.075	0.000	0.022	0.011	0.014	0.006	0.048
Zn, mg/l	0.265	0.189	0.157	0.255	0.114	0.176	0.407	0.105	0.147	0.258	0.147	0.133	0.099
Total Coliforms	460	43	23	≥2400	≥2401	≥2402	150	≥2402	≥2404	460	43	9	≥2404
Fecal Coliforms	0	23.00	9.00	1100.00	43.00	210.00	4.00	≥2402	460.00	460.00	23.00	0.00	28.00
E-Coli	Absent	Absent	Present	Present	Present	Present	Absent	Present	Present	Present	Present	Absent	Present

Table 5.5 Correlation analysis of the groundwater samples collected from the areas around Vembanad Lake

	pH	EC	Temp	Colour	Turb	Na	K	Ca	Mg	F	Cl	HCO3	SO4	NO3-N	PO4-P	Fe,	Zn	Mn
pH	1.00	-0.05	-0.27	-0.15	-0.01	-0.22	-0.02	-0.15	-0.21	-0.21	-0.33	0.16	-0.28	0.54	-0.13	-0.09	0.18	-0.23
EC		1.00	0.32	-0.24	-0.21	0.70	0.41	0.80	0.58	0.82	0.77	0.51	0.69	-0.01	-0.26	-0.02	0.43	0.50
Temp			1.00	-0.41	-0.35	0.57	0.37	0.03	0.09	0.89	0.58	0.56	-0.10	-0.27	-0.30	-0.32	0.05	-0.37
Color				1.00	0.95	-0.10	-0.10	-0.20	0.00	-0.36	-0.21	-0.57	-0.06	-0.14	0.48	0.95	-0.36	0.00
Turb					1.00	0.00	0.00	-0.24	0.03	-0.27	-0.14	-0.54	-0.11	-0.11	0.35	0.96	-0.38	-0.08
Na						1.00	0.76	0.62	0.54	0.84	0.96	0.56	0.53	-0.03	-0.25	0.07	-0.04	-0.01
K							1.00	0.59	0.67	0.53	0.68	0.49	0.34	0.42	-0.17	-0.04	-0.03	-0.08
Ca								1.00	0.73	0.56	0.68	0.47	0.88	0.22	-0.18	-0.09	0.29	0.61
Mg									1.00	0.35	0.64	0.23	0.49	0.05	-0.18	0.10	0.50	0.38
Fluoride										1.00	0.89	0.80	0.73	0.23	0.13	0.27	0.41	0.50
Chloride											1.00	0.53	0.55	-0.12	-0.31	-0.03	0.17	0.09
HCO3												1.00	0.32	0.11	-0.21	-0.48	0.20	-0.11
SO4													1.00	-0.04	-0.14	0.04	0.03	0.75
NO3-N														1.00	-0.04	-0.19	-0.09	-0.09
PO4-P															1.00	0.37	-0.07	-0.04
Fe																1.00	-0.28	0.05
Zn																	1.00	0.28
Mn																		1.00

Table 5.6 Basic statistics for groundwater samples

Parameters	Maximum	Minimum	Mean	SD
pH	7.34	6.17	6.87	0.35
EC, µS/cm	2850.00	50.50	1048.72	957.16
Temp, °C	31.70	26.60	28.67	1.78
Colour, Hazen	69.00	2.30	15.68	18.81
Turbidity, NTU	17.00	1.00	3.46	4.35
TH, mg/l	440.00	40.00	215.54	124.90
CaH, mg/l	280.00	24.00	125.54	73.40
MgH, mg/l	200.00	16.00	90.00	60.75
Na, mg/l	356.72	6.60	118.28	105.21
K, mg/l	49.20	4.10	20.99	13.45
Ca2+, mg/l	112.00	9.60	50.22	29.36
Mg2+, mg/l	48.60	3.89	21.87	14.76
Fluoride, mg/l	3.39	0.04	0.99	1.12
Chloride, mg/l	618.61	15.09	192.68	183.78
Alkalinity, mg/l	304.00	20.00	149.23	87.08
Sulphate, mg/l	86.40	1.60	23.20	24.49
NO3-N, mg/l	2.012	0.005	0.342	0.56
PO4-P, mg/l	1.750	0.038	0.385	0.50
Fe, mg/l	3.791	0.056	0.710	0.99
Zn, mg/l	0.407	0.099	0.189	0.09
Mn, mg/l	0.563	0.000	0.072	0.15

6.0 Core sediment quality of Vembanad Wetland System

6.1 Introduction

Sediment is a general term which is used to describe both suspended and deposited materials. In aquatic system sediment include all particulate materials which are washed or blown in a river or lake or are formed in the water body itself. Sediments are the layers of relatively finely divided matter covering the bottom of rivers, streams, lakes, reservoirs, bays estuaries and ocean. Unlike water quality which is susceptible to seasonal variation, dependent on in and out flow and weather, sediment quality is more constant and will have more farfetched implications. Assessment of sediments in a complex aquatic system resulted in a better understanding of the adverse impacts that contaminants in sediments pose to fish, wild life and humans who depend this impacted waterways. Therefore apart from polluted water, fate of contaminated sediment has been chosen as one of the aspects responsible for ecological decline. Lake sediments provide a useful archive of information on changing lacustrine and watershed ecology (Cohen 2003). Sediments enter a lake from its water shed, the water column and the atmosphere. Each of these sources has its own distinct characteristics that enable scientists to track changes within the relative contribution of the sources to the sediment. This can be related to natural and anthropogenic impacts on the lake and its watershed.

Depending upon the limnological conditions, the sediment can act both as source as well as sink for the nutrients and other elements. Under favorable conditions the sediment releases these nutrients into water body leading to the enhanced productivity of ecosystem. Sediments are ecologically important components of the aquatic habitat and also a reservoir of contaminants which play a significant role in maintaining the trophic status of any water body. Sediment not only reflects the current quality of water but also provide vital information on the transportation and fate of pollutants.

6.1.1 Core sediments

Among the sediments, bottom sediments are very important as it undergoes leaching and also it has got the ability to exchange cations with the surrounding aquatic medium. Core sediments provide useful information on the changes in the quality of the lake from a past period. Sediment core contain information about the events that occurred in precultural time in the lakes and its catchments area. The sediment history broadly reflects the contamination history of an area. Vertical profiles of pollutant species in sediment cores have been commonly used as “pollution records”.

6.1.2 Sediment contamination

Sediments are known to effectively sequester hydrophobic chemical pollutants entering water bodies such as lakes, rivers and estuaries. Apart from being a sink for pollutants, sediments are also a potential source of pollution toxicity to aquatic organisms. Core sediments can be used to study the pollution history of aquatic ecosystem (Karbassi et al. 2005, Ahmad W. Mohamed 2005, Lopez and Lluch 2000). Geochemical studies of sediment cores are helpful in the assessment of pollution and changes in climatic conditions (Karbassi and Amirnezhad 2004), rate of sedimentation (Karbassi 1996), weathering trend and the source of pollution etc. Over the last few decades the study of the sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. Coastal and estuarine region are the important region for many persistent pollutants and they accumulate in organisms and bottom sediments (Szefer et al. 1995). The study of dated sediment profile from industrialized estuaries is indeed a valuable tool for sediment quality assessment (Grant and Briggs 2002, White et al. 2005).

6.1.3 Sediment quality guidelines

It is accepted that without defensible sediment quality guidelines it would be difficult to assess the extend of sediment contamination (Jones-Lee and Lee 2005). During the last years several efforts have been devoted to develop environmental quality guidelines designed specifically to support contaminated sediment and dredged material management and to implement policies and regulatory strategies. Different technical approaches have been used to develop numerical SQGs.

The need for chemical guidelines that could be used to predict adverse biological effects in contaminated sediments lead to the development of sediment quality guidelines (USEPA 1992, Long et al. 1995, Long and Mc Donald 1998, Mc Donald et al. 2000).

Generally the primary purpose of SQGs is to protect animals living in or near sediments from the deleterious effects associated with sediment bound contaminants. SQGs are also used to rank and/or prioritize contaminated areas or chemicals of concern for further investigation (Long and Mc Donald 1998) or used to evaluate spatial pattern of sediment contamination (Birch and Taylor 2002) or used in the design of monitoring programs (Crane and MacDonald 2003).

Numerical sediment quality guidelines (SQGs) have been used to identify contaminants of concern in aquatic ecosystem (MacDonald et al. 2000). According to this sediments were classified as: non-polluted, moderately polluted and heavily polluted, based on SQG of USEPA (Perin et al. 1997). Taylor's (1972), crustal abundance was used as reference lines. Effects-range SQGs are empirically derived and do not consider factors affecting the bioavailability of contaminants. They differ from mechanistic SQGs, such as those derived from equilibrium partitioning theory, which consider geochemical that bind contaminants.

The National Oceanic and Atmospheric Administration (NOAA) developed a set of empirical SQGs (Long et al. 1995) that provides two values, effects range low (ERL) and effects range high(ERM), which delineate three concentration ranges for each particular chemical and the corresponding estimation of the potential biological effect. These guidelines were derived from the collection of concurrent sedimentary chemical and biological data collected from the three seaboards of North America, incorporating field and laboratory data from many different methodologies, species and biological endpoints.

Chemical concentration corresponding to the 10th and 50th percentiles of adverse biological effects was called the effects range-low (ERL) and effects-range median (ERM) guidelines, respectively (Long et al. 1995). These two guideline values delineated three ranges in chemical concentrations, where adverse effects were rarely (<ERL), occasionally (≥ERL and <ERM) and frequently observed (≥ERM). The guidelines were derived for 25 chemicals, 9 trace metals, 13 PAHs 2 OCs and total PCB.

The concentrations below ERL represent a minimal-effects range, which is intended to estimate conditions where biological effects are rarely observed. Concentrations equal to or grater than ERL, but less than ERM represents a range with in which biological effects occur occasionally. Concentrations at or above ERM values represents a probable effect range with in which adverse biological effects frequently occur. These set of SQGs have been shown to have some predictive ability although do not account for chemical bioavailability and was not based upon experiments in which causality was determined. According to the concept of SQG, adverse biological effects are not expected when the concentrations of the contaminants are below the TEL values, where as concentrations of contaminants higher than the PEL values will probably results in adverse biological effects.

The potential acute toxicity of contaminants in sediment sample can be estimated as the sum of the toxic units (∑TU) defined as the ratio of the determined concentration to PEL value (Pederson et al. 1998)

Hakanson et al. (1980), had suggested a contamination factor ($C^i{}_f$) and the degree of contamination (C_d) to describe the contamination of given toxic substance, which is given

by $C^i{}_f = \frac{C^i{}_{0-1}}{C^i n}$ and $C_d = \sum_{i=1}^{7} C^i{}_f$

Where $C^i{}_{0-1}$ is the mean content of the substance;

$C^i{}_n$ is the reference value for the substance.

The following terminologies are used to describe the contamination factor.

C^i_f	C_d	Description
$C^i_f \leq 1$	$C_d < 7$	low degree of contamination
$1 \leq C^i_f < 3$	$7 \leq C_d < 14$	moderate degree of contamination
$3 \leq C^i_f < 6$	$14 \leq C_d < 28$	considerable degree of contamination
$C^i_f \geq 6$	$C_d \geq 28$	very high degree of contamination

Tomlinson et al. (1980), had employed a simple method based on pollution load index (PLI), to assess the extend of pollution by metals in estuarine sediments. Sediment pollution load index (PLI) was calculated using the equation

$$\text{PLI} = (\text{Product of n number of CF values})^{1/n}$$

CF is the contamination factor, n the number of metals, and world average concentration of elements reported for shale was taken as their background values.

This chapter presents the environmental quality of the wetland system from the assessment of sediment cores in different parts of the wetland through their geochemical and toxicological study. The main goal of this work are to determine the chronological distribution of pollutants especially metals and to correlate the toxicity distribution with chemical concentration in sediment profiles in order to obtain a global picture of the sediment quality of Vembanad wetland system.

6.2 Methodology

The core samples of sediments were collected using gravity type sediment corer of 50cm length. The sampling stations were selected based on the criteria that they were near the urban and domestic effluent discharge points, agricultural dewatering areas, places of tourism activities, industrial discharge points and estuarine region. A total of eight sediment cores, including five from southern region and three from northern part, were collected for the present study.

The cores collected from the freshwater region include 3/V, sliced into 9 pieces, 7/V sliced into 12 pieces, C/V sliced into 19 pieces, 15/V sliced into13 pieces and 18/V sliced into 12 pieces. The details of the sampling stations are indicated in Figure 6.1. The sampling stations in the estuarine region include Boat jetty (1/P) of Cochin bar mouth, Pathalam downstream of industrial area (2/P) and the industrial area site of Pathalam (3/P). The core 1/P was sliced into 10 pieces, 2/P into 12 pieces and 3/P into 11 pieces. The details of the sampling stations are indicated in Figure 6.2.

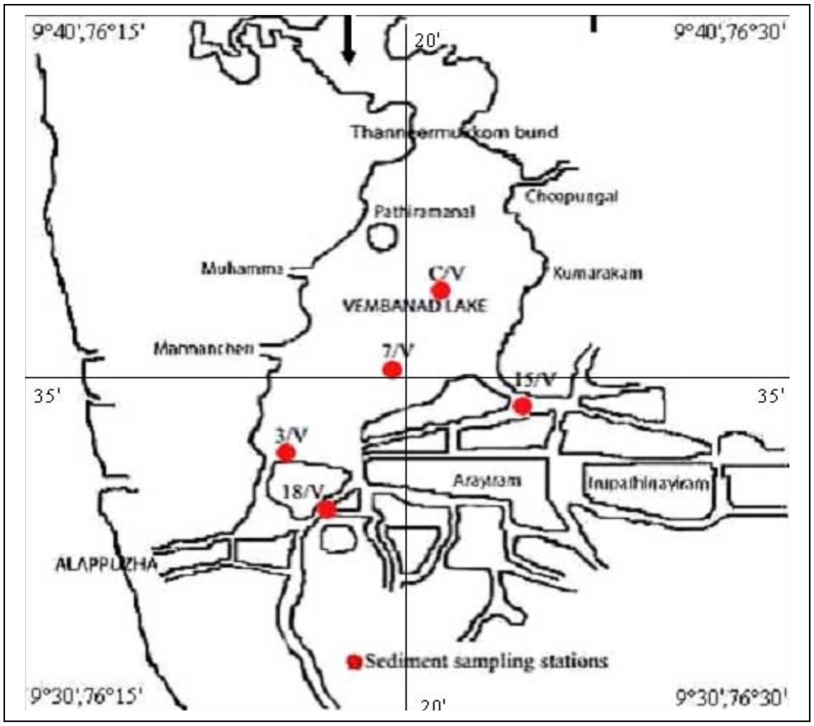


Figure 6.1 Map of core sediment sampling sites in the southern region

The collected sediment cores were cut into slices of approximately 2-4cm length from the field itself and properly labeled (Plate 1,&2). The samples (each slices of the core) were brought to the laboratory using ice bags and stored in a deep freeze unit until the drying procedure (UNEP 1985). The various physicochemical parameters like pH, electrical conductivity, alkalinity, chloride and sulphate were estimated following soil analysis procedures. Using the ammonium acetate extract did extraction of exchangeable sodium, potassium, calcium and magnesium. Organic matter was determined by wet oxidation-redox titration method using an acid dichromate solution. Inorganic phosphorous was extracted using 1N hydrochloric acid. Hydrolysable phosphorous was extracted using 0.1N sulfuric acid. The total phosphorous was extracted with a mixture of nitric acid and perchloric acid. Pesticides were extracted using hexane-acetone mixture. The total heavy metal extraction was done using an acid mixture of HNO_3 and $HClO_4$. The analytical procedure for the determination of different geochemical parameters was further discussed in section 3.5. The concentration of different ions were expressed in units of mg/Kg. The organic carbon content was reported as percentage values.

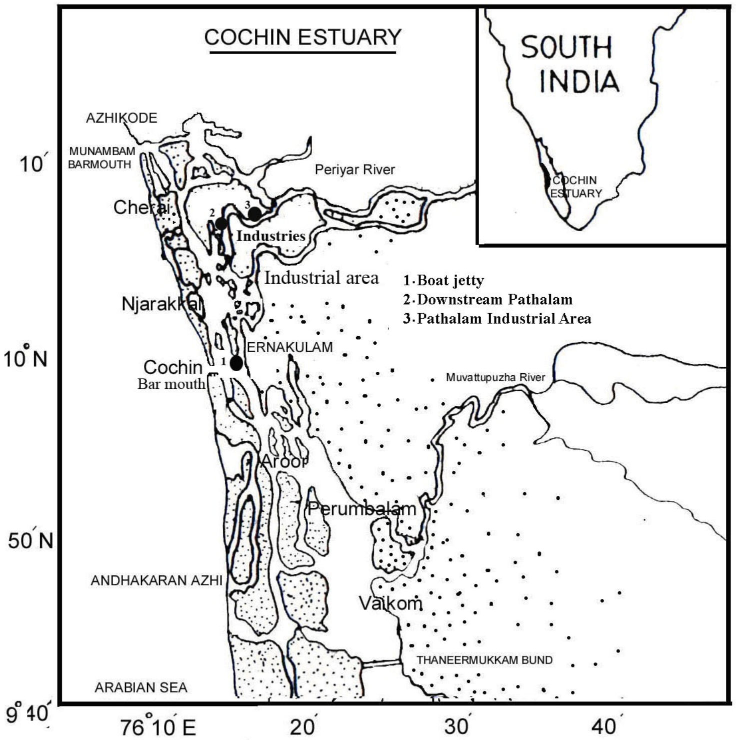


Figure 6.2 Map of core sediment sampling sites in the northern region

6.3 Results and Discussion

6.3.1 Core sediments from the southern region of Vembanad wetland system

The results of the geochemical and toxicological analysis of the five sediment core collected from the southern region is given in Table 6.1 to 6.5 and are discussed below.

6.3.1.1 Texture

The textural classes of surface sediments of three core samples were analyzed and are plotted in the ternary diagram (Figure 6.3). It revealed that the eastern side of the Vembanad Lake is blanketed mainly with sand dominated sediments with sandy loam. The content of sand is 81.25%. The ranges of silt and clay fractions are 5.0%, 13.75% respectively. At the middle portion, the percentage sand is 56.25, with silty loam and in the western side the texture class becomes completely loam (sand 61.25%, silt 17.5% and clay 21.25%).

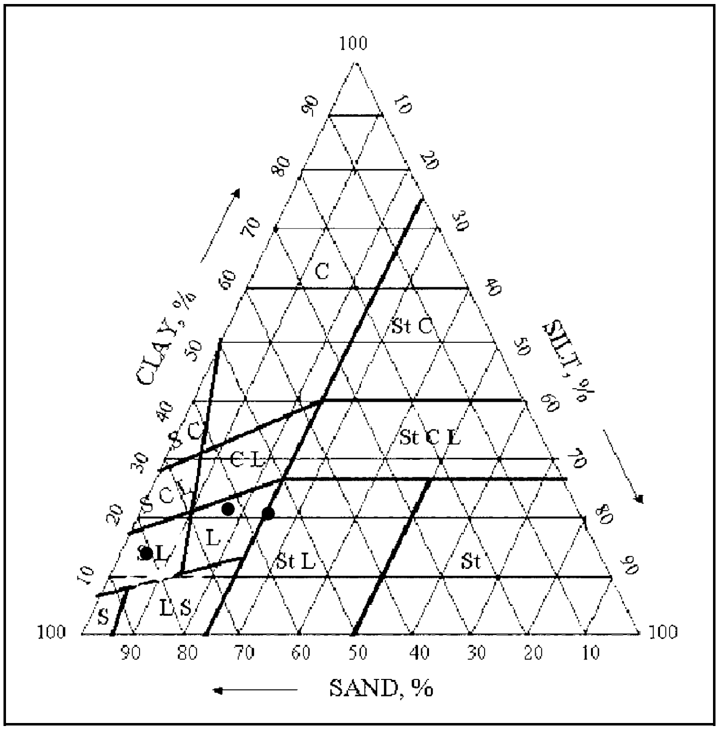


Figure 6.3 Ternary diagram showing the various textural classes of the sediments of Vembanad Lake

6.3.1.2 pH

Sediment pH is the most informative parameter that can be used to predict other chemical properties of sediments (Mohamed et al. 2003). Many chemical and biological reactions in sediments are controlled by the pH in equilibrium with soil particle surface

(Hendershot et al. 1993). The soil pH was probably due to active acidity of hydrogen ion and dissolved aluminum.

Moving from top to bottom a gradual increase in the pH was noticed (Figure 6.4). Sediments of 11/V and 18/V were acidic whereas the surface part of the core 3/V, 7/V and 15/V were found to be alkaline. Most agricultural soils have pH value lying between 4 and 8, which is reflected in our study. It is already established that excessive decomposition makes the soil anaerobic and acidic (Hannu et al. 2000). Oxidation of organic sulphur compounds results in the production of sulfuric acid, which produce acidic nature to the sediment. The highest alkaline pH (8.93) at 15/V indicated the presence of more hydroxyl ions in the sediments. The pH can become more alkaline if the soil solution contains high sodium ion, which is reflected in the station 15/V. Sulphate reduction, decomposition of organic matter and other anaerobic environment might have resulted in the decrease in pH towards the surface of the core (Robert G Wetzel 2001).

6.3.1.3 Sediment organic carbon

Organic matter in lake sediments is derived from primary production with in the aquatic ecosystem (autochthonous sources) and also from terrestrial biota (allochthonous sources) by transport of leached and eroded material in to the lake. Although organic matter makes up only a small portion of lake sediments, it can indicate ecosystem changes within a lake (Cohen 2003). Natural organic matter plays an important role in the biogeochemical cycles of many trace elements and the quality of aquatic environment (Robert G Wetzel 2001). Increased production of plants in the lake, generally results in increased accumulation of organic matter in the sediment, which is reflected by increased percentage of organic carbon (Hodell and Schelske 1998).

The percentage of organic carbon ranges from 1.84% to 11.84%. Comparatively low organic carbon was reported for the core samples 7/V and 11/V, which is due to greater distance from the shore, as terrestrial inputs decreases. High value of organic carbon was reported in the station 15/V, which may be due to high organic load in nearby area.

Decay process by heterotrophic organism caused a gradual decrease of organic carbon from surface to bottom (Figure 6.5). C/N ratio calculated from elemental analysis of %C and % N provides insight into relative contribution of algal vs. vascular organic matter into the sediment. In the present study, the variation of C/N ratios from 15 to 98 indicated maximum contribution from terrestrial sources and a few aquatic sources. The high value of C/N ratio was observed at the station 15/V, which may be due to the large quantity of carbon rich cellulose in terrestrial plants (Meyers 1997, Meyers and Teranes 2001).

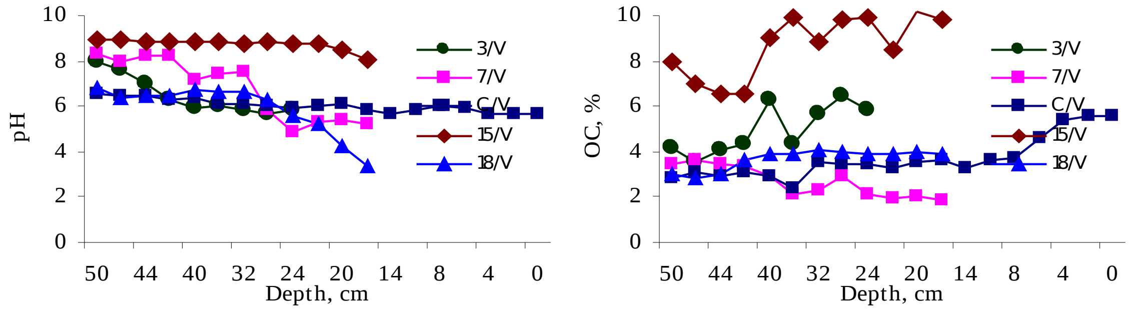


Figure 6.4 & 6.5 Variation of pH and % organic carbon along the core

6.3.1.4 Exchangeable cations and anions

Cations like calcium, magnesium, sodium and potassium and anions like chloride were also present in high amounts in the sediments These are the ions arising mainly due to salinity intrusion into this backwater. Higher concentrations in these samples may be due to larger salinity in pore waters which leads higher adsorption of sodium and potassium into sediments (Evangelou 1998). The spatial and temporal variations are shown in Figures 6.6-6.9. The station 15/V recorded highest concentration of these ions, which was attributed to more contribution from the agricultural land or due to the higher exchangeability at neutral pH. High concentration of calcium observed in the station 15/V may be due to the over deposits of lime stone and other calcium bearing rocks. The spatial variation in the concentration of cations was due to the difference in particle size of the sediment which adsorbs the ions in different proportion.

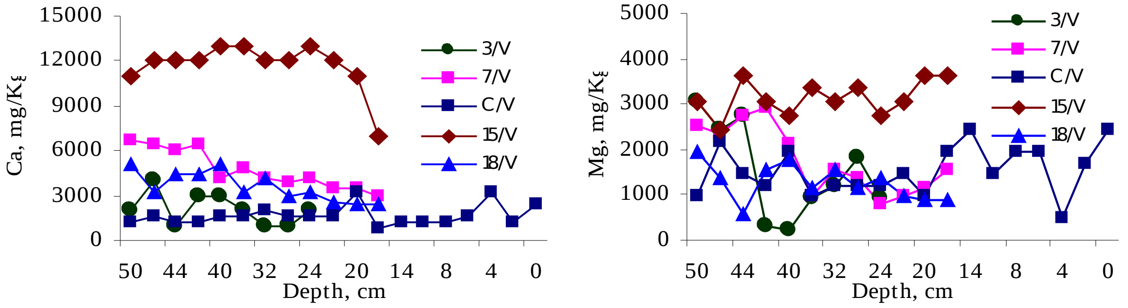


Figure 6.6 & 6.7 Variation of ex-calcium and ex-magnesium along the sediment core

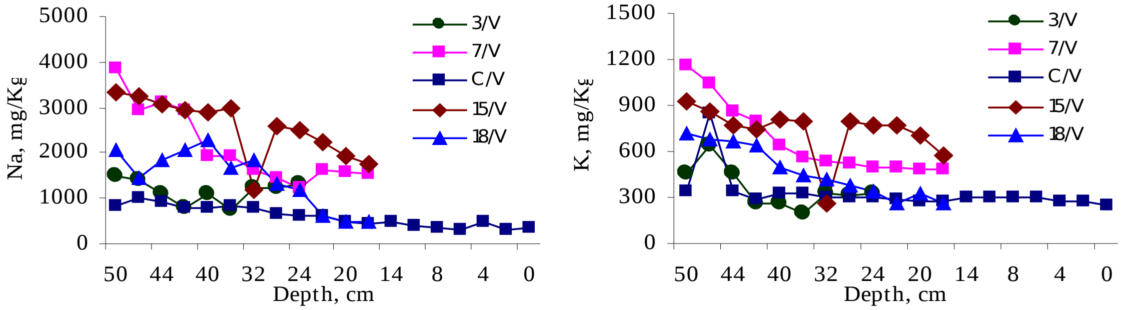


Figure 6.8 & 6.9 Variation of ex-sodium and ex-potassium along the sediment core

The leachate from the agricultural field and the canal waters contributes potassium in the sediments. The adsorption and exchange behavior of alkali metals in sediments is strongly a function of their hydrated radii (Helmke et al. 1996). Moving from bottom to the surface of the core the concentration of exchangeable cations is found to be decreasing. The decrease in the exchangeable cation concentration may be due to the decrease in pH from bottom to the surface, which affects the ion exchange capacity of cations (Francesco et al. 1999) and was confirmed from the correlation matrix.

6.3.1.5 Sulphate and chloride

The concentration of sulphate in the lake was found to be increasing towards the surface (Figure 6.10). Under anoxic conditions sulfate reduction takes place and promotes the release of phosphorous from sediment (Roden and Edmonds 1997), which leads to eutrophication. Relative to the sulfate concentration in the seawater (Boyd 2000), high concentration in sediments were recorded (5772 mg/Kg) in the core 18/V, which was contributed from excess fertilization. There was no gradual trend in the chloride values (Figure 6.11). Most of the chloride input may be from sea water intrusion and sewage disposal. Domestic and industrial waste discharge, leaching of sedimentary rocks and soils also contribute to the present level of chloride in the sediment core. High concentration of chloride was recorded at the station 7/V which is due to salinity intrusion.

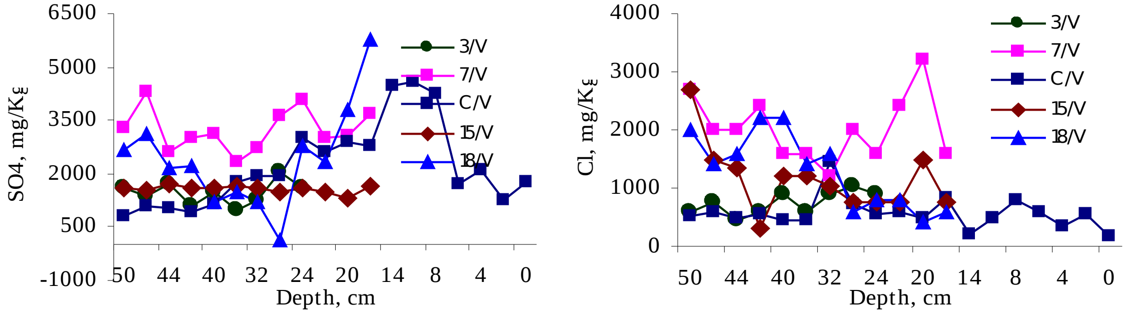


Figure 6.10 & 6.11 Variation of sulphate and chloride along the sediment core

6.3.1.6 Nitrate

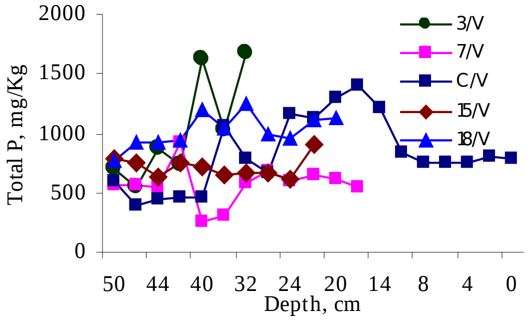
Nitrogen in sediment plays a crucial role in determining the trophic status of the lake in the absence of external sources. The total nitrogen content of the lake indicated an increasing trend with time and varies from 4480 mg/Kg to 1512 mg/Kg, 3304 to 1008 mg/Kg for 3/V and 15/V respectively. The higher concentration was due to the increased agricultural activities in the catchments of the lake, which contribute high amount of nutrients to the lake.

6.3.1.7 Fractionation of phosphorous

The biogeochemical cycle of phosphorous plays a significant role in eutrophication process (Hong Wang et al. 2003). Phosphorous flux from sediments in many lakes are sometimes sufficient to maintain anthropogenic eutrophication when external phosphorous sources have been reduced (Zhou et al. 2001). Several studies have evaluated the ability of sediments to release P under aerobic and anaerobic conditions using intact sediment-water cores (Anderson, 1975; Holder and Amstrong, 1980; Moore e al. 1998). The knowledge of phosphorous speciation is essential to evaluate the environmental changes, phosphorous cycle, bioavailability, carbon, nitrogen, sulfur and oxygen cycles (Schenau and De Lange, 2001). Due to the many different extraction schemes and their modifications it is quite difficult to compare literature data in the field of phosphorous fractionation. However the percentage of different forms of phosphorous calculated in the sediment cores of Vembanad Lake revealed different sources are contributing phosphorous to the lake system.

Inorganic phosphate plays a dynamic role in aquatic ecosystems and is one of the most important nutrients if present in low concentration, but in excess along with nitrates causes algal blooms. Different forms of phosphorous are tabulated in Table 6.6. The total phosphorous content in the sediments varied from 255mg/Kg to 1680mg/Kg (Figure 6.12). From the correlation diagram it is noted that there are two types of relationships. In the case of 3/V and C/V samples, inorganic phosphorous shows a negative correlation with pH and a positive correlation with Fe, whereas in 7/V and 15/V inorganic phosphorous showed a positive correlation with pH and a negative correlation with Fe. The core 18/V showed no such correlation. High concentration of ortho-phosphorous observed at the station, 15/V indicated its source as agricultural runoff. Municipal effluents from Alappuzha town might have caused high load of organic-phosphorous for the station 3/V.

The relative order of the average concentrations of ortho-phosphorous and organic-phosphorous are C/V<7/V<3/V<18/V<15/V and 15/V<7/V<18/V<3/V<11/V. The data indicate the input of high organic load at the areas of 3/V and high inorganic load to the surroundings of 15/V. The station 3/V reported higher rate of vertical deposition of phosphate, which may be due to the continuous discharge of urban waste from Alappey. The mean values of the percentage concentration of inorganic, organic and hydrolysable form of the phosphorous fractions were calculated and are showed in the Figure 6.13. The study revealed that even if the source of phosphorous to the lake system is banned, the lake wills receive the phosphorous from sediments to undergo eutrophication for along period of time.



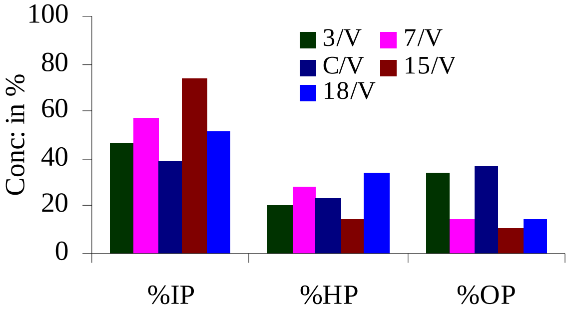


Figure 6.12 Total phosphorous along the core **Figure 6.13** % fraction of phosphorous

6.3.1.8 Pesticides

Organochlorine pesticides are ubiquitous and persistent pollutants used widely throughout the world. Due to the extensive use in agriculture, organic environmental contaminants such as HCH, DDT along with other organochlorine pesticides are distributed globally by transport through air and water. They are chemically stable, lipid soluble and have a low rate of biotransformation and degradation, and hence they are persistent in the environment which results in biomagnifications (Miliadis 1994).

Five slices of the core samples of sediment (C/V) were analyzed for the concentration of chlorinated pesticides, such as lindane, aldrin endo-alpha, dieldrin, DDE, endo-beta and DDD. The concentrations of each pesticide were found to be very high in all the segments of core. The highest concentration was reported for lindane with a value of 16.15mg/Kg. For endo-beta the concentration came up to 2.02 mg/Kg. For DDD the highest concentration is 1.06mg/Kg. Among the core the variation is approximately uniform for all pesticides except lindane. The variation is shown graphically in Figures 6.14&6.15.

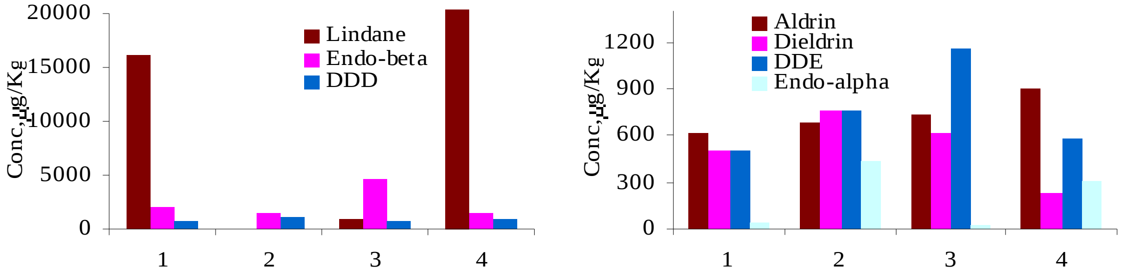


Figure 6.14&6.15 Variation of organochlorine pesticides in the sediment core.

6.3.1.9 Heavy metals

Heavy metals are distributed between the aqueous phase and the suspended sediments. The presence of heavy metals in sediments is affected by the mass transport of heavy metals to the ocean. Trace element pollution in aquatic environment sediments caused by industrialization has been reported by many researchers around the world (Al-Masri et al. 2002). Human activities have lead to accumulation of toxic heavy metals in aquatic sediments (Heyvaert et al. 2000, Sadiq 1992). Many researchers have used sediments to study the behavior of metals over time of sedimentation (Bellucci et al. 2003 and Bertolotto et al. 2003). The occurrence of elevated levels of trace metals especially in the sediments can be a good indication of man induced pollution and high level of heavy metals can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering.

In long-term, the contaminated sediments could be a second source of pollution to the overlying water when the environmental conditions to which the sediment is exposed are altered. Concentration of trace metals in coastal estuaries can be elevated due to high inputs from natural as well as anthropogenic sources. Hence understanding the transport and distribution of trace metals in estuaries is a goal of environmental chemists (Unnikrishnan and Nair 2004).

Five sediment cores from the fresh water region of the Vembanad Wetland System were studied for the trace element contents. The average concentration of iron, manganese, nickel, copper, zinc, cadmium, lead, mercury and chromium were determined and are given in Tables 6.7 to 6.11. The spatial and temporal variation given below

6.3.1.9.1 Variation of heavy metals along the core

The concentration of iron varied from 25.55g/Kg to 82.37g/Kg, and highest distribution was reported in the sample C/V, which was collected from the middle of the lake. There is an increase in the concentration from bottom to the surface of the sediment core, which confirmed the increased anthropogenic activities with time. Spatial variation of average concentration of iron is in the order 15/V<3/V<7/V<18/V<C/V. The longitudinal variation is shown in Figure 6.16. Concentration of manganese varied from 281.67mg/Kg to 1311.67mg/Kg with a mean value of 610.48mg/Kg. The order of distribution along the lake is 3/V<C/V<15/V<18/V<7/V. The stations 3/V and 7/V showed an increasing trend from bottom with maximum concentration at a depth of 32 cm and then a decrease towards the surface slice, which is shown in Figure 6.17.

The concentration of copper with respect to the station follow the order 7/V<15/V<3/V<C/V<18/V and varied from 16.73mg/Kg to 56.13mg/Kg (Figure 6.18). Highest deposition of copper was present in the sample 18/V, with a deceasing trend towards the surface, whereas at all other stations, an increasing trend in the upward direction was noticed. The level of nickel with respect to stations is in the order 7/V<3/V<15/V<C/V<18/V. The concentration of nickel varied from 36.53 to 74.47mg/Kg (Figure 6.19), which is in agreement with the results of Venugopal et al. (1982). Highest conc. of the zinc was observed in the top layers of the core sediments and varied from 103.39mg/Kg to 305.29mg/Kg. The longitudinal variation is shown in the Figure 6.20. Higher chromium was observed for the sample 18/V (4.629mg/Kg) and the values are in agreement with the earlier studies reported for Vembanad Lake (Harikumar et al. 2007). MacDonald et al. (2000) reported a threshold effect concentration (TEC= the concentration above which toxicity may be observed) and a probable effect concentration (PEC= the concentration above which toxicity is frequently observed) of approximately 43 and 111 mg/Kg of chromium for total sediment. The source of chromium includes industrial and municipal effluents. The effluent from chromium plating industries is one of the major sources of lead. Lead concentration varied from 0.61 mg/Kg to 80.03 mg/Kg, in the core sediment samples, which is shown in Figure 6.21. The values are close to concentration of lead reported in the coastal region of Visakhapatnam (Satyanarayana et al. 1994). Most of the samples have concentration less than the EPA criteria for heavily polluted sediments > 60 mg/Kg (Tuley Alemdaroglu et al. 2003). The concentration of cadmium varied from 0.07mg/Kg to 2mg/Kg and is uniformly distributed without any trend (Figure 6.22). The highest concentration of mercury reported was 1.6 mg/Kg and the variation of Hg vertically is shown in Figure 6.23.

6.3.1.9.2 Sediment contamination by comparison with effect based sediment quality guideline (SQG)

Average concentration of heavy metals in the core sediments are summarized in Table 6.12. In the present study Taylor’s (1972), crustal abundance was used as reference lines. From the table it is found that the sediments in Vembanad Lake were polluted in moderate rate for Cu, moderate to heavy rate for zinc and nickel and non polluted to moderate rate for lead.

6.3.1.9.3 Assessment of sediment contamination by comparison of concentration with those of background sediments

The contamination factor and degree of contamination for the core sediment samples at each station was calculated according to Hakanson et al. (1980) and are given in the Table 6.13. All the stations except 15/V indicate moderate degree of contamination. The station 15/V showed low degree of contamination.

6.3.1.9.4 Assessment of pollution by calculating the pollution load index (PLI)

The PLI values calculated for each of the stations were summarized in Table 6.14. Concentration levels of Pb, Cd, Zn and Fe in most of the stations exceeded the world average concentration of shale (Satyanarayana et al. 1994). The station, Ranimangalam (15/V) showed less concentration than the shale value except the elements Cr and Zn.

The PLI values showed a high pollution load at stations Kuppapuram (18/V) and in the centre of the lake (C/V).

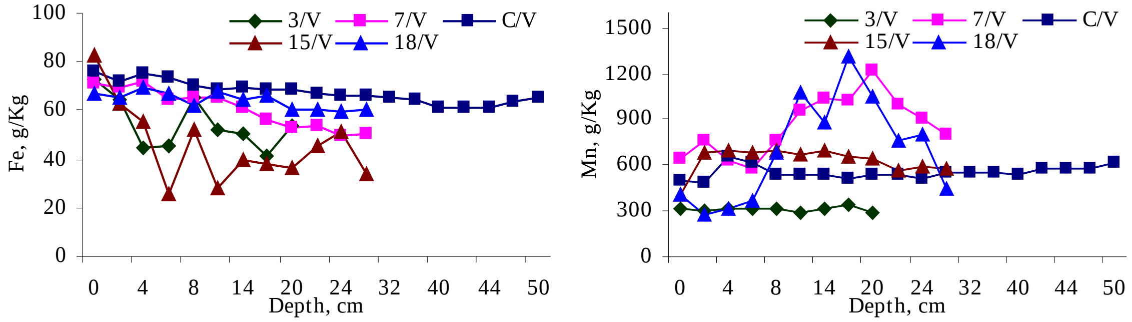


Figure 6.16&6.17 Variation of iron and manganese along the sediment core

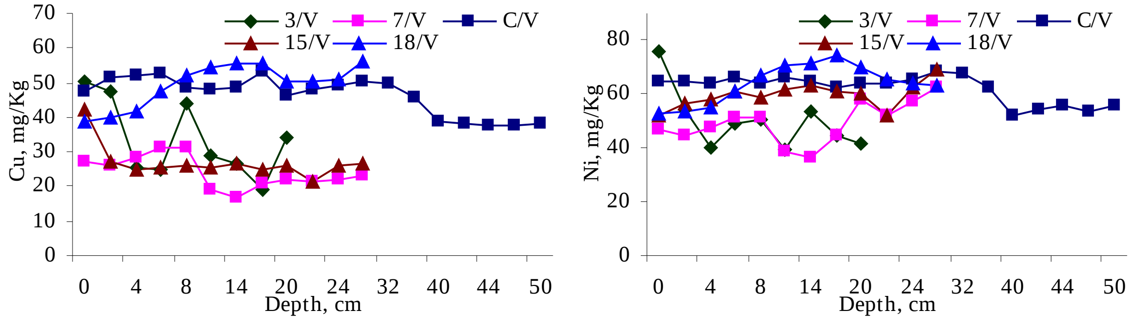


Figure 6.18&6.19 Distribution of copper and nickel in core sediments

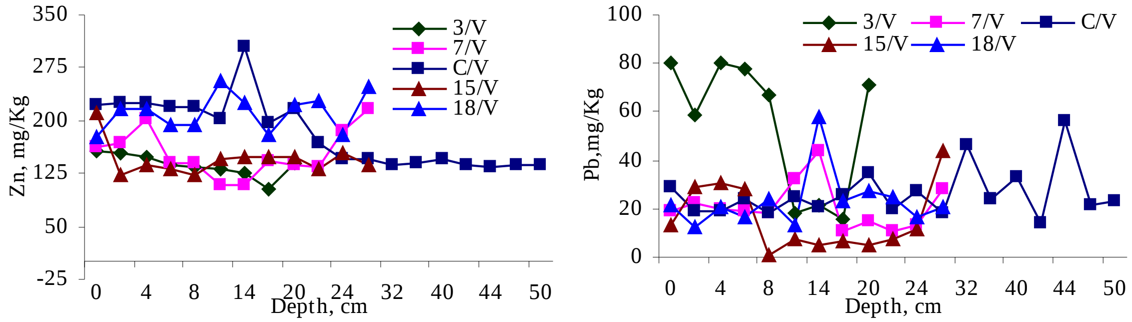


Figure 6.20&6.21 Depth wise variation of zinc and lead

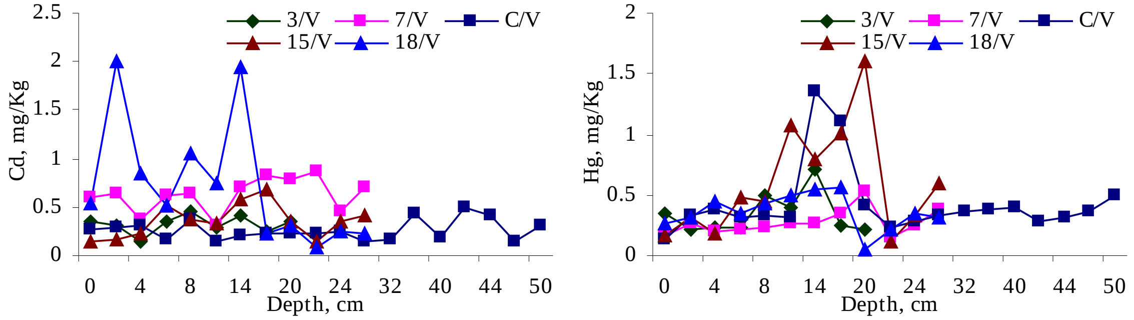


Figure 6.22&6.23 Depth wise distribution of cadmium and mercury

6.3.1.9.5 Ecotoxicological sense of heavy metal contamination

The average concentrations of different heavy metals were compared with the sediment quality guidelines developed for marine and estuarine ecosystem. From the Table 6.15 it is found that except nickel all other elements are at low to moderate range according to TEL and PEL values. For the metal nickel the stations C/V (Centre of the lake), 15/V (Ranimangalam) and 18/V (Kuppapuram) exceeded the ERM levels. The potential acute toxicity of contaminants in sediment sample can be estimated as the sum of the toxic units (∑TU) defined as the ratio of the determined concentration to PEL value (Pederson et al. 1998). From the toxic unit values the stations 18/V (Kuppapuram) and C/V (Centre of the lake) are more polluted compared to others.

6.3.1.9.6 Comparison with different rivers of the world

A comparison of metal concentration with different values reported for different rivers is generally taken as the quick and practical method for tracing heavy metal enrichment. The average values of the metal concentrations reported by other workers on some of the important rivers of the world (Jain 2004) have been summarized in Table 6.16. The comparison study with different rivers of the world revealed that the average metal load of Vembanad Lake is quit higher in the sediments.

6.3.2 Core sediments from the northern side of the wetland system

Three sediment cores from the Cochin estuary were collected to study geochemical behavior of the sediment core and the impact of industrialization to the estuary. More over it is also aimed to understand the impact of these pollutants to the freshwater side of the wetland system. The analytical results are tabulated in table 6.17 and are discussed below.

6.3.2.1 pH

The sediment sample at station Boat jetty showed highly alkaline pH, which was due to saline contribution. There is a decreasing trend in alkalinity towards the surface of the core. Similarly the station Pathalam industrial site also recorded high pH. It may be due to the alkaline pH of the effluents discharged from the industries. Comparatively acidic pH was reported in the station downstream Pathalam which is due to changes in sediment organic carbon, and texture

6.3.2.2 Electrical conductivity

Electrical conductivity of sediments points the presence of soluble salts. The conductivity is a function of total dissolved ions, types of ions and their potential to form charged or non-charged pairs or complexes (Evangelou 1998). The present study reported very high conductivity ranged from 434 μS/cm to 12810 μS/cm, which is primarily due to saline contribution.

6.3.2.3 Organic carbon

The percentage of organic carbon ranged from 5.35 to 8.41. Spatial variation indicated higher values in downstream Pathalam. Down core variation signified uniform distribution in all stations (Figure 6.24). Comparative to most of the stations in Vembanad Lake, the concentration of organic carbon in the estuary was high.

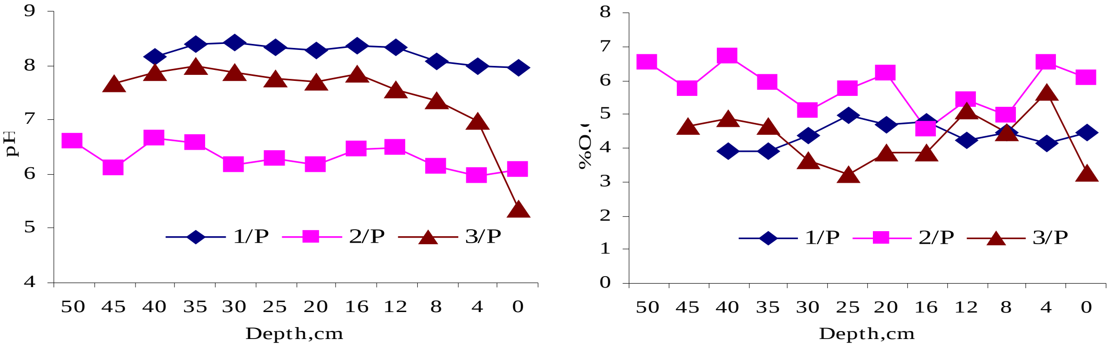


Figure 6.24&6.25 Down core variation of pH and % OC in the sediment core

6.3.2.4 Exchangeable cations and anions

The concentration of different ions present in the sediment core of Boat Jetty was the highest and is many times higher than that of sea water (Boyd 2000). Relatively higher concentration of magnesium was observed in the sediments of Boat jetty compared to calcium, which is in agreement with that of sea water. The station Pathalam industrial area recorded huge concentration of calcium (4000 to 11200 mg/Kg) with decreasing trend towards the surface. It is highly due to the contribution from the industrial waste. Whereas at the same station the concentration of magnesium increases towards the surface layer, which indicates the variability in ion exchange capacity of sediments in different regions of Cochin estuary. The spatial and temporal variation of the cations are showed in Figures 6.26-6.29.

The concentration of alkali metals such as sodium and potassium were also high in sediment core. In Vembanad fresh water region the concentration of exchangeable calcium is higher than sodium. But in estuarine region the sodium concentration exceeds that of calcium. The more concentration of calcium in freshwater region is due to clam deposition whereas the saline interaction made higher sodium in estuarine region. The exchangeability of sodium and potassium increases towards the surface whereas it is reverse in freshwater region. The concentration and variation of different exchangeable cations varied differently in each cores and it depends on factors like mineral deposition in sediments, saline mixing, industrial and municipal contribution and ion exchange capacity.

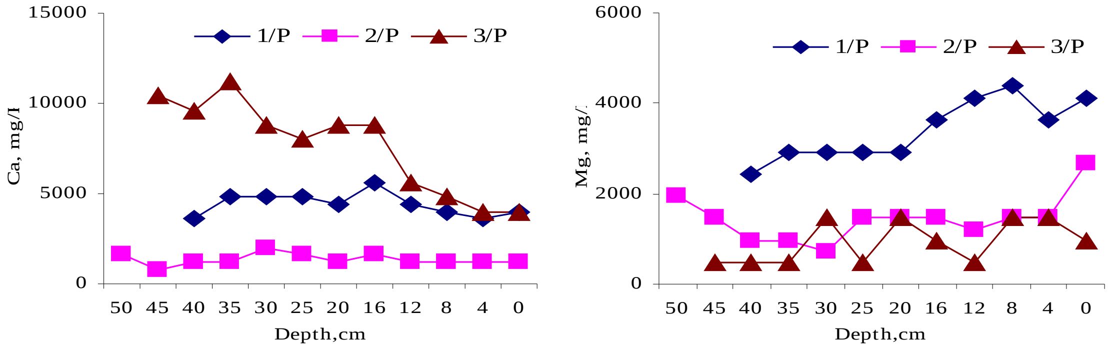


Figure 6.26&6.27. Down core variation of calcium and magnesium in the sediment core

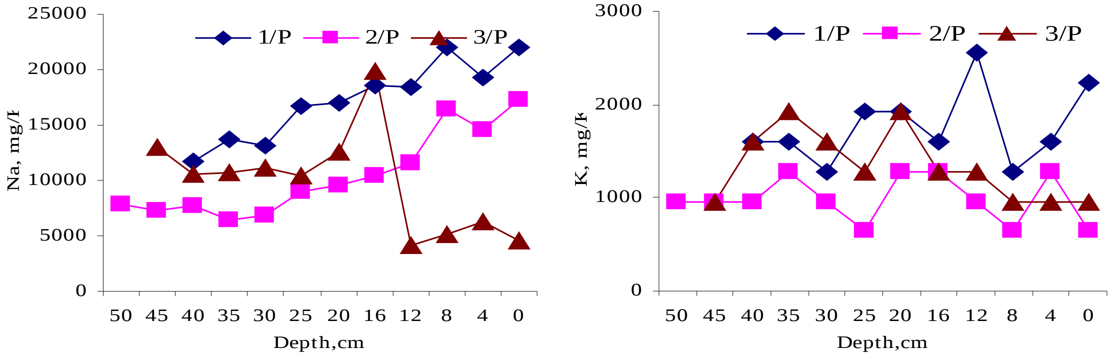


Figure 6.28&6.29 Down core variation of sodium and potassium in the sediment core

The major anions determined include chloride, sulphate, bicarbonate and phosphate. The concentration of chloride at Boat jetty came to a level of 39388mg/Kg in the uppermost layer, which is approximately double to that in sea water (Mohamed et al. 2003). The other two stations, Pathalam downstream and Pathalam industrial area also recorded higher values, 16602mg/Kg, 8138mg/Kg respectively which is mainly due to industrial discharge. Down core variation showed increasing trend towards the surface layer. The surface layer of the core sediment at Pathalam industrial site has a concentration of 10448mg/Kg of sulfate, which is an impact of industrialization. Down core variation indicated increasing trend in Boat jetty, and uniform distribution in other sites. The bicarbonate variation showed uniform distribution along the core. Highest concentration is 2560mg/Kg. Boyd (2000) has reported 142mg/l of bicarbonate in sea water. The concentration of phosphate is sever at the top layer of Pathalam industrial site (9510mg/Kg), which indicates excessive input of fertilizer residues from fertilizer industries in this area. The spatial and temporal variations of the major anions are depicted in Figures 6.30-6.33.

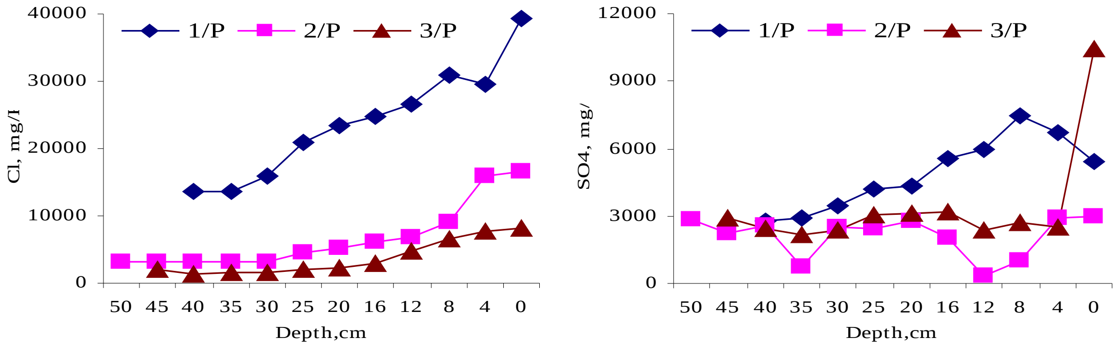


Figure 6.30&6.31 Down core variation of chloride and sulfate in the sediment core

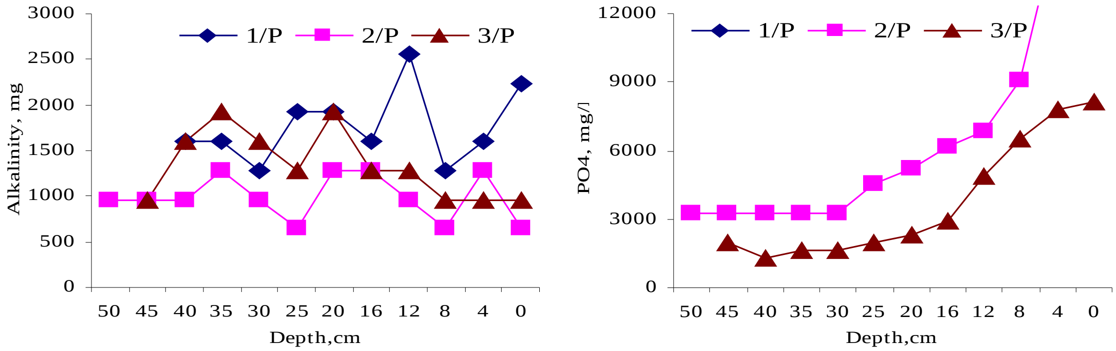


Figure 6.32&6.33 Down core variation of alkalinity and phosphate in the sediment core

6.3.2.5 Variation of heavy metals along the core

The concentration of various trace metals present in each core sample was given in Table 6.18. The concentration of iron varied from 107.38g/Kg to 6.76g/Kg, with an average value of 52.76g/Kg. The highest distribution was found at the station 2/P, which is the downstream of industrial area. The distribution pattern is almost uniform along the core with small increasing trend at stations 1/P and 3/P. Spatial variation of average concentration of iron was in the order 2/P>1/P>3/P and its longitudinal variation is shown in Figure 6.34. Concentration of manganese varied from 19.8g/Kg to 3.73g/Kg with a mean value of 11.42g/Kg. The average Mn contents in 1/P, 2/P and 3/P were 4.10g/Kg, 15.49g/Kg, and 14.68g/Kg respectively; all are higher than the average shale value of 850mg/Kg. The order of distribution along the estuary is 2/P>3/P>1/P with a slight increasing rate of deposition. The spatial and temporal variation is shown in the Figure 6.35.

Overall copper content of the sediments varied from 2.383 g/Kg to 0.58 g/Kg. The average copper content in 1/P, 2/P and 3/P are 1.19g/Kg, 1.68g/Kg, and 1.35g/Kg respectively. The down core variation of copper follows a decreasing trend in the station 2/P and a small increasing trend in stations 1/P and 3/P (Figure 6.36). The pollution of the estuary with respect to copper is very high and exceeds the EPA criteria for heavily polluted sediments of >50 mg/Kg. The level of nickel with respect to stations is in the order 2/P>1/P>3/P. The concentration of nickel varied from 49.59mg/Kg to 83.21mg/Kg (Figure 6.37). The average nickel content of 1/P, 2/P and 3/P are 70.56mg/Kg, 72.82mg/Kg and 62.6mg/Kg respectively. EPA criteria for heavily polluted sediments for Ni is >50mg/Kg. The pollution due to zinc in the sediment is very severe at the station 2/P with an average concentration of 1964g/Kg, compared to the average shale value of 95mg/Kg and EPA criteria of >200mg/Kg for heavily polluted sediments. This is due to the discharge of effluents from zinc based industry near the station. The spatial variation of zinc follows the order 2/P>1/P>3/P with uniform distribution through out the core (Figure 6.38).

The station 3/P recorded the highest concentration of lead, 244.37mg/Kg at a depth of 15cm from the surface. All the stations showed an increasing rate of deposition. The average concentration of lead ranged from 244.37mg/Kg to 7.38mg/Kg. The spatial and temporal variation was given in the Figure 6.39. Cadmium content varied from 41.73mg/Kg to 4.28mg/Kg. The spatial and temporal variation of cadmium revealed that all the stations were heavily polluted with respect to an average shale value of 0.3 mg/Kg

(Figure 6.40). The station 3/P is heavily polluted by mercury and its concentration at this station ranged from 23.41mg/Kg to 3.91mg/Kg. The average concentration of mercury at the stations 1/P, 2/P and 3/P are 0.52 mg/Kg, 0.75mg/Kg and 10.74 mg/Kg respectively. The spatial and temporal variation is given in the Figure 6.41.

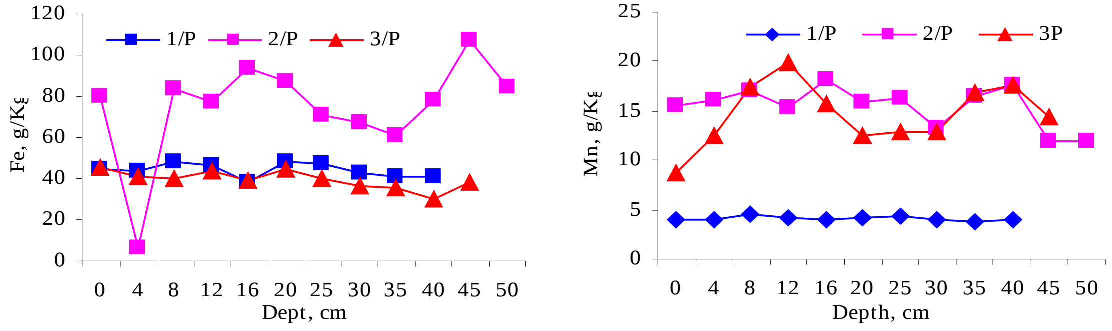


Figure 6.34&6.35 Distribution of iron and manganese in the core sediments

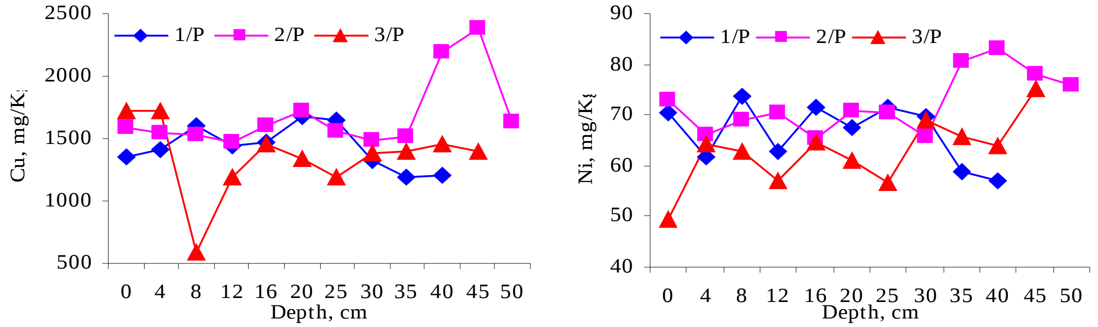


Figure 6.36&6.37 Down core variation of copper and nickel in Cochin estuary

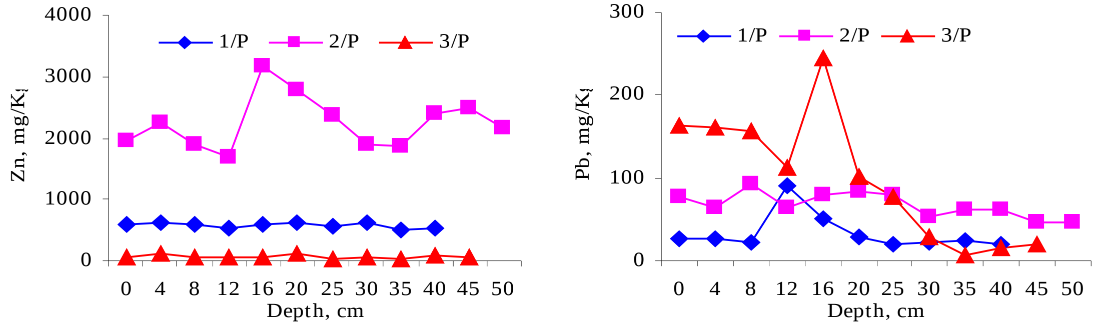


Figure 6.38&6.39 Down core variation of zinc and lead in Cochin estuary

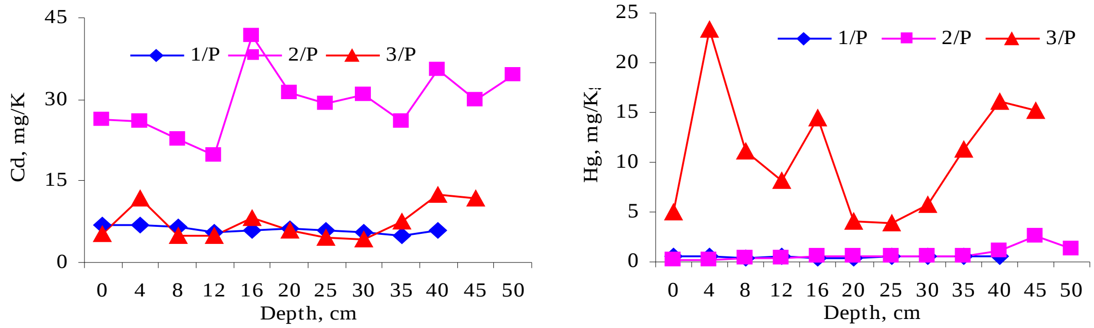


Figure 6.40&6.41 Down core variation of cadmium and mercury in Cochin estuary

6.3.2.6 Statistical analysis

The geochemistry of iron and organic matter affects the behavior of trace metals in aquatic environment (Fang and Hong 1999). Following their release to the environment the heavy metals are efficiently scavenged by newly precipitated iron and manganese hydroxides (Sarika and Chandramohanakumar 2008). The concentration and distribution of heavy metals in the aquatic systems are influenced by adsorption and co-precipitation with Fe and Mn oxides (Hatje et al. 2001). Correlation among metals and different sedimentary parameters in each core samples were determined.

The present study reveled that the correlation among different parameters differs with respect to stations. In the station 1/P, the organic carbon showed good positive correlation with all the heavy metals except mercury. Mercury showed a strong negative correlation with TOC. But for 2/P Fe, Mn, Cd, Pb and Zn showed negative correlation with TOC whereas Ni, Hg and Cu showed positive correlation with TOC. The metals Fe and Mn showed positive correlation with other metals (except mercury) and micronutrients such as Na, K, Mg, Cl and SO4 in core collected from station 1/P. At the station 2/P there is a positive correlation of different metals with Fe and Mn. But at station 3/P Fe showed a negative correlation with Mn Ni and Cd. Manganese showed a negative correlation with Fe and Cu. The correlation of Fe and Mn with different metals was given in Table 6.19.

6.3.2.7 Sediment contamination by comparison with effect based sediment quality guidelines

Sediments were classified as: non-polluted, moderately polluted and heavily polluted, based on effect based sediment quality guideline (SQG) of USEPA (Perin et al. 1997). Average concentration of heavy metals in the core sediments were compared with the SQGs. In all the stations the concentration of copper was above 50 mg/Kg, which belong to the class of heavily polluted sediments according to SQG. The concentration of zinc was above 200 mg/Kg at the stations 1/P and 2/P, which belongs to the class of heavily polluted sediment. At the station 3/P average concentration of zinc is less than 90mg/Kg which is in the category of non-polluted sediments. The average concentration of lead was above 60 mg/Kg at stations 2/P and 3/P, which indicates heavily polluted zone. At the station 1/P concentration of zinc was less than 40 mg/Kg and is nonpolluted according to SQG. The nickel concentration in all the stations was above 50 mg/Kg and hence is heavily polluted.

6.3.2.8 Assessment of sediment contamination by comparison of concentration with those of background sediments

The contamination factor and degree of contamination for the core sediment samples at each station were calculated according to Hakanson et al. (1980). From the results it was found that the contamination factor was below one for nickel at all the stations. For zinc at the station 3/P it is in the range of moderate degree of contamination. For manganese at the station 1/P and lead at stations 1/P and 2/P, the contamination factor is in the range of considerable degree of contamination. But the degree of contamination calculated for the stations 1/P, 2/P and 3/P were 72.6, 232.52 and 86.75 respectively, which are very high. This indicates severe degree of contamination in Cochin estuary.

6.3.2.9 Assessment of pollution by calculating the pollution load index (PLI)

The method employed by Tomilson et al. (1994) has been used to determine the pollution load index (PLI) of the estuary. The PLI values for each of the stations were calculated. The average concentration and the concentration present at the surface of the sediment core were compared with the average concentration of world shale. The trace element concentration along with the PLI values was given in Table 6.20. From the comparison table it is found that the pollution load at the station 2/P, downstream of industrial area is very severe.

6.3.2.10 Ecotoxicological sense of heavy metal contamination

The sediment quality guidelines developed for marine and estuarine ecosystem were used in the present study to determine the ecotoxicological sense of heavy metal contamination in the core sediments of Cochin estuary. Chemical concentrations corresponding to the 10th and 50th percentiles of adverse biological effects were called the effects range-low (ERL) and effects-range median (ERM) guidelines, respectively (Long et al. 1995). Considering the results, the heavy metal concentration of zinc at station 3/P and lead at 1/P were below ERL, which represent a minimal-effects range, which is intended to estimate conditions where biological effects are rarely observed. For cadmium at stations 1/P and 3/P, lead at stations 2/P and 3/P concentrations are grater than ERL and less than ERM, which represents a range with in which biological effects occur occasionally. For the copper and nickel at all stations, zinc at stations 1/P and 2/P and cadmium at station 2/P exceeded the ERM levels, which represents a probable effect range with in which adverse biological effects frequently occur. The potential acute toxicity of contaminants in sediment sample was estimated as the sum of the toxic units (∑TU) defined as the ratio of the determined concentration to PEL value (Pederson et al. 1998). The toxic unit values at stations 1/P, 2/P and 3/P are 18.44, 32.93 and 16.66 respectively.

6.4 Summary

The geochemical analysis of core sediments from southern and northern regions of the Vembanad wetland system revealed that, irreparable ecological damage is being happened to the system. pH, organic carbon, and texture in different regions have a great impact on the exchangeability of major ions to the aquatic system. There is high accumulation of organic matter in the lake. The relative concentration of exchangeable cations like $Ca^{2+,}$ Mg^{2+}, Na^{+} and K^{+} in the lake decreases with time in freshwater region and increases towards the surface in estuarine region. The ionic concentrations in sediments of Boat jetty were many times higher than that of seawater. Determination of nutrient concentration indicated hypereutrophic stage of lake with vertical increase in the rate of deposition of nitrate, sulphate, and phosphate. Fractionation studies indicated different sources which are contributing phosphorous to the wetland system. The amount of phosphorous in sediments is so severe that even if the source of phosphorous to the system is banned, it contributes phosphorous to the water column to maintain the hypereutrophic stage for a long period of time. The concentrations of pesticides were very high. The heavy metal levels are so dangerous that it threatens the aquatic life frequently. The spatial variation indicated industrial discharge as the main source of trace metals to the northern as well as southern region. Other sources of trace metals include those from sea water, agricultural runoff and soil type.

Table 6.1 Physico-chemical characteristics of core sample collected from station 3/V

Depth ,cm	32	28	24	20	16	12	8	4	0
Sample ID (3/V)	1	2	3	4	5	6	7	8	9
pH	7.95	7.64	6.97	6.30	5.96	6.03	5.81	5.63	5.85
EC, µS/cm	418	421	370	285	366	285	393	464	441
OC %	4.18	3.50	4.10	4.30	6.30	4.30	5.70	6.50	5.80
OM %	7.23	6.05	7.09	7.43	10.89	7.43	9.86	11.24	10.03
Ca, mg/Kg	2000	4000	1000	3000	3000	2000	1000	1000	2000
Mg, mg/Kg	3037.5	2430.0	2733.8	303.8	200.0	911.3	1215.0	1822.5	911.3
Na, mg/Kg	1479.5	1404.5	1099.5	799.5	1079.5	754.5	1214.5	1219.5	1314.5
K, mg/Kg	462.00	638.00	462.00	264.00	264.00	198.00	330.00	308.00	330.00
$Cl^{-,}$ mg/Kg	599.80	749.70	444.80	599.80	899.70	599.80	899.70	1049.60	899.70
SO_4^{2-} ,mg/Kg	1615.2	1380.0	1732.0	1086.0	1506.0	988.8	1260.0	2026.0	1578.0
PO_4-P, mg/Kg	350.0	170.0	320.0	390.0	720.0	540.0	930.0	930.0	800.0
Available-N, mg/Kg	252.00	252.00	364.00	224.00	560.00	280.00	504.00	420.00	616.00
TJN, mg/Kg	1848.0	1792.0	2128.0	2240.0	3752.0	1512.0	2968.0	4480.0	4088.0

Table 6.2 Physico-chemical characteristics of core sample collected from station 7/V

Depth ,cm	44	40	36	32	28	24	20	16	12	8	4	0
Sample ID (7/V)	1	2	3	4	5	6	7	8	9	10	11	12
pH	8.28	7.94	8.23	8.24	7.15	7.4	7.55	5.85	4.85	5.33	5.37	5.22
EC, µS/cm	1133	1121	918	936	758	591	553	640	769	688	721	773
OC %	3.43	3.59	3.43	3.35	2.95	2.15	2.31	2.95	2.15	1.92	2.00	1.84
OM %	5.92	6.19	5.92	5.78	5.09	3.71	3.99	5.09	3.71	3.30	3.44	3.16
Ca, mg/Kg	6720	6400	6080	6400	4160	4800	4160	3840	4160	3520	3520	2880
Mg, mg/Kg	2527	2333	2722	2916	2138	972	1555	1361	778	972	1166	1555
Na, mg/Kg	3860	2940	3100	2940	1940	1940	1620	1460	1220	1620	1580	1520
K, mg/Kg	1160	1040	860	800	640	560	540	520	500	500	480	480
Cl^-, mg/Kg	2700	2000	2000	2400	1600	1600	1200	2000	1600	2400	3200	1600
SO_4^{2-} ,mg/Kg	3299	4308	2596	3008	3112	2328	2728	3596	4048	3000	3068	3676
PO_4-P, mg/Kg	505	480	470	780	210	130	190	230	210	250	240	215
Alkalinity , mg/Kg	2667	1067	1467	1467	533	533	533	333	250	350	300	250

Table 6.3 Physico-chemical characteristics of core sample collected from C/V

Depth cm	ID (C/V)	pH	EC, µS/cm	OC %	OM %	Ca, mg/Kg	Mg, mg/Kg	Na, mg/Kg	K, mg/Kg	Cl^- mg/Kg	SO_4^{2-} mg/Kg	F^- mg/Kg	PO_4 P mg/Kg	NO_3 N mg/Kg
50	1	6.52	285	2.87	4.66	1200	972.0	820.0	345.0	508.2	784.6	6.80	220	5.0
47	2	6.44	327	3.07	5.29	1600	2187.0	1000.0	850.0	591.4	1076.2	4.60	160	4.8
44	3	6.48	356	2.91	5.02	1200	1458.0	900.0	345.0	494.8	1013	6.00	170	5.0
42	4	6.29	274	3.11	5.36	1200	1215.0	800.0	285.0	558.8	938.8	4.60	150	3.8
40	5	6.37	284	2.95	5.09	1600	1944.0	800.0	320.0	452.6	1157.8	5.80	230	4.8
36	6	6.12	380	2.35	5.78	1600	972.0	850.0	325.0	455.2	1788.2	4.00	190	4.0
32	7	6.08	350	3.55	6.12	2000	1215.0	800.0	295.0	1432.4	1960.2	5.40	390	3.4
28	8	6.06	377	3.47	5.98	1600	1215.0	650.0	300.0	715.6	1955.4	5.00	310	4.2
24	9	5.95	473	3.47	5.98	1600	1215.0	625.0	295.0	545.6	2984	12.00	210	4.2
22	10	6.04	416	3.31	5.71	1600	1458.0	625.0	290.0	602.2	2629.6	10.60	330	3.8
20	11	6.10	411	3.51	6.05	3200	972.0	500.0	280.0	481.8	2916.8	ND	320	1.8
16	12	5.80	455	3.63	6.26	800	1944.0	450.0	275.0	818.4	2794.8	3.80	390	3.2
14	13	5.70	510	3.31	5.71	1200	2430.0	475.0	305.0	190.6	4453.6	8.40	250	2.2
12	14	5.80	515	3.59	6.19	1200	1458.0	400.0	295.0	474	4580.8	10.00	310	2.6
8	15	6.00	500	3.71	6.39	1200	1944.0	350.0	295.0	778	4227.6	ND	400	2.2
6	16	5.90	235	4.59	7.91	1600	1944.0	315.0	295.0	596.2	1701.8	ND	500	2.8
4	17	5.70	262	5.38	9.28	3200	486.0	500.0	280.0	338.6	2074	4.00	490	1.8
2	18	5.70	170	5.54	9.64	1200	1701.0	300.0	275.0	550	1283.2	4.40	340	2.0
0	19	5.70	223	5.59	9.64	2400	2430.0	350.0	245.0	187.8	1735.8	4.00	380	2.2

Table 6.4 Physico-chemical characteristics of core sample collected from station 15/V

Depth ,cm	44	40	36	32	28	24	20	16	12	8	4	0
(15/V)	1	2	3	4	5	6	7	8	9	10	11	12
pH	8.93	8.95	8.84	8.85	8.83	8.82	8.72	8.81	8.78	8.73	8.51	8.09
EC µS/cm	769	794	795	698	688	664	708	592	569	575	533	653
OC %	7.98	6.98	6.58	6.58	9.04	9.91	8.84	9.78	9.91	8.51	10.17	9.78
OM %	13.76	12.03	11.34	11.81	15.58	17.08	15.24	16.86	17.08	14.67	17.53	16.86
Ca, mg/Kg	11000	12000	12000	12000	13000	13000	12000	12000	13000	12000	11000	7000
Mg, mg/Kg	3037.5	2430.0	3645.0	3037.5	2733.8	3341.3	3037.5	3341.3	2733.8	3037.5	3645.0	3645.0
Na, mg/Kg	3344.5	3244.5	3069.5	2929.5	2884.5	2980.5	1189.5	2604.5	2514.5	2239.5	1949.5	1774.5
K, mg/Kg	924.00	858.00	770.00	748.00	814.00	792.00	264.00	792.00	770.00	770.00	704.00	572.00
Cl^-, mg/Kg	2699.2	1499.5	1349.5	299.9	1199.6	1199.6	1049.6	749.7	749.7	749.7	1499.5	749.7
SO_4^{2-} ,mg/Kg	1598.4	1557.6	1725.6	1598.4	1578.0	1664.4	1584.0	1454.4	1567.2	1502.0	1292.4	1648.8
PO_4-P, mg/Kg	700.00	630.00	570.00	490.00	490.00	500.00	600.00	580.00	510.00	570.00	600.00	440.00
Available N,mg/Kg	168.00	280.00	196.00	196.00	280.00	168.00	168.00	252.00	168.00	112.00	168.00	252.00
TJN, mg/Kg	1624.0	1568.0	1680.0	1288.0	1736.0	1008.0	1904.0	1624.0	1288.0	1456.0	1232.0	2128.0

Table 6.5 Physico-chemical characteristics of core sample collected from 18/V

Depth ,cm	44	40	36	32	28	24	20	16	12	8	4	0
ID (18/V)	1	2	3	4	5	6	7	8	9	10	11	12
pH	6.84	6.38	6.46	6.47	6.71	6.66	6.64	6.32	5.61	5.19	4.29	3.38
EC, µS/cm	662	685	591	676	541	467	462	440	490	360	454	945
OC %	3.03	2.87	3.03	3.59	3.91	3.91	4.07	3.99	3.91	3.91	3.99	3.91
OM %	5.23	4.95	5.23	6.19	6.74	6.74	7.02	6.88	6.74	6.74	6.88	6.74
Ca, mg/Kg	5120	3200	4480	4480	5120	3200	4160	2880	3200	2560	2400	2400
Mg, mg/Kg	1944	1360.8	583.2	1555.2	1749.6	1166.4	1555.2	1166.4	1360.8	972	874.8	874.8
Na, mg/Kg	2060	1440	1840	2040	2300	1660	1840	1320	1200	620	490	480
K, mg/Kg	720	680	660	640	500	440	420	380	340	260	320	260
Cl^- mg/Kg	2000	1400	1600	2200	2200	1400	1600	600	800	800	400	600
SO_4^{2-} mg/Kg	2660	3112	2144	2228	1200	1492	1208	132	2760	2332	3788	5772
PO_4 -P, mg/Kg	410.0	550.0	450.0	530.0	580.0	620.0	460.0	460.0	520.0	550.0	570.0	510.0
Alkalinity , mg/Kg	400.0	333.3	333.3	400.0	266.7	400.0	466.7	666.7	133.3	200.0	200.0	666.7

Table 6.6 Fractionation of phosphorous in different core sediments

3/V					**C/V**				
Slice No	Ortho-P, mg/Kg	Hydrolysable-P, mg/Kg	Organic-P, mg/Kg	Total-P, mg/Kg	Slice No	Ortho-P, mg/Kg	Hydrolysable-P, mg/Kg	Organic-P, mg/Kg	Total-P, mg/Kg
1	350	100	250	700	1	220	40	340	600
2	170	140	230	540	2	160	40	200	400
3	320	140	420	880	3	170	90	180	440
4	390	50	300	740	4	150	270	40	460
5	720	520	380	1620	5	230	190	40	460
6	540	290	190	1020	6	190	470	400	1060
8	930	280	470	1680	7	390	150	240	780
7/V					8	310	190	160	660
1	505	45	20	570	9	210	390	560	1160
2	480	70	10	560	10	330	350	440	1120
3	470	30	50	550	11	320	240	740	1300
4	780	30	105	915	12	390	290	720	1400
5	210	20	25	255	13	250	430	540	1220
6	130	160	25	315	14	310	190	340	840
7	190	290	105	585	15	400	40	320	760
8	230	260	200	690	16	500	60	200	760
9	210	280	110	600	17	490	20	250	760
10	250	280	115	645	18	340	120	340	800
11	240	180	195	615	19	380	220	180	780
12	215	215	110	540	**18/V**				
15/V					Slice No.	Ortho-P, mg/Kg	Hydrolysable-P, mg/Kg	Organic-P, mg/Kg	Total-P, mg/Kg
Slice No.	Ortho-P, mg/Kg	Hydrolysable-P, mg/Kg	Organic-P, mg/Kg	Total-P, mg/Kg	1	410	290	65	765
2	630	70	90	790	2	550	290	90	930
3	570	120	60	750	3	450	300	165	915
4	490	20	120	630	4	530	300	115	945
5	490	200	70	760	5	580	380	240	1200
7	600	90	30	720	6	620	300	115	1035
8	580	60	10	650	7	460	310	475	1245
9	510	110	50	670	8	460	420	110	990
10	570	0	90	660	9	520	420	20	960
12	440	110	70	620	10	550	400	160	1110
14	340	340	230	910	11	570	340	215	1125

Table 6.7 Concentration of trace metals in the core sediment collected from station 3/V

Depth, cm	Slice No:	Fe g/Kg	Mn mg/Kg	Cu mg/Kg	Ni mg/Kg	Hg, mg/Kg	Cd, mg/Kg	Cr mg/Kg	Zn mg/Kg	Pb, mg/Kg
32	9	72.32	320.51	50.3	75.7	0.345	0.353	NA	156.7	80.03
28	8	64.40	301.67	47.67	54.20	0.222	0.310	2.48	155.1	59.03
24	7	44.44	310.33	25.67	40.15	0.229	0.153	NA	148.1	79.95
20	6	45.60	313.33	24.73	49.13	0.234	0.355	1.008	136.4	78.09
16	5	64.93	313.33	44.07	50.47	0.495	0.450	2	133.0	66.65
12	4	52.03	291.67	28.80	39.73	0.400	0.290	NA	132.2	17.93
8	3	50.05	316.67	26.47	53.27	0.713	0.423	NA	124.2	21.09
4	2	41.60	335.00	19.07	44.80	0.245	0.253	1.963	103.4	15.72
0	1	54.10	288.33	34.13	41.80	0.209	0.347	1.5	139.9	71.33

Table 6.8 Concentration of trace metals in the core sediment collected from station 7/V

Depth, cm	Slice No:	Fe g/Kg	Mn mg/Kg	Cu mg/Kg	Ni mg/Kg	Hg, mg/Kg	Cd mg/Kg	Cr mg/Kg	Zn mg/Kg	Pb, mg/Kg
0	12	70.95	646.67	27.00	47.07	0.170	0.600	1.787	163.63	19.00
4	11	69.50	760.00	25.80	44.73	0.272	0.647	1.408	167.41	22.00
8	10	71.62	635.00	28.20	47.40	0.194	0.380	NA	202.95	20.00
12	9	64.33	580.00	31.27	51.53	0.214	0.627	4.199	141.05	19.22
16	8	65.62	763.33	31.40	51.60	0.239	0.640		139.02	18.55
20	7	64.93	963.33	19.27	38.80	0.267	0.307	1.995	107.85	32.05
24	6	61.38	1031.67	16.73	36.53	0.265	0.707	NA	108.21	43.47
28	5	56.52	1016.67	20.67	44.53	0.354	0.820	1.644	142.07	10.97
32	4	52.88	1225.00	21.80	58.13	0.535	0.780	NA	136.62	14.70
36	3	53.65	996.67	21.53	52.40	0.153	0.867	1.8	133.04	10.81
40	2	49.35	910.00	22.07	57.33	0.245	0.447	NA	185.46	13.41
44	1	50.50	803.33	23.27	62.33	0.383	0.693	1.419	217.16	28.20

Table 6.9 Concentration of trace metals in the core sediment collected from station C/V

Depth, cm	Slice No:	Fe g/Kg	Mn mg/Kg	Cu mg/Kg	Ni mg/Kg	Hg, mg/Kg	Cd, mg/Kg	Cr mg/Kg	Zn mg/Kg	Pb, mg/Kg
0	19	76.09	501.67	47.60	64.73	0.136	0.267	0.30	223.00	28.65
2	18	72.27	486.67	51.33	65.00	0.334	0.287	-----	225.11	18.86
4	17	75.37	658.33	52.33	63.87	0.374	0.313	2.38	223.85	19.19
6	16	73.15	615.00	52.47	65.93	0.315	0.167	----	219.06	23.59
8	15	70.36	540.00	48.87	63.73	0.326	0.373	3.90	219.93	17.96
12	14	68.78	536.67	48.27	66.13	0.315	0.153	----	200.96	24.39
14	13	69.22	538.33	48.80	64.73	1.359	0.200	4.05	305.29	20.53
16	12	68.36	515.00	53.13	62.33	1.103	0.227	----	196.33	25.30
20	11	68.28	541.67	46.13	63.60	0.411	0.227	1.80	215.97	34.47
22	10	66.91	543.33	47.93	63.73	0.230	0.233	----	167.22	19.64
24	9	65.93	513.33	49.13	65.20	0.289	0.253	2.20	144.35	26.92
28	8	66.17	553.33	50.53	68.27	0.332	0.140	----	146.38	18.21
32	7	65.01	550.00	49.87	67.67	0.356	0.167	1.86	137.01	45.97
36	6	64.77	555.00	45.60	62.20	0.376	0.433	1.86	140.38	24.05
40	5	61.03	531.67	38.60	52.20	0.400	0.180	----	144.99	32.89
42	4	61.42	580.00	38.20	54.47	0.283	0.487	1.94	137.26	14.13
44	3	60.80	578.33	37.60	55.67	0.308	0.413	1.50	133.91	55.80
47	2	63.57	571.67	37.60	53.67	0.371	0.147	----	136.21	21.41
50	1	65.19	615.00	38.20	55.53	0.489	0.307	----	136.94	23.05

Table 6.10 Concentration of trace metals in the core sediment collected from station15/V

Depth cm	Slice No:	Fe g/Kg	Mn mg/Kg	Cu mg/Kg	Ni mg/Kg	Hg, mg/Kg	Cd, mg/Kg	Cr mg/Kg	Zn mg/Kg	Pb, mg/Kg
0	12	82.37	410.00	42.40	51.87	0.164	0.153	1.848	211.56	13.333
4	11	62.53	681.67	27.13	56.33	0.318	0.167	NA	123.82	28.650
8	10	55.70	696.67	24.80	57.67	0.178	0.233	1.176	136.61	30.330
12	9	25.55	683.33	25.20	61.00	0.478	0.513	NA	130.23	28.113
16	8	52.45	696.67	26.27	58.67	0.442	0.367	1.68	123.32	0.613
20	7	28.02	666.67	25.73	61.67	1.068	0.333	NA	145.41	7.180
24	6	39.65	691.67	26.73	63.00	0.789	0.573	1.932	146.97	5.367
28	5	38.00	656.80	24.82	61.23	1.004	0.673	NA	147.85	6.250
32	4	36.00	646.67	25.80	60.47	1.601	0.347	2.709	149.48	5.107
36	3	45.25	570.00	21.60	51.80	0.117	0.147	NA	131.95	7.25
40	2	51.38	596.67	25.87	62.27	0.334	0.347	3.388	154.37	11.567
44	1	33.68	575.00	26.80	69.40	0.595	0.413	1.344	136.41	44.040

Table 6.11 Concentration of trace metals in the core sediment collected from station18/V

Depth cm	Slice No:	Fe g/Kg	Mn mg/Kg	Cu mg/Kg	Ni mg/Kg	Hg, mg/Kg	Cd mg/Kg	Cr mg/Kg	Zn mg/Kg	Pb, mg/Kg

0	12	66.65	410.00	38.87	52.67	0.270	0.547	2.096	177.75	21.70
4	11	65.35	281.67	40.20	53.47	0.306	2.000	1.496	216.09	12.03
8	10	69.58	310.00	41.60	54.73	0.440	0.853	NA	217.04	20.87
12	9	67.05	370.00	47.27	60.87	0.353	0.513	4.629	193.07	16.82
16	8	62.38	678.33	51.87	67.20	0.429	1.060	NA	194.25	24.19
20	7	67.43	1076.67	54.47	71.00	0.503	0.747	3.668	256.21	13.03
24	6	64.77	876.67	55.40	71.40	0.542	1.933	NA	224.20	58.23
28	5	65.95	1311.67	55.80	74.47	0.561	0.233	1.559	180.50	22.79
32	4	60.32	1045.00	50.53	69.87	0.055	0.307	NA	222.15	26.96
36	3	60.30	761.67	50.40	65.67	0.217	0.073	1.553	227.97	24.74
40	2	59.57	795.00	50.67	64.00	0.344	0.240	NA	178.74	16.90
44	1	60.23	440.00	56.13	62.93	0.314	0.235	1.53	248.77	20.41

Table 6.12 Average concentration of heavy metals in the core sediment and its assessment with respect to Sediment Quality Guidelines

Element mg/Kg	Sampling Stations					Elemental Back-ground Conc.	SQG non-polluted	SQG moderate polluted	SQG heavily polluted
	3/V	7/V	C/V	15/V	18/V				
Cu	33.43	24.08	46.43	26.93	49.43	55.0	<25	25-50	>50
Zn	136.5	153.7	181.8	144.8	211.3	70.0	<90	90-200	>200
Mn	310.0	860.9	553.9	630.9	696.3	950.0	_	_	_
Cr	1.79	2.04	2.18	2.01	2.36	100.0	<25	25-75	>75
Cd	0.33	0.63	0.26	0.36	0.73	0.2	_	_	_
Pb	54.42	21.03	52.51	15.65	23.22	12.5	<40	40-60	>60
Ni	49.92	49.37	62.04	59.61	64.02	75.0	<20	20-50	>50

Table 6.13 Contamination factor and degree of contamination of Vembanad lake sediments

Sampling Station ID	C^i_f for different metals						C_d
	Cu	Zn	Cr	Cd	Pb	Ni	
3/V	0.61	1.95	0.02	1.63	4.35	0.67	8.56
7/V	0.44	2.20	0.02	3.13	1.68	0.66	7.47
C/V	0.84	2.60	0.02	1.31	4.20	0.83	8.97
15/V	0.49	2.07	0.02	1.78	1.25	0.79	5.61
18/V	0.90	3.02	0.02	3.64	1.86	0.85	9.44
Reference	1.00	1.00	1.00	1.00	1.00	1.00	6.00

Table 6.14 Concentration of various heavy metals and their assessment with average shale value and the pollution load index

Sampling stations	Heavy metal, mg/Kg (Fe in g/Kg)							PLI
	Cu	Pb	Cd	Zn	Mn	Fe	Ni	
3/V	33.43	54.42	0.33	136.55	310.09	54.39	49.92	0.99
7/V	24.08	21.03	0.63	153.71	860.97	60.94	49.37	1.11
C/V	46.43	52.51	0.26	181.80	553.95	67.51	62.04	1.30
15/V	26.93	15.65	0.36	144.83	630.98	45.88	59.61	0.87
18/V	49.43	23.22	0.73	211.39	696.39	64.13	64.02	1.47
Average shale	45	20	0.3	95	900	46.7	68	

Table 6.15 Sum of the toxic units (∑TU) of core sediments and various guidelines for heavy metals

Element, mg/Kg	Sampling stations					TEL	PEL	ERL	ERM
	3/V	**7/V**	**C/V**	**15/V**	**18/V**				
Cu	33.43	24.08	46.43	26.93	49.43	18.70	110.00	34.00	270.00
Zn	136.55	153.71	181.80	144.83	211.39	124.00	270.00	150.00	410.00
Cr	1.79	2.04	2.18	2.01	2.36	52.30	160.00	81.00	370.00
Cd,	0.33	0.63	0.26	0.36	0.73	0.68	4.20	1.20	9.60
Pb,	54.42	21.03	52.51	15.65	23.22	30.20	110.00	46.70	218.00
Ni	49.92	49.37	62.04	59.61	64.02	15.90	43.00	20.90	51.60
TU	2.55	2.29	3.09	2.41	3.12				

Table 6.16 Comparison of heavy metal concentration with other rivers of the world

Rivers	Heavy metal, mg/Kg				Rivers	Heavy metal, mg/Kg			
	Cu	**Pb,**	**Cd,**	**Zn**		**Cu**	**Pb,**	**Cd,**	**Zn**
Ganga	10.8	25.6	2.55	36.1	Illinois, USA	19	28	2	81
Ganga	21	25	-	46	Yamuna	52	57	-	123
Brahmaputhra	17	-		47	Yamuna	22.2	60	9.5	59.2
Genesse, USA	18	40	-	69	Average shale	45	20	0.3	95
Toyohira, Japan	22	24	0.2	152	*Vembanad*	*36.06*	*33.37*	*0.46*	*165.66*
Average shale	45	20	0.3	95					

Table 6.17 Physico-chemical characteristics of core sample collected from estuary

Depth, cm	Parameters	pH	OC %	EC, mS/cm	Ca, mg/kg	Mg, mg/kg	Na, mg/kg	K, mg/kg	Alkalinity, mg/Kg	Cl-,mg/kg	SO4, mg/kg	PO4-P,mg/kg

1/P												
40	1	8.17	3.91	2830	3600	2430	11766	1500	1600	13672	2752	782
35	2	8.40	3.91	2810	4800	2916	13727	1700	1600	13672	2925	472
30	3	8.41	4.39	3240	4800	2916	13139	1725	1280	15950	3430	648
25	4	8.33	4.95	4150	4800	2916	16670	2200	1920	20833	4224	600
20	5	8.28	4.71	4530	4400	2916	17062	1950	1920	23437	4339	234
16	6	8.35	4.79	4930	5600	3645	18631	2050	1600	24740	5555	638
12	7	8.33	4.23	5230	4400	4131	18435	1900	2560	26693	5952	728
8	8	8.08	4.47	6220	4000	4374	21966	2150	1280	30924	7424	1048
4	9	8.00	4.15	5840	3600	3645	19220	1975	1600	29622	6694	750
0	10	7.96	4.47	7270	4000	4131	21966	2250	2240	39388	5402	738
2/P												
50	1	6.60	6.54	839	1600	1944	7843	675	960	3255	2832	427
45	2	6.12	5.75	764	800	1458	7255	500	960	3255	2266	197
40	3	6.67	6.70	664	1200	972	7647	575	960	3255	2595	358
35	4	6.57	5.91	552	1200	972	6470	600	1280	3255	726	314
30	5	6.16	5.11	766	2000	729	6862	500	960	3255	2531	364
25	6	6.27	5.75	937	1600	1458	9020	575	640	4557	2413	220
20	7	6.16	6.22	1142	1200	1458	9608	550	1280	5208	2768	200
16	8	6.46	4.55	1203	1600	1458	10393	525	1280	6185	2048	173
12	9	6.48	5.43	1239	1200	1215	11570	525	960	6836	362	154
8	10	6.15	4.95	1655	1200	1458	16474	525	640	9115	986	95
4	11	5.97	6.54	3330	1200	1458	14512	1000	1280	15950	2947	154
0	12	6.08	6.06	12810	1200	2673	17258	1200	640	16602	3008	233
3/P												
45	1	7.68	4.63	499	10400	486	12943	425	960	1953	2906	3530
40	2	7.86	4.87	464	9600	486	10589	1250	1600	1302	2413	6470
35	3	7.99	4.63	488	11200	486	10785	1000	1920	1628	2179	5850
30	4	7.87	3.63	434	8800	1458	11178	1050	1600	1628	2384	2200
25	5	7.77	3.23	529	8000	486	10393	925	1280	1953	3024	2530
20	6	7.71	3.87	707	8800	1458	12551	1025	1920	2279	3114	3490
16	7	7.84	3.87	809	8800	972	19808	1125	1280	2930	3171	6780
12	8	7.55	5.11	1025	5600	486	4116	1550	1280	4883	2397	9510
8	9	7.35	4.47	1328	4800	1458	5097	2275	960	6510	2688	5210
4	10	6.97	5.67	1660	4000	1458	6274	2550	960	7812	2528	3630

0	11	5.35	3.27	2180	4000	972	4508	1825	960	8138	10448	1275

Table 6.18 Concentration of various trace metals in the core sample collected from estuary

1/P									
Depth, cm	Slice	Fe,g/kg	Mn,g/kg	Cd,mg/kg	Cu,mg/kg	Pb, mg/Kg	Hg, mg/Kg	Ni, mg/Kg	Zn, mg/Kg
0	1,10	44.54	4.04	7.03	1346.25	27.18	0.56	70.56	578.11
4	1,9	43.27	4.03	6.98	1412.50	27.54	0.53	61.91	620.87
8	1,8	47.75	4.45	6.63	1598.13	22.29	0.46	73.82	586.76
12	1,7	46.48	4.18	5.53	1439.38	89.99	0.49	62.78	526.02
16	1,6	37.89	4.00	5.85	1468.75	51.28	0.45	71.46	584.34
20	1,5	48.37	4.17	6.30	1676.88	28.16	0.46	67.38	622.73
25	1,4	47.65	4.35	5.88	1653.75	20.94	0.51	71.48	577.73
30	1,3	42.54	4.00	5.45	1322.50	22.81	0.52	69.87	630.63
35	1,2	41.31	3.73	4.98	1192.50	24.85	0.53	59.00	496.80
40	1,1	40.51	4.02	5.85	1206.88	18.77	0.60	57.06	538.89
2/P									
Depth, cm	Slice	Fe,g/kg	Mn,g/kg	Cd,mg/kg	Cu,mg/kg	Pb, mg/Kg	Hg, mg/Kg	Ni, mg/Kg	Zn, mg/Kg
0	3,12	79.70	15.59	26.35	1588.13	78.27	0.23	72.82	1963.67
4	3,11	6.76	16.04	25.83	1540.00	63.18	0.15	65.99	2259.00
8	3,10	83.90	17.02	22.75	1525.00	92.50	0.37	68.84	1910.02
12	3,9	77.13	15.40	19.58	1465.00	65.01	0.37	70.42	1695.87
16	3,8	93.20	18.26	41.73	1608.75	79.78	0.62	65.37	3157.62
20	3,7	86.83	15.92	31.05	1713.75	83.68	0.55	70.64	2783.00
25	3,6	70.83	16.30	29.33	1558.13	79.50	0.59	70.45	2364.44
30	3,5	67.45	13.27	30.75	1480.63	52.18	0.51	65.68	1911.00
35	3,4	61.20	16.46	25.88	1515.63	61.36	0.59	80.59	1864.39
40	3,3	78.06	17.63	35.45	2197.50	62.64	1.13	83.21	2389.07
45	3,2	107.38	11.99	30.00	2383.75	45.35	2.64	78.08	2503.15
50	3,1	84.31	12.01	34.48	1629.38	46.63	1.21	75.98	2152.93
3/P									
Depth, cm	Slice	Fe,g/kg	Mn,g/kg	Cd,mg/kg	Cu,mg/kg	Pb, mg/Kg	Hg, mg/Kg	Ni, mg/Kg	Zn, mg/Kg
0	7,11	45.59	8.71	5.23	1723.75	162.59	4.91	49.59	70.07
4	7,10	40.96	12.48	11.93	1727.50	160.78	23.41	64.26	121.35
8	7,9	40.04	17.50	5.03	583.13	156.28	11.14	62.85	50.07
12	7,8	43.91	19.87	4.90	1191.25	112.89	8.08	57.11	54.04
16	7,7	39.39	15.69	8.13	1457.50	244.37	14.46	64.46	56.97
20	7,6	44.61	12.53	5.78	1337.50	100.50	4.03	61.19	127.66
25	7,5	39.69	12.82	4.48	1196.88	77.96	3.91	56.51	42.69
30	7,4	36.55	12.79	4.28	1378.13	28.60	5.72	68.91	50.70
35	7,3	35.85	16.92	7.55	1392.50	7.38	11.22	65.84	42.68
40	7,2	30.04	17.69	12.33	1463.13	16.14	16.12	63.78	102.38
45	7,1	37.87	14.44	11.78	1403.13	20.63	15.18	75.05	61.14

Table 6.19 Correlation of Iron and Manganese with other metals

Parameter /Station		Fe	Mn	Ni	Cu	Cd	Pb	Hg	Zn
Fe	1/P	1	0.745	0.34	0.705	0.32	0.017	-0.312	0.219
	2/P	1	-0.194	0.281	0.435	0.319	0.049	0.553	0.277
	3/P	1	-0.401	-0.571	0.016	-0.512	0.585	-0.398	0.107
Mn	1/P	0.745	1	0.585	0.802	0.418	0.029	-0.405	0.327
	2/P	-0.194	1	-0.126	-0.224	-0.074	0.747	-0.563	0.259
	3/P	-0.401	1	0.272	-0.534	0.127	-0.163	0.257	-0.265

Table 6.20 Comparison of heavy metals with average shale value and the pollution load index

Element	1/P		2/P		3/P		Average Shale
	Average	Surface	Average	Surface	Average	Surface	
Fe, g/kg	44.0	44.5	74.7	79.7	39.5	45.6	45.70
Mn, mg/kg	4096.8	4040.0	15490.5	15586.9	14675.9	8714.4	850
Cd, mg/kg	6.0	7.0	29.4	26.4	7.4	5.2	0.30
Cu, mg/kg	1431.7	1346.2	1683.8	1588.1	1350.4	1723.8	45.00
Pb, mg/Kg	33.3	27.2	67.5	78.3	98.9	162.6	20.00
Ni, mg/Kg	66.5	70.6	72.3	72.8	62.7	49.6	68.00
Zn, mg/Kg	576.2	578.1	2246.2	1963.7	70.9	70.1	95.00
PLI	4.3	4.3	9.8	9.7	4.5	4.3	

7.0 Biomonitoring using Aquatic Macrophytes

7.1 Introduction

Macrophytes are aquatic plants that grow in or near water and can be classify as emergent, submerged or floating plants. There has been considerable interest in using aquatic plants for removal of various pollutants, including heavy metals from water bodies because of their fast growth rate and simple growth requirements, which are favorably compared to those of fish (Lewis 1995, Wang 1991). Moreover, aquatic plants are particularly important in heavy metal pollution studies, since the analysis of these plants can give an indication of the state of water environment to which they have been exposed (Hellawell 1986). Studies had been done in investigating the capabilities of some macrophytes to remove different concentration of heavy metals (Maine et al. 2004, Skinner et al. 2007) in the role as biomonitors of environmental metal levels(Mishra et al. 2007) and in their ability as biological filters of the aquatic environment (Upadhyay et al. 2007). In aquatic environment, where pollutant inputs are discontinuous and pollutants are quickly diluted, analysis of plant tissues provides time-integrated information about the quality of the system (Baldantoni et al. 2005).

The biomonitoring of pollutants using accumulator species is based on the capacity with which some plant and animal has to accumulate relatively large amounts of certain pollutants, even from much diluted solutions without obvious noxious effects. Biomonitoring has several advantages and is the most significant study of sublethel levels of bioaccumulated contaminants with in the tissues of organism, which indicate the net amount of pollutants integrated over a period of time (Lowett–Doust et al. 1994). It may be performed in two ways, based on the kind of sample organism: 1, endemic or native organisms (passive biomonitoring) and 2, introduced organisms (active biomonitoring) (Chaphekar 1991).

Vembanad Kol Wetland System is a Ramsar site having importance in the point of biodiversity, water quality, mineral resources, flora and fauna, hydrology etc. The environmental problems of the wetland system with reference to heavy metal content of water, sediment and animals had been reported by many authors (Harikumar et al. 2007, Balachandran et al. 2003, Unnikrishnan and Nair 2004, Sankaranarayanan et al. 1998, Pillai and Valsala 1995). But very few studies have reported on the accumulation of heavy metals in the aquatic macrophytes. In fact, additional information is needed to provide a database for the ecological status of the Vembanad Wetland System that helps the policy makers to take effective decision for proper management of the lake. This chapter focuses on the distribution of trace metals such as iron, manganese, copper, nickel, cadmium, mercury, zinc, lead and chromium in different parts of the five native aquatic macrophytes of the Vembanad Lake and classification of macrophytes based on their capability as biomonitors.

7.2 Methodology

The study area included the southern upstream part of the Thanneermukkom barrier, which prevents the salinity intrusion towards the fresh water region. In this part the hydrography is mainly controlled by discharges from four rivers namely Pamba, Manimala, Meenachil and Achancovil. Six native aquatic macrophytes from the fresh water region of Vembanad Lake, were selected as passive biomonitors for the present study. The selected plant species were *Eichornia crassipes, Sacciolepis interrepta, Alternanthera pheloxeroides, Salvenia molesta and Pistia stratiotes*.

The plants were washed with lake water to remove periphyton and sediment particles then under running tap water and distilled water to eliminate debris. The samples were then separated into roots, stalk and leave sections. They were oven dried overnight at 65^{0}C until constant weight and cut into small pieces. The finely ground material was stored in sealed polyethylene bottles at room temperature until digestion.

A sample of approximately 1.5g of ground plant was weighed and digested with concentrated nitric acid and perchloric acid (3:1 by volume). The digests were diluted with distilled water and made up to 25ml. The digested samples were analyzed for heavy metals using (AAS by Thermo M5 series). A reagent mixture blank was carried following the same procedure as the plant samples. Metal accumulation in plant body is reported as milligram of metal per kilogram of dry plant weight.

7.3 Results and discussion

The analytical results of the metal accumulation in different aquatic macrophytes showed that the concentration and the distribution of the metals were different in different species. The aquatic plant growing in the study area exhibited different trace element concentrations, depending on the plant organ, plant species, and both the sampling time and the sampling site. Roots of aquatic plant absorb heavy metals from interstitial water (or pore water) and accumulate high concentrations (Baldantoni et al. 2004).

7.3.1 Variation of heavy metals in different parts of the macrophytes

In the species *Eichornia crassipes*, the average concentration of the heavy metal was in the order Fe>Mn>Zn>Ni>Pd>Cu>Cr >Cd>Hg. The different parts of the plant showed different accumulation rate for the specific metal and it varied for different metals. The above species showed highest metal distribution in the roots followed by stem and leaf. Copper was found high in the stem, and the leaf showed highest concentration of mercury. *Sacciolepis interrepta* showed the distribution pattern as Fe> Mn> Zn> Cu> Ni> Pb> Hg> Cr > Cd. The order of accumulation is root>stem>leaf. Trace element distribution in *Alternanthera pheloxeroides* followed the same order as *Eichornia crassipes.* The order of accumulation in the parts of the plant followed the same order as *Sacciolepis interrepta* except cadmium where the leaf showed least distribution. But the concentration of mercury was highest in the leaves. The total trace element concentration of *Salvenia molesta and Pistia stratiotes* showed the pattern Fe>Mn>Zn>Cu>Ni>Pb> Cd> Hg>Cr and Fe>Mn>Zn> Pb> Ni> Cu> Cd> Hg>Cr respectively.

The maximum and the minimum concentration of different heavy metals present in aquatic macrophytes of Vembanad Lake are given in the Table 7.1, and its variation is shown in the Figures 7.1-7.8. The present study showed higher concentration of all heavy metals in the roots of *Alternanthera pheloxeroides* except for mercury, which is high in the leaves. *Sacciolepis interrepta* recorded the least concentration in the stem except for nickel, cadmium, where it is minimum in the leaves. The minimum concentration of manganese, nickel, cadmium, zinc and lead was found in *Sacciolepis interrepta* and *Pistia stratiotes* showed the minimum distribution of iron, copper, mercury, and chromium.However, comparison of metal content in macrophytes is often difficult because of the difference in age of plants and the presence of pollution sources (Vardayan and Ingole 2006).

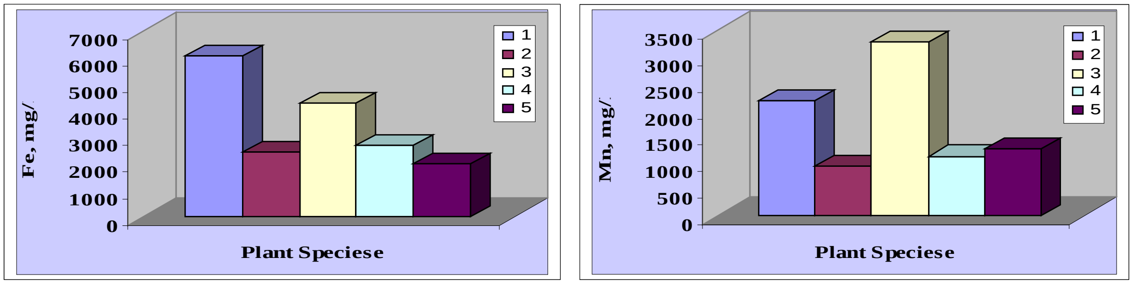


Figure 7.1 & 7.2 Average concentration of Fe and Mn in different macrophytes

7.3.2 Comparison with the sediment

A comparison of the concentration of different trace elements present in the macrophytes with the background concentration present in the sediment was given in Table 7.2.

The comparison table indicated higher concentration of manganese and zinc in the all the macrophytes compared to the sediment. Chromium and mercury were high in *Alternanthera pheloxeroides* compared with that of sediment. *Salvinia molesta* recorded same concentration of cadmium as present in the sediment. The concentration of iron present in the sediment was 10-20 times higher than that of the plants, which indicated its contribution from the soil type of the particular area.

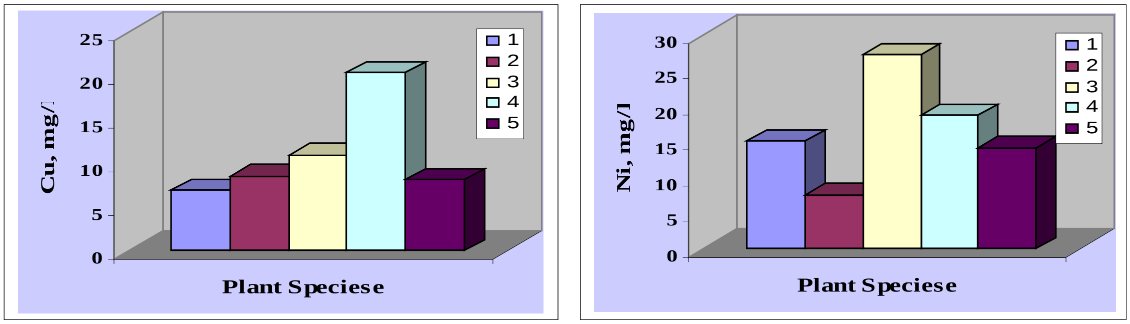


Figure 7.3 & 7.4 Average concentration of Cu and Ni in different macrophytes

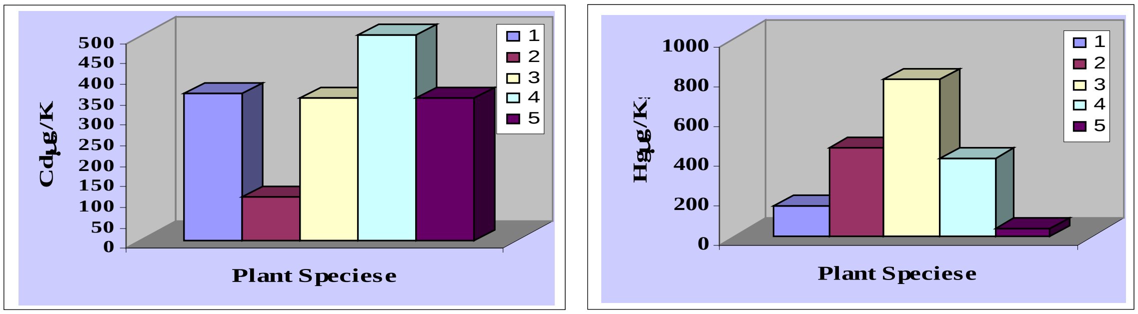


Figure 7.5 & 7.6 Average concentration of Cd and Hg in different macrophytes

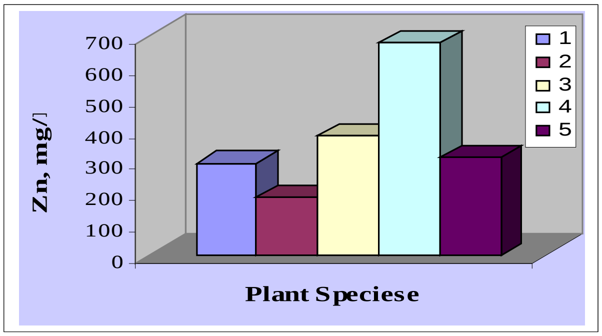


Figure 7.7 Average concentration of Zn in different macrophyte

7.3.3 Comparison with lake water

Concentration factor (CF) of each plant was calculated (Rai et al. 1995, Espinoza-Quinones et al. 2005) as the ratio between the metal concentration in plants (mg kg^{-1} dry weight) and the ambient metal concentration in lake water (mg l^{-1}). Metal concentration factor determined for metals such as iron, manganese, copper, nickel, zinc and lead in different plants are given in Table 7.3.

The concentration factor determined for each metal can be used as a tool for the comparative suitability of particular macrophyte among the selected plants of Vembanad Lake for the biomonitoring technique. For the trace element, iron the concentration factor was high for *Eichornia crassipes.* Hence this species can be used as the most suitable biomonitor for iron. *Alternanthera pheloxeroides* showed highest concentration factor for manganese, nickel and lead and can be used as the suitable indicator for the toxicity of above metals. For copper and zinc the highest concentration factor was reported for *Salvinia molesta,* which indicate its capacity as a suitable biomonitor for the above metals. The concentration of cadmium, mercury and chromium in lake water were below the detectable limit and hence the contamination factor was not calculated. But the macrophytes containing the highest concentration, *Alternanthera pheloxeroides* can be used as the best biomonitor.

7.4 Summary

Since the measurement of pollutants in the organism can be conveniently used for evaluating the bioavailability of pollutants in an environment, the use of biomonitoring is widespread in marine and fresh water environment. The present study showed that concentration and the order of accumulated metals were different in each macrophytes and the maximum concentration was reported in the roots of *Alternanthera pheloxeroides*. Stem showed least concentration for most trace elements. The minimum concentrations of trace elements were detected in *Sacciolepis interrepta* and *Pistia stratiotes*. All the macrophytes showed higher concentration of manganese and zinc compared to that of sediment. Comparison of the trace elements with the background concentration of sediment showed more chromium and mercury in *Alternanthera pheloxeroides.* The concentration factor calculated showed the suitability of different macrophytes among the selected plants as the biomonitor for specific heavy metal in the study area. *Eichornia crassipes* is the suitable biomonitor for iron, *Alternanthera* *pheloxeroides* for manganese, nickel, lead, mercury and chromium and *Salvinia molesta* for copper, cadmium and zinc. Above all *Alternanthera pheloxeroides* is the best hyper accumulator, which can be used for phytoremediation of the aquatic eco-system. The above results confirmed that the Vemband Lake is facing serious environmental pollution due to trace metals. The major source for the metal contamination is the industrial effluents discharged to Periyar River, which is reaching Vembanad Lake through Cochin estuary.

Table 7.1 Concentration of heavy metals in different parts of the macrophytes

Heavy metal	Maximum	Part of plant	Minimum	Part of plant
Fe, mg/Kg	16857	1, Root	136.0	2, Stem
Mn, mg/Kg	9236	3, Root	36.3	2, Stem
Cu, mg/Kg	21.1	3, Root	2.3	2, Stem
Ni, mg/Kg	65.3	3, Root	2.5	2, Leaf
Cd, µg/Kg	940.9	3, Root	25.0	1,3 Leaf
Hg, µg/Kg	1410.8	3, Leaf	36.4	5, Plant
Zn, mg/Kg	966.5	3, Root	25.9	2, Stem
Pb, mg/Kg	24.4	3, Root	5.3	2, Root
Cr, mg/Kg	2.04	2, Root	0.026	5, Plant

Table 7.2 Comparison of heavy metals present in the macrophytes with metals present in sediment samples

Species	Fe, mg/Kg	Mn, mg/Kg	Cu, mg/Kg	Ni, mg/Kg	Cd, mg/Kg	Hg, mg/Kg	Zn, mg/Kg	Pb, mg/Kg	Cr, mg/Kg
Eichornia crassipes.	6071	2181	6.87	15.09	0.36	0.15	292	13.68	1.64
Sacciolepis interrepta.	2464	938	8.53	7.57	0.11	0.45	184	5.32	0.14
Alternanthera pheloxeroides	4289	3294	10.98	27.22	0.35	0.80	380	24.37	2.04
Salvinia molesta	2686	1129	20.35	18.69	0.50	0.40	674	13.89	0.34
Pistia stratiotes	2021	1266	8.16	14.15	0.35	0.04	312	19.72	0.03
Sediment(Av)	58570	610	36.06	56.99	0.50	0.5	166	33.37	2.03

Table 7.3 Concentration factor calculated for the various heavy metals in different macrophytes

Plant	Concentration Factor(CF/10^3)					
Element	Fe	Mn	Cu	Ni	Zn	Pb
1	11.039	90.490	3.121	3.654	26.846	1.287
2	4.481	38.909	3.878	1.833	16.954	0.500
3	7.799	136.694	4.991	6.591	34.970	2.293
4	4.884	46.836	9.250	4.525	62.015	1.306
5	3.674	52.539	3.709	3.425	28.697	1.855
1, Eichornia crassipes. 2, Sacciolepis interrepta. *3, Alternanthera pheloxeroides. 4, Salvinia molesta. 5, Pistia stratiotes*						

8.0 Isotopes studies of Vembanad wetland system

8.1 Introduction

The last two decades of 19th century witnessed tremendous development in the field of physical sciences notably physics and chemistry which had far reaching influence on the other discipline of science and technology notably engineering technology, medicine and agriculture. The discovery of X-rays followed by radioactivity at the end of 19th century paved way for increased scientific research activities all over the world notably in the laboratories in Europe, USA, Soviet Union and including countries like Japan. Early 20th century witnessed the discovery of isotopes of several elements. The invention of mass spectrograph with in a few years of discovery of isotopes added development in physical and chemical sciences.

The introduction of the concept of isotopes disproved many ideas of Dalton who was first to give the theory on atoms. Added to this, the chemical purity of almost all the compounds became a matter of question. This includes water also. Thus, water, which is a common material of natural origin and is essential for the human beings and animal kingdoms for their existence on the earth is also subjected to variation in their isotopic composition. With the three isotopes of hydrogen and the equal number of isotopes of oxygen which exist naturally came to be known, the possibility of water having several isotopic compositions exist. The complexity further increases when we consider the artificially produced isotopes of oxygen numbering nine to be a part of water molecule.

The original studies on isotopes in water were concerned with seawater and precipitation. The first was primarily a survey on variations in $^{18}O/^{16}O$ concentration ratios, soon to be followed by a study of the $^{2}H/^{1}H$ ratios in natural waters (Friedman 1953). Dansgaard (1964) observed in great detail about the $^{18}O/^{16}O$ variations in global precipitation, including a discussion on the meteorological patterns. His work was the start of the global "isotopes-in-precipitation" network of the international organizations WMO and

IAEA. In more recent years the observations became supported by theoretical and numerical modeling.

The revolutionary development of the introduction of nuclear accelerators as mass spectrometers has greatly stimulated the hydrological application of isotopes with extreme low abundances in nature. Also ^{14}C research has gained tremendously by this new technological approach.

The nature of the isotopic applications is of course dictated by the specific character of isotopes, radioactive and non-radioactive. We can distinguish three different types of applications.

1) Stable and radioactive isotopes can be used as *tracers*, marking a water body or a certain quantity of water; a nice example is the phenomenon that the rain water during a heavy storm is often depleted in the heavy isotope (stable ^{2}H, deuterium, or stable ^{18}O) with respect to the most abundant isotope (^{1}H and ^{16}O, respectively). This offers the possibility to follow the rain water in the surface runoff and even quantitatively analysing the runoff hydrograph.

2) During the transition of compounds such as water or carbon dioxide from one phase to another, the concentration ratio of the isotopes of an element often changes, undergoes so-called *isotope fractionation*. Conversely, observing differences in especially the stable isotopic concentration ratios informs us about certain geochemical or hydrological processes that took place. For instance, as a result of a series of processes, the isotopic composition of carbon as well as oxygen of calcium carbonate is different for the marine and the freshwater origin. Furthermore, the isotopic composition of oxygen and hydrogen in rainwater varies with latitude, altitude, climate and time of the year.

3) *Radioactive decay* offers the possibility to determine an age, provided certain conditions are met. Noteworthy in this respect is the frequent application of dating groundwater –i.e. determining the time elapsed since the infiltration of the water- by comparing the ^{14}C or

^{3}H (tritium) activities in a groundwater sample with that of the recharge water. Moreover, also concentration differences of radioactive isotopes can also be used as a tracer.

8.1.1 Environmental stable isotopes

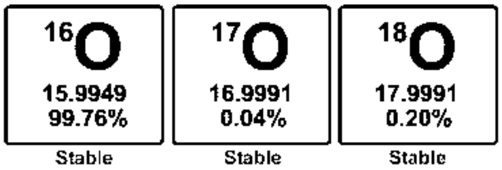
Environmental isotopes may be defined as those isotopes, both stable as well as radioactive, which occur in the environment in varying amounts and over which the investigator has no direct control. The environmental isotopes most commonly used as tracers in hydrology are the deuterium, oxygen-18 and tritium (isotopes of the water molecule), carbon-13, carbon-14, nitrogen-15 and sulphur-34(isotopes of dissolved solute in water). Of these deuterium, oxygen-18, cabon-13, nitrogen-15 and sulphur-34 are the stable and the remaining are the radioactive. The use of stable isotopes in hydrology depends on its variations in the natural waters, which results from isotope fractionation occur during some physical and chemical reactions.

8.1.2 Isotopes of hydrogen

Hydrogen is the chemical element with atomic number1. With an atomic mass of 1.00794 amu, hydrogen is the lightest element. Hydrogen is the most abundant of the chemical elements, constituting roughly 75% of the universe's elemental mass. Stars in the main sequence are mainly composed of hydrogen in its plasma state. The most common naturally occurring isotope of hydrogen, known as protium, has a single proton and no neutrons. Besides protium hydrogen has two isotopes namely deuterium and tritium. Protium and deuterium are stable isotopes. I.e., which do not disintegrate spontaneously. Tritium is a radioactive isotope, which disintegrates spontaneously by emitting beta rays.

8.1.3 Isotopes of oxygen

Oxygen (Z=8) is the most abundant chemical element in the crust of the earth and is combined with hydrogen to form water. Oxygen has three stable isotopes whose approximate abundances are ^{16}O = 99.76 %, ^{17}O =0.04% and ^{18}O =0.20% and is represented below.



Besides the tree stable isotopes mentioned above, fourteen radio isotopes of oxygen have been characterized, with the most stable being ^{15}O with a half life of 122.24 sec and ^{14}O with a half-life of 70.61 sec. All of the remaining radioactive isotopes have half-lives that are less than 27 sec and the majority of these have half-lives that are less than 83 milliseconds.

8.1.4 Abundance and fractionation of stable isotopes

The isotope *effects* can be described in terms of isotope abundances. *Isotope (abundance) ratios* are defined by the expression

$$R = \frac{\text{abundance of rare isotope}}{\text{abundance of abundant isotope}} \qquad (1)$$

The ratio carries a superscript before the ratio symbol R, which refers to the isotope under consideration. For instance

$$^{13}R(CO_2) = \frac{[^{13}CO_2]}{[^{12}CO_2]} \qquad ^{18}R(CO_2) = \frac{[C^{18}O^{16}O]}{[C^{16}O_2]}$$

$$^{2}\mathrm{R(H_2O)} = \frac{[^{2}\mathrm{H}^{1}\mathrm{HO}]}{[^{1}\mathrm{H_2O}]} \qquad ^{18}\mathrm{R(H_2O)} = \frac{[\mathrm{H_2}^{18}\mathrm{O}]}{[\mathrm{H_2}^{16}\mathrm{O})}$$

The *isotope ratio* and an *isotope concentration* are represented by different equations. In the case of CO_2 isotope ratio can be defined by the following equation

$$\frac{[^{13}\mathrm{CO_2}]}{[^{13}\mathrm{CO_2}] + [^{12}\mathrm{CO_2}]} = \frac{[^{13}\mathrm{CO_2}]}{[\mathrm{CO_2}]} = \frac{^{13}\mathrm{R}}{1 + {}^{13}\mathrm{R}} \qquad (2)$$

especially if the rare isotope concentration is very large, as in the case of labeled compounds, the rare isotope concentration is often given in *atom %*. This is then related to the isotope ratio

by: $$R = (\text{atom }\%/100) / [1 - (\text{atom }\%/100)] \qquad (3)$$

8.1.5 Isotope fractionation

The use of stable isotopes in hydrology depends on its variation in the natural waters. Stable isotope variation results from isotope fractionation which occurs during some physical and chemical processes. Examples of physical process which could lead to isotope fractionation are evaporation of water or condensation of vapour. During evaporation the residual liquid is enriched in heavier isotope molecules because the lighter isotope molecule move more rapidly and has a grater tendency to escape from the liquid phase i.e., there is a difference in the volatility between the two molecular species. Chemical fractionation effects occur because a chemical bond involving a heavy isotope will have a lower vibrational frequency than an equivalent bond with a lighter isotope. The bond with the heavy isotope thus will be stronger than that with the light isotope. Fractionation may occur during both equilibrium and non equilibrium chemical reactions. During non equilibrium of irreversible reactions, kinetic fractionation leads to the enrichment of the lighter isotope in the reaction product, because of the ease with which the light isotope could be broken.

8.1.6 Kinetic and equilibrium isotope fractionation

The process of isotope fractionation is mathematically described by comparing the isotope ratios of the two compounds in chemical equilibrium ($A \Leftrightarrow B$) or of the compounds before and after a physical or chemical transition process ($A \rightarrow B$). The *isotope fractionation factor* is then defined as the ratio of the two isotope ratios:

$$\alpha_A(B) = \alpha_{B/A} = \frac{R(B)}{R(A)} = \frac{R_B}{R_A} \qquad \text{———} \qquad (4)$$

which expresses the isotope ratio in the phase or compound B relative to that in A.

If changes in isotopic composition are dealt with, for instance C is oxidised to CO_2, the carbon isotope fractionation refers the "new" $^{13}R(CO_2)$ value to the "old" $^{13}R(C)$, in other words $^{13}\alpha = {}^{13}R(CO_2)/{}^{13}R(C)$.

In general isotope effects are small: $\alpha \approx 1$. Therefore, the deviation of α from 1 is widely used rather than the *fractionation factor*. The fractionation is defined by the equation 5.

$$\varepsilon_{B/A} = \alpha_{B/A} - 1 = \frac{R_B}{R_A} - 1 \quad (10\times10^3‰) \qquad \text{———} \qquad (5)$$

ε represents the *enrichment* ($\varepsilon > 0$) or the *depletion* ($\varepsilon < 0$) of the rare isotope in B with respect to A. The symbols $\alpha_{B/A}$ and $\varepsilon_{B/A}$ are equivalent to $\alpha_A(B)$ and $\varepsilon_A(B)$. In the one-way process ($A \rightarrow B$) ε is the change in isotopic composition, in other words: the new isotopic composition compared to the old.

Because ε is a small number, it is generally given in ‰ (per mill, equivalent to 10^{-3}). An ε value of, for instance, 5‰ is equal to 0.005. The consequence is that in mathematical equations it is incorrect to use $\varepsilon/10^3$ instead of merely ε.

The second type of fractionation is *equilibrium* (or *thermodynamic*) *fractionation*. This is essentially the isotope effect involved in a (thermodynamic) equilibrium reaction. As a formal example in the isotope exchange reaction:

$$^*A + B \Leftrightarrow A + {}^*B \qquad \text{———} \qquad (6)$$

where the asterisk points to the presence of the rare isotope. The fractionation factor for this equilibrium between phases or compounds A and B is the equilibrium constant for the exchange reaction

$$K = \frac{[A]}{[*A]}\frac{[*B]}{[B]} = \frac{[*B]/[B]}{[*A]/[A]} = \frac{R_B}{R_A} = \alpha_{B/A} \qquad (7)$$

Isotope fractionation processes in nature which are not purely kinetic (i.e. one-way processes) will be referred to as *non-equilibrium fractionations*. An example is the evaporation of ocean or fresh surface water bodies: the evaporation is not a one-way process (certainly water vapor condenses), neither an equilibrium process as there is a net evaporation.

Equilibrium fractionation, on the other hand, can be determined by laboratory experiments and in several cases reasonable agreement has been shown between experimental data and thermodynamic calculations.

8.1.7 Fractionation by diffusion

Isotope fractionation might also occur because of the different mobilities of isotopic molecules. An example in nature is the diffusion of CO_2 or H_2O through air.

8.1.8 Expression of stable isotopic compositions – The delta (δ) notation

Isotope ratios such as

$${}^{2}R = \frac{{}^{2}H}{{}^{1}H} \qquad {}^{13}R = \frac{{}^{13}C}{{}^{12}C} \qquad {}^{18}R = \frac{{}^{18}O}{{}^{16}O} \qquad (8)$$

are generally not reported as absolute numbers. The main reasons are:

a) the type of mass spectrometers, suitable for measuring isotope abundances with high sensitivity in order to detect very small natural variations, are basically not suitable for obtaining reliable absolute ratios

b) the necessity of international comparison requires the use of references to which the samples have to be related

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c) the use of isotope ratios would lead to reporting results as numbers consisting of a large number (5 or 6) of digits

d) absolute ratios are in principle less relevant than the changes in ratios occurring during transitions between phases or molecules.

Therefore, an isotope abundance is generally reported as a deviation of the isotope ratio (δ) of a sample 'A' relative to that of a reference sample or standard, r:

$$\delta_{A/r} = \frac{R_A}{R_r} - 1 \qquad (\times 10^3 ‰) \qquad (9)$$

$$\delta = \frac{R_{sample} - R_{s\tan dard}}{R_{s\tan dard}} \; (\times 10^3 ‰) \qquad (10)$$

For the specific isotopes of hydrogen and oxygen, the respective δ values are indicated by the symbols:

$$^{2}\delta = \frac{(^{2}H/^{1}H)_A}{(^{2}H/^{1}H)_r} - 1 \qquad ^{18}\delta = \frac{(^{18}O/^{16}O)_A}{(^{18}O/^{16}O)_r} - 1 \qquad (11)$$

where the more often used symbols are δ^{2}H or δD, and δ^{18}O, respectively..

R_{Sample} is the ratio of ^{18}O/^{16}O or ^{2}H/^{1}H, for example in the sample and $R_{Standard}$ is the ratio of the international standard for oxygen and hydrogen, say VSMOW (Vienna Standard

Mean Ocean Water). The analytical precision for $\delta^{18}O$ and $\delta^{2}H$ are 0.2 and 2.0 ‰, respectively. Other stable isotopes will have a different reference standard and different analytical precision, but their ratios can be expressed in the same manner. From the above relation it is obvious that negative δ values indicate lower abundances of the rare isotope in these samples than in the reference material, positive δ values point to higher abundances.

8.1.9 The reference standard

Since Stable isotope concentrations are expressed as the difference between the measured ratio of the sample and the measured ratio of a reference standard, a correct calibration of reference samples used by different laboratories in routine measurements with respect to the international standard was necessary for the inter-comparison of results.

The standard almost universally adopted as reference for oxygen and hydrogen stable isotope variations in natural waters was SMOW (standard mean ocean water). A serious disadvantage is that SMOW does not actually exist as a real water sample and there for can not be used to directly calibrate laboratory measurement. The isotopic ratio of SMOW where defined by Craig (1961) with respect to the existing water standard.

Craig evaluated the isotopic ratios of SMOW as

$$^{18}O/^{16}O = (1993.4 \pm 2.5)\ 10^{-6} \quad \text{———————————} \quad (12)$$

$$D/H = (158 \pm 2)\ 10^{-6} \quad \text{———————————} \quad (13)$$

The preparation of a large water sample having an isotopic composition as close as possible to that of the defined SMOW was entrusted in 1966 by the International Atomic Energy Agency (IAEA) to professor H Craig of the university of California. This water sample was obtained by mixing distilled ocean water with small amount of other waters to adjust the isotopic ratios to the required values. Such a water sample, called Vienna

SMOW (V- SMOW), or Vienna Standard Mean Ocean Water, is an isotopic water standard defined in 1968 by the international atomic energy agency. VSMOW serves as a reference standard for comparing hydrogen and oxygen isotope ratios, mostly in water samples. VSMOW remains one of the major isotopic water benchmarks in use today.

8.1.10 Composition of VSMOW

The isotopic ratios of VSMOW water are defined as follows:

$^{2}H / ^{1}H$ = 155.76 ±0.1 ppm (a ratio of 1 part per approximately 6420 parts)

$^{3}H / ^{1}H = 1.85 \pm 0.36 \times 10^{-11}$ ppm (a ratio of 1 part per approximately 5.41×10^{16} parts)

$^{18}O / ^{16}O$ = 2005.20 ±0.43 ppm (a ratio of 1 part per approximately 498.7 parts)

$^{17}O / ^{16}O$ = 379.9 ±1.6 ppm (a ratio of 1 part per approximately 2632 parts)

According to Craig measurements, the V-SMOW has the same ^{18}O content as the defined SMOW, but its D content is 0.2‰ lower. Other water samples distributed by the IAEA for inter calibration purposes of stable isotope measurement in natural waters are Standard Light Antarctic Precipitation (SLAP) & Greenland Ice Sheet Precipitation (GISP). SLAP has been obtained by melting an amount of ice and firn collected in 1967 at plateau station, Antarctica. It's ^{18}O & D contents are very low. GISP is a water sample with an ^{18}O & D content intermediate between that of V-SMOW and SLAP. The isotopic compositions of different reference standards are given in the chart shown below.

	Hydrogen Isotope		Oxygen Isotope	
IAEA Name	δ^{2}Hvsmow(‰)	Standard deviation (‰)	δ^{18}Ovsmow(‰)	Standard deviation(‰)
V-SMOW	0	0	0	0
GISP	-189.5	1.2	-24.78	0.09

SLAP	-428.0	0	-55.5	0

8.1.11 Deuterium and oxygen-18 variations in the hydrologic cycle

Large variations in the isotopic composition of natural waters occur in the atmospheric part of the water cycle and surface waters which are exposed to the atmosphere. Soil and subsurface waters inherit the isotopic composition of the atmospheric and surface water inputs and further changes take place negligibly except as a result of mixing of waters of different isotopic composition. Individual rainfall events have little impression on most hydrological systems and long term average data of the isotopic composition of the precipitation should be used as the input to the system. A global IAEA/WMO(International Atomic Energy Agency/World Meteorological Organization) network was established to conduct a world wide survey of δD and $\delta^{18}O$ in the precipitation since 1961. From this the following observations were made.

a) **Latitude effect**:- A gradual decrease of δD and $\delta^{18}O$ content when going from lower to higher latitude. Stations located in the northern and southern hemisphere are depleted in isotopic values compared to those located near the equator. The depletion in the isotopic values towards the poles is related to decrease in temperature.

b) **Continental effect**: - A decrease in δD and $\delta^{18}O$ values when going from the coast to a continent inland. Moist air masses originating from the ocean when it condenses, near the coast, the first condensate will have the heavy isotopic content similar to the ocean water. As the moist air masses moves inland the vapour gets continually decrease in the heavy isotopes since the precipitation leaving the system is enriched in D and 18O

c) **Altitude effect**: - A decrease in the δD and $\delta^{18}O$ content with increase in altitude. The magnitude of the altitude effect depends on local climate and topography. Typical gradients in δD observed is 1.5 to 4‰ per 100m and in $\delta^{18}O$ is 0.2 to 0.5‰. One reason for the altitude effect is the progressive rainout of the heavy isotopes during orographic ascent of the moist air masses (which occurs in the windward side of the mountain range). The depletion in the isotopic composition with altitude is also related to decrease of temperature.

d) **Seasonal effect: -** Seasonal variation of δD and δ^{18}O is related to seasonal variation of temperature. Seasonal fluctuations are more predominant in places far away from the coastal stations, whereas in coastal stations seasonal variation is relatively small.

e) **Amount effect**: - For some tropical stations a strong negative correlation between δD and δ^{18}O and the amount of rainfall is observed. The amount effect results in average depletion of -1.5‰ in δ^{18}O per 100mm of rainfall in these stations. This has been partly explained as being due to the evaporation of the falling raindrops and also due to exchange with atmospheric water vapor during periods of light rains.

8.1.12 $\delta\,^{2}$H and δ^{18}O correlation

Tthe relation between the $^{2}\delta$ and $^{18}\delta$ values of natural waters is determined by equilibrium fractionations $^{2}\varepsilon_{v/l}$ and $^{18}\varepsilon_{v/l}$. Craig (1961b) and Dansgaard (1964) found a relation between the $^{2}\delta$ and $^{18}\delta$ values of precipitation from various parts of the world:

$$^{2}\delta = 8\ ^{18}\delta + 10\ ‰ \qquad (14)$$

This relation, known as the *Global Meteoric Water Line* (GMWL), with a slope of 8 and a certain *intercept* with the ^{2}H axis (= the $^{2}\delta$ value at $^{18}\delta$ = 0‰) (Fig. 8.1, 8.2)

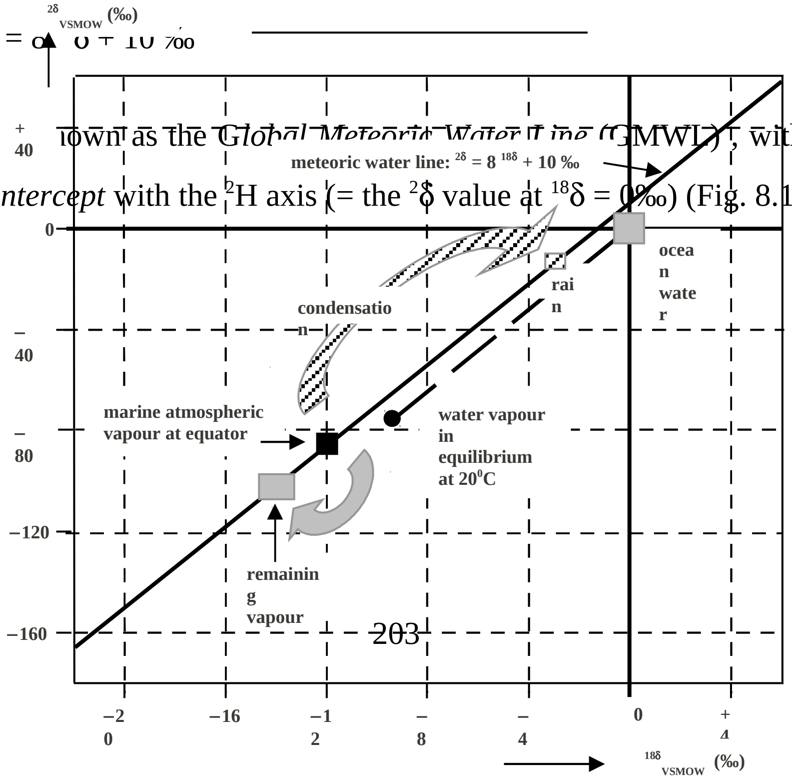

Figure 8.1 Relation between natural variations of $^{18}\delta$ and $^{2}\delta$ ocean water, atmospheric vapour and precipitation

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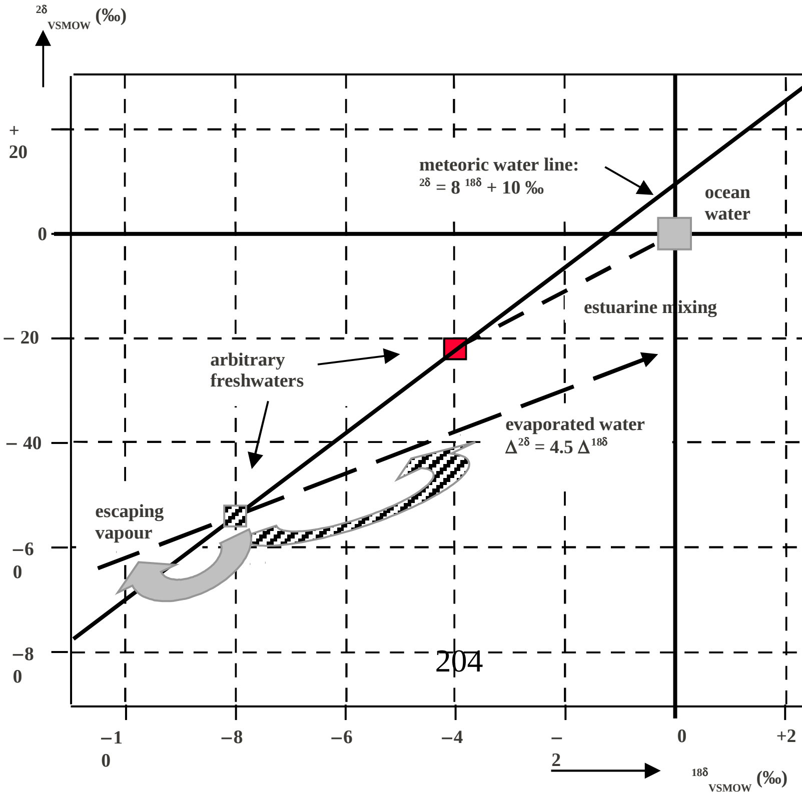
The general relation of the MWL is:

$$^{2}\delta = s\cdot{}^{18}\delta + d \tag{15}$$

where the slope s = 8, as is explained by the ratio between the equilibrium isotope fractionations of hydrogen and oxygen for the rain condensation process; d is referred to as the *deuterium excess* (*d-excess*), the intercept with the $^{2}\delta$ axis. In several regions of the world as well as during certain periods of the year and even certain storms the $^{2}\delta$ value is



different from 10 ‰, depending on the humidity and temperature conditions in the evaporation region.

Figure 8.2 Relation between $^{18}\delta$ and $^{2}\delta$ for estuarine mixing and for evaporating surface water

The isotopic composition of water vapor over seawater with $^{2}\delta = {}^{18}\delta = 0$ ‰ vs VSMOW is somewhat lighter than would follow from isotopic equilibrium with the water: the evaporation is a non-equilibrium (partly kinetic) process. However, from the observed vapour composition onward the vapor and precipitation remain in isotopic equilibrium, because the formation of precipitation is likely to occur from saturated vapor (i.e. vapor in physical equilibrium with water). Consequently the $^{18}\delta$ and $^{2}\delta$ values both move along the meteoric water line.

The δD $\delta^{18}O$ relationship for precipitation in any giver region however differs from the global equation. The δD-$\delta^{18}O$ relationship of local precipitation will give the local meteoric water line (LMWL).

In order to relate the isotopic content of water sample to the meteoric water line a deuterium excess parameter was introduced by Dansagaard as $d= \delta D-8\delta^{18}O$. The *d*-excess may vary from place to place, owing to various origins and conditions of formation of the vapor. For instance the vapors escaping from the open tropical oceans give rise to condensation process with *d*-excess of about 10. This value may be representative of oceanic precipitation. However condensation of vapors produced from closed sea gives rice to a value much higher than 10. This has been observed for stations in the Mediterranean region where the mean value of d is about 22‰. The deviation in the deuterium excess occurs possibly as result of evaporation occurring into a high continental air i.e. lower humidity compared to the ocean. Since d is closely correlated to the average relative humidity over the area of production, (*d*=10 for relative humidity of

75%), it represent a climatic index of major interest for detecting global paleo climatic fluctuations and identify paleo precipitation.

In some areas the linear correlation between δD and δ^{18}O values of precipitation samples does not have a slop of 8 and is between 4 and 6. This has also been observed for surface waters such as lakes reservoirs etc. which are subject to intense evaporation. During evaporation the surface water becomes enriched in δD and δ^{18}O. The enrichment continues as the evaporation progress up to a constant value.

The isotopic composition of evaporating water tends towards a constant value known as isotopic stationary state even though the remaining fraction of liquid continues to diminish. This is due to the exchange of surface water with the atmospheric vapor. The enrichment of δD and δ^{18}O produced by evaporation has a complex relationship which is a function of temperature, relative humidity of atmosphere, the speed of evaporation as well as differential diffusion of isotopic molecules in air. Hence the increase in the heavy isotopic content varies from one evaporating system to another due to all these factors which depend on climatic conditions.

8.1.13 Deuterium and oxygen-18 in groundwater

In most groundwater system the stable isotopic content of water may be considered conservative. However numerous processes could modify the stable isotopic content of groundwater during or after it is recharged.

The first process which may modify the stable isotopic content of groundwater is the evaporation in the unsaturated zone of the infiltrating precipitation. This generally occurs in arid areas, where the vapor transport controlled by thermal gradient may mainly occur and one can expect an isotopic enrichment of the liquid phase. In the δD and δ^{18}O diagram, points will fall below the local meteoric water i.e. δD and δ^{18}O correlation of local precipitation samples.

The second process which may distort the stable isotopic composition is the exchange with oxygen bearing (and possibly the hydrogen bearing) minerals. This exchange is importance in geothermal environments. With low reaction rates in low temperature environments a long time of contact is needed for significant exchange to take place and equilibrium generally will not be reached.

Another process which may modify the initial stable isotopic content of groundwater is the isotopic exchange with a gas phase which is not in equilibrium with the environmental water. Requirements for a significant deviation of the initial stable isotopic of pore water are a large fractionation factor and or molar ratio of the gas phase either in static or dynamic system. Exchange of water with CO_2 is an example to illustrate this process. In some gases system the oxygen atomic ratio of CO_2/H_2O may reach significantly higher than 1%. Since as mentioned earlier, the fractionation factor for CO_2(g) and H_2O(l) is 1.0412 at 25°C one would expect ^{18}O content of water of such a system to be depleted. Such an effect in which an oxygen-18, shift towards negative values have been observed in geothermal systems.

8.1.14 Significance of δD and $\delta^{18}O$ in hydrological studies

Groundwater is recharged either directly by local precipitation or remotely from distant outcrop areas. Some recharge could also occur from nearby surface water bodies. Ion groundwater investigations, the interest is to estimate the amount of recharge and to identify the source of recharge. Stable isotope variation could be applied in the following studies.

a) The seasonal variation in D and ^{18}O of precipitation in some areas could be used to estimate recharge to the groundwater. The seasonal variation of snow precipitation can be used to identify age stratification in some deposits.
b) For studying the source of recharge to a groundwater system, altitude effect could be made use of it.

c) Since the surface water system such as rivers, lakes etc have D and ^{18}O contents significantly different from that of recharge by local precipitation, recharge of surface water bodies to groundwater system could be identified.

d) Source of salination to a groundwater body due to dissolution or leaching of salts from soils or aquifer material, sea water intrusion etc. could be identified using stable isotopes δD and $\delta^{18}O$ in combination with chemistry.

8.1.15 Stable sulphur-34

Sulphur has four stable isotopes: ^{32}S (95.02%), ^{33}S(0.75%), ^{34}S(4.21%) and ^{36}S(0.02%). The 34S/32S ratio expressed as $\delta^{34}S$ with respect to CDT(Canyon Diablo Troilite) is of interest in isotope hydrology.

The stable isotopic content of aqueous sulphur compounds (chiefly SO_4^{2-}, H_2S, HS^-) may provide information on the origin of the sulphur compound and the kind of redox reaction involving sulphur. There are three main reservoirs of sulphur; evaporate sulphates, marine sulphates and sedimentary sulphides. Hydrological interest is confined to evaporates and marine sulphates. Whereas $\delta^{34}S$ values of evaporates cover a wide range, the value for marine sulphates remained constant at +20‰ for several millions of years. The $\delta^{34}S$ of sulphates of precipitation falls in the range of +3.2 to 8.2 % in non industrialized areas and values up to 15.6‰ in industrialized areas.

Groundwater may contain sulphate derived from precipitation, from oxidation of sulphide minerals or organic sulphur or from dissolution of evaporate minerals. Sulphur isotope variation in the subsurface could occur due to the following reactions.

a) Kinetic effect, bacterial reduction of sulphate to H2S or oxidation of sulphides to sulphates

b) Various chemical exchange reactions e.g. between sulphates and sulphides or between sulphide themselves.

The principal organism which transforms sulphates to H_2S are the sulphate reducing bacteria belonging to the genera Desulfovibrio and Desulfatomaculam. When the product H2S is continually extracted from the system-for instance by degassing of precipitation of iron sulphides, the bacteria continues to reduce sulphate until no more sulphate is available. The $\delta^{34}S$ of the residual sulphate increases with decreasing sulphate concentration.

A general problem with sulphur isotopes is that isotopic values of certain compounds may vary greatly, even if the compounds that have in principle the same type of origin. Despite that, many exchange processes between S (and O) containing compounds mutually, and between these and water is that in the aqueous environment the isotopes can often be used to identify their sources. Furthermore, $^{34}S/^{32}S$ –occasionally in combination with $^{18}O/^{16}O$– is applied to observe special biochemical processes in surface- and groundwater (Pearson et al. 1980,).

8.1.16 Limnochronology

Radioactive nuclide's present in the environment have proved very useful for the introduction of time parameter in a variety of earth science problems. Last few decades have shown marked development in the field of limnochronology. Lakes receive most of its radioactivity either through land-derived or atmospheric sources. Among the land derived, most of the isotopes in the U-Th series, are derived through weathering of rocks and soil layers. They are carried to the lakes by rivers and groundwater's. Radionuclides are also contributed by the physical erosion of soil horizons.

Those nuclides which are continuously, directly produced in the earth atmosphere by cosmic ray radiation, and those nuclides which have been injected into the earths environment due to testing of nuclear weapons, are brought down to the earths surface by wet precipitation and dry fall out processes. They ultimately sink into the water bodies present on the earth.

Radioactive chronologies are generally based on either (1) the decay of the radioactive nuclide or (2) the build up of the daughter nuclide to attain secular equilibrium with its parent

In the first technique based on the decay of a nuclide with depth in the sediment, then the basic requirements are (1) the flux of the radionuclides to the sediment-water interface has remained constant and (2) no migration of the radionuclides are occurred in the dating intervals, i.e., the change in the concentration of the nuclide in the system is only due to its radioactive decay. Then the activity of the nuclide in the sediment at any depth z, from the sediment water interface is given by

$$A_{(z)} = A_o e^{-\lambda t} \qquad \text{———————————} \qquad (16)$$

Where A_o is the activity of the nuclide in a freshly deposited sediment at time t=0, λ is the radioactive decay constant. The value of A_o is the ratio of the deposition rate of the nuclide to the deposition rate of sediment at the interface. If the sediment accumulation rate S (cm/time) is constant over the interval t, then t=z/2 substituting for A_o and t

$$Az = \frac{\theta\lambda}{S\rho z}\ e^{-\lambda z/s} \qquad \text{———————————} \qquad (17)$$

Where θ is the flux of the nuclide, atoms/cm/time and p(z) is the insitu density at depth z.

If the sedimentation rate has changed during the dating interval, the age of different strata in the sediment column can b e calculated from the integrated activity of the isotopes in the core. The time t taken to deposit a sediment layer of thickness z, in continuously depositing sediment in a constant radio nuclide flux is given by

$$t = \frac{1}{\lambda}\ln(Qo/Qz) \qquad (18)$$

Where Q is standing crop (activity/unit area) of the nuclide below the sediment-water interface, Qz is equal to the standing crop remaining below depth ‘z’ from the surface. In addition, since the value of Q(z) is known for various depth intervals for the core, it is possible to calculate their age and hence the sedimentation rate between them.

On the other hand, when the chronology relies on the in growth of a daughter from its parents, then the ratio of the daughter to parent activity at any time t is

$$\frac{Ad}{Ap} = \frac{\lambda d}{\lambda(d-\lambda)p}(1-e(\lambda p-\lambda d)t) \qquad (19)$$

Where Ao = activity λ=decay constant and subscripts dap refers to daughter and parent nuclides respectively. In this equation it is assumed that the activity of the daughter Ad=0 at t=0, ie the time of formation of the deposit. If Ad≠0 at t=o then it is essential to have a precise knowledge of Ad/Ap at the tome of formation. In this case also the common requirement of the closed system is necessary for both the parent and daughter nuclides.

8.1.17 Dating technique

There are a number isotopes available to estimate the age and rate of sedimentation in lakes and reservoir. These techniques include both the environmental isotopes (eg., ^{14}C, ^{13}7Cs, ^{210}Pb etc) as well as artificial isotopes(eg. ^{240}Pu, ^{241}Am). Dating by ^{14}C method is used to give sedimentation age for a longer period of time. However recent advances in measuring environmental radio nuclides have given two promising methods (1) ^{210}Pb method from present to 150 years and (2) ^{137}Cs method from the present to 1954. The present study adopted ^{137}Cs method for the determination of sedimentation rate of Vembanad lake.

8.1.18 ^{137}Cs method

Considerable amount of ^{137}Cs were produced in the atmosphere by nuclear weapon tests. These are now been deposited on the earth as fallout. Since nuclear weapons were mostly tested in the northern hemisphere, the ^{137}Cs fallout is about four times greater in the northern hemisphere than in the southern parts. ^{137}Cs is absorbed in clay, silt and humic materials. The amount of ^{137}Cs deposited in the earth has been measured at precipitation stations at many locations. The rate of sedimentation can be calculated from sediment core sections, by using the depth where the 1963 peak is found and the depth (1954) were the ^{137}Cs is firs detected. The procedure to apply ^{137}Cs for estimation of sedimentation rates is to identify the position of 1963 fallout peak in a sediment core. The amount of sediment accumulated above the peak divided by the number of years since 1963will yield sedimentation rate.

8.2 Methodology

8.2.1 Collection of water samples

The precipitation (rain) samples were collected from three sampling stations which are marked in the area map (Figure 8.3). Samples were collected daily as and when there was rain. A composite sample was prepared after the end of each month by pooling the samples collected at daily/weekly /whenever rain during the month. Care was taken to prevent air entry into the collecting vessel to avoid exchange tritium from air into the sample. Water samples were collected during 2007 to 2008, daily basis, during the summer, southwest monsoon and northeast monsoon periods.

Surface water samples from 20 representative stations of Vembanad lake were collected for ^{2}H and ^{18}O measurement in three seasons, pre-monsoon, monsoon and post-monsoon. Samples from the depth were also collected in two seasons. The sampling stations were marked in the area map (Figure 8.3.). Thirteen groundwater samples including shallow open well, deep bore well and a small pond were also collected from the basins of the Vembanad Lake, which is marked in Figure 5.3. Large volumes, around 20 litters of surface water sample from five stations were collected in the pre-monsoon season for the determination of $\delta^{34}S$. A total of 56 samples including surface and bottom water, from different stations of Cochin estuary were collected indifferent time intervals in pre-rinsed Tarson bottles. A core sediment sample was collected from the middle of the lake (C/V) to find out the sedimentation rate of the lake by finding the cesium-137 activity.

5.2.1 Preservation of the sample

The samples were collected in clean polythene bottles of 60 ml capacity. The bottles were filled with water samples to the maximum, leaving only a little space to account for the expansion during the transport. While filling the bottles, only a little space was left in order to prevent air, which may introduce error due to the exchange of the ^{18}O present in the air with water.

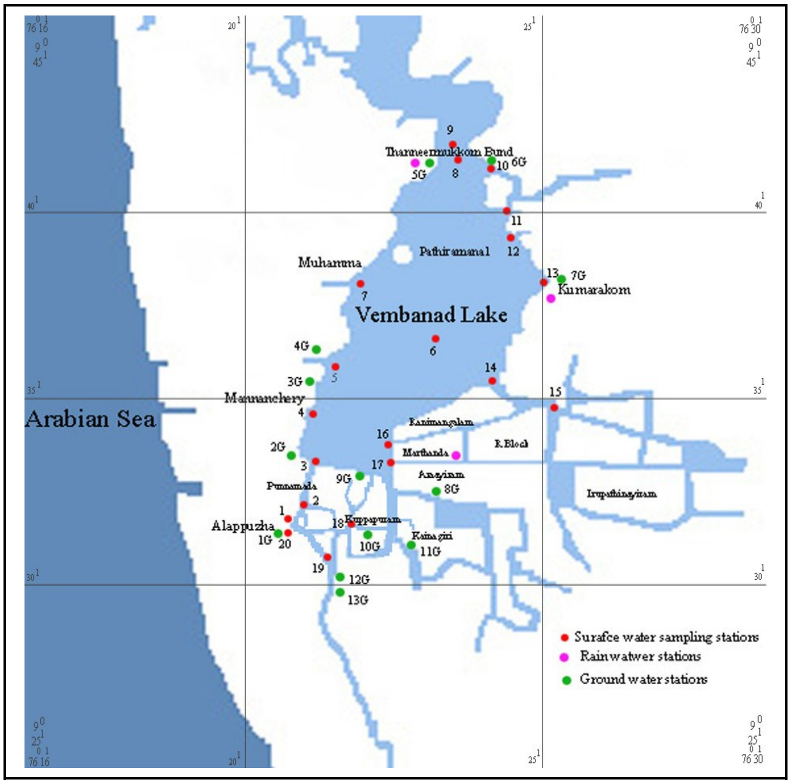


Figure 8.3 Area map of Vembanad wetland system showing sampling stations

8.3 Results and Discussion

The δ^2H and $\delta^{18}O$ values of the water samples of precipitation, lake water and groundwater were analyzed using IR-MS. The average delta values in different seasons and the mean values are tabulated in Table1, 2&3. Mean annual values of δD and $\delta^{18}O$ in precipitation collected at many locations around the world plot along a line with a slope of 8 and intercept of +10 ($\delta D=8\delta^{18}O+10$), commonly referred to as the global meteoric water line (MWL) (Craig 1961).

8.3.1 Precipitation

The variability in isotopic composition of rainfall from one site to another is a function of several factors, including storm-track origin, rainfall amount and intensity, atmospheric temperature, and the number of evaporation and condensation cycles (Dansgaard 1964). The precipitation samples of the area follows the equation $\delta D = 5.32\delta^{18}O+9.0$ with a slope of 5.33 (Figure 8.4). The monthly stable isotopic ratio of the precipitation ranged from -30.88‰ to +16.24‰ for δ^2H and from -7.4‰ to -0.26‰ for $\delta^{18}O$ during the observation period, and showed seasonal variation with lower values in winter and higher values in summer.

The variation of $\delta^{18}O$ in different periods showed highly enriched values (-0.20‰) in the month of February and March. This distinct isotopic signature of precipitation is due to local recycling of evaporated vapor of land origin and also indicate marine vapor source from the southern Bay of Bengal, evaporating under low relative. The highest depleted $\delta^{18}O$ value of -7.40‰ was observed in the month of November, which is due to winter precipitation. But this depleted $\delta^{18}O$ value is not so contributed in enhanced d-excess values over the wetland region.

The low *d*-excess value of 7.5‰ was observed in the wetland region during summer monsoon (May-August), which is characteristic of the indication of evaporation from falling rain drops of southwest coast of India. Moving to the month of November in the middle of the NE winter monsoon, δ^{18}O values is depleted (-7.40‰) indicating vapor source from isotopically light surface water of Bay of Bengal, which is further confirmed by the d-excess value of 10‰.

8.3.2 Surface water

The results of δ^{2}H and δ^{18}O values are listed in Table 8.1 and plotted as *X–Y* plot with reference to GMWL in Figure 8.5. Three clusters of values are clearly distinguished in the plot which represents the temporal variation of δ^{18}O and δ^{2}H values in the region. Temporal variation in isotopic composition can be used to estimate subsurface components of the water balance to the lake (Nachiappan et al. 2002).

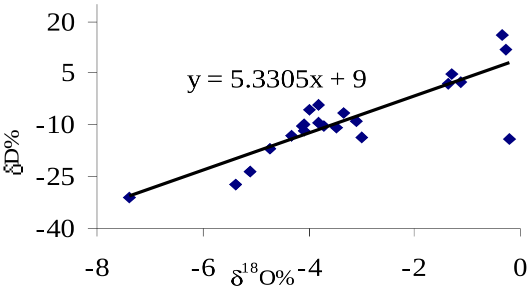


Figure 8.4 LMWL for precipitation in Vembanad Region

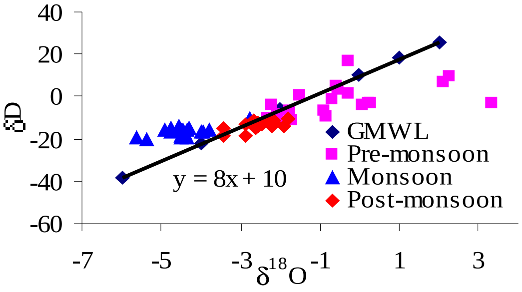


Figure 8.5 *X–Y* plot of surface water samples of Vembanad Lake

In the case of lake having large inflow and outflow, local additions of precipitation can be of minor importance, except during floods. In such cases, contributions from different surface and subsurface sources, each with their characteristic isotope ratio, determine the isotopic composition of the lake water. Vembanad Lake has relatively the most depleted values of δ^{18}O and δ^{2}H in the monsoon season with values ranged from -20.21‰ to -10.81‰ and -5.6‰ to -2.77‰ for δ^{2}H and δ^{18}O respectively. The most depleted δ values observed in the monsoon season are due to the amount effect. In contrast samples from Vembanad Lake itself are the most enriched in heavy isotopes with values ranged from

-11.9‰ to +17.0‰ and -2.3‰ to +3.34‰ in the pre-monsoon season. The enriched δ values in the summer samples collected in the pre-monsoon season showed that the lake have undergone variable degree of evaporation. The post monsoon season is characterized by intermediate δ values. Most of the data points in the pre and post monsoon season plot below the LMWL following a general evaporation/mixing line.

The spatial variation of $\delta^{18}O$ showed most enriched value at the station 9, Thanneermukkom north, through which saline water enters to the fresh water region (Figure 8.6). The highest enriched $\delta^{2}H$ value was observed at the station 12, Kanavattinkara (Figure 8.7), where the lake is stagnant with high rate of evaporation. The continuous decrease in $\delta^{18}O$ and δD values towards the south from the station Thanneermukkom confirmed the partial contribution of sea water for determining the isotopic composition of the lake in pre-monsoon season. Since the lake as a whole is facing evaporation, the dominant factor which contributed highly enriched value of $\delta^{18}O$ at this station is sea water mixing. This is confirmed from the highest salinity at this station. The most enriched $\delta^{2}H$ value observed at the station Kanavattinkara, with gradual decrease towards the south indicated the role of $\delta^{2}H$ for predicting the evaporation loss, since the station have low salinity. Thus it is concluded that in a system undergoing both evaporation and salinity intrusion, the $\delta^{18}O$ is an indicator of salinity mixing and $\delta^{2}H$ indicates the evaporation effect. The above fact is also concluded from the value of electrical conductivity and water temperature. The samples collected from the bottom of the lake showed more depleted delta values with more variation for δD than $\delta^{18}O$, further confirming the value of $\delta^{2}H$ as an indicator of the evaporation effect. Hence in a system undergoing both evaporation and salinity mixing, the combined measurement of ^{18}O and ^{2}H can be used to quantify the evaporation effect and to study mixing processes between lake water and adjacent sea water.

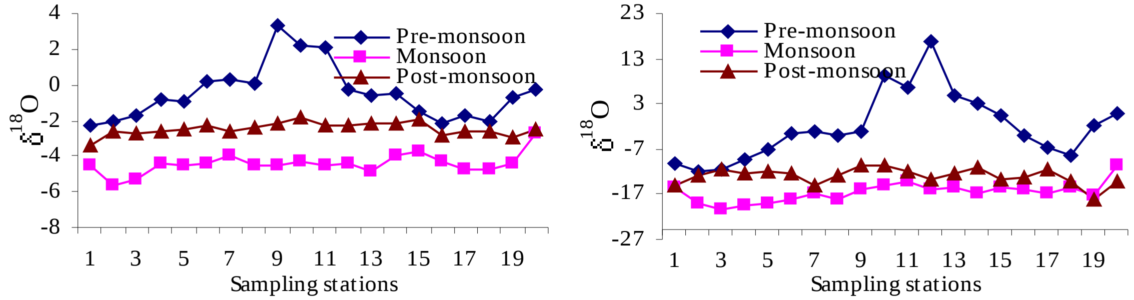


Figure 8.6&8.7 Spatial and temporal variation of $\delta^{18}O$ and $\delta^{2}H$ of Vembanad lake water

The variation of $\delta^{18}O$ with chloride is shown in the Figure 8.8. The plot indicated one clustered value in monsoon season signifying complete mixing in the lake. The variation of salinity and $\delta^{18}O$ in pre-monsoon season confirmed mixing of saline water, where as the post-monsoon samples plot in both fresh and saline region

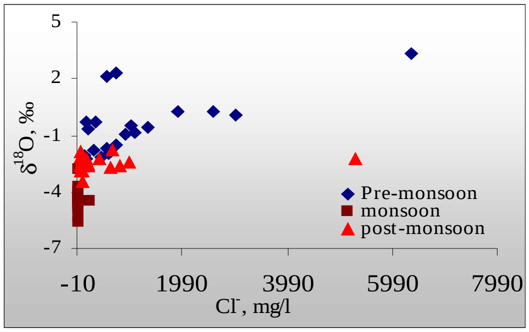


Figure 8.8 A plot $\delta^{18}O$ versus chloride concentration

8.3.3 Groundwater

A compilation of published data on groundwater samples from across India analyzed over the last three decades revealed that the country can be broadly divided into three contiguous regions A, B and C with transition areas in between. Based on $\delta^{18}O$ of the three regions A, B and C, the entire data set is subdivided in three broad subgroups namely, <-4‰, between -4‰ and -2‰ and >-2 ‰. The region C covers nearly all of Tamil Nadu, southern Andra Pradesh, south-eastern Karnataka and southern part of

Kerala (study area). The δ^{18}O of groundwater in this region is mostly <-3‰ and the *d*-excess mostly <5‰ except in parts of Tamil Nadu coast and some hill regions around Bangloor, where lower (<-4‰) values of δ^{18}O are also seen (Gupta and Deshpande 2005). The stable isotopic ratio of the study area samples ranged from -20.87‰ to -7.65 ‰ for δ^{2}H and -4.23 ‰ to -2.07‰ for δ^{18}O during the observation period. The δ^{18}O-δD regressions of the groundwater samples included in this study is shown in Figure 8.9. The slope of the best fit line to all groundwater data in δ^{18}O-δD plot is 6.5 with a *d*-excess of 7.3‰. The high *d*-excess (>5‰) seen in groundwater in this area is inherited from precipitations having a component of kinetically controlled re-evaporated vapor.

The similarity in isotopic composition between rainfall and upgradient groundwater indicates rapid recharge rate with evapotranspiration processes not affecting the stable isotopic composition of water (Gupta and Deshpande 2005b). Water samples from the station Thanneermukkom have isotopic compositions (δ^{18}O = -4.23‰) similar to meteoric water (δ^{18}O = -4.09‰), indicating the direct recharge from precipitation. The highest δ^{18}O (-2.07‰) value at the station Mannancheri obviously reflects the southwest monsoon source under the influence of high potential evapotranspiration.

The deep aquifers of the area have comparatively higher salinity than the open wells. The δ^{18}O-δ^{2}H plot indicates evaporative enrichment of saline waters. In the δ^{18}O-Cl- plot of the deep saline water, the δ^{18}O value remain largely unchanged with increase in salinity indicating that, these waters derived their salinity by leaching salts from the aquifer matrix, in addition to evaporation (Figure 8.10).

The stable-isotopic composition of waters relative to the MWL reveals important information on groundwater recharge patterns, the origin of waters in hydrologic systems, and mixing of groundwater and surface water. From the δ^{18}O-δD diagram four groups of samples were identified, which are depicted in the Figure 8.11. The first group consist of sample collected from an open well at Thannermukkom station which have depleted isotopic compositions (δ^{18}O = -4.23‰) similar to meteoric water (δ^{18}O = -4.09), indicating the direct recharge from precipitation. The similarity in isotopic composition between rainfall and upgradient groundwater indicated a rapid recharge rate with evapotranspiration processes not affecting the stable isotopic composition of water. The second group consists of open wells very near to the lake and has isotopic composition in the mixing zone of surface water and subsurface water. The mixing line connects the isotopic composition of the groundwater with lake water in between the two seasons, monsoon and post monsoon samples of lake water. The third group consists of samples from bore wells of 800 feet and from a shallow open well very near to the lake, have little different isotopic composition. Progressively smaller fractions of lake water leakage have mixed with groundwater at these sites. The last group consists of samples from bore wells and pond water near to the lake, have enriched isotopic composition. Evaporation in the unsaturated zone of infiltrating precipitation is the reason for enriched data. Hence there is no interconnection between the lake water and sub surface waters of this particular group. Groundwater source is likely outside of the watershed.

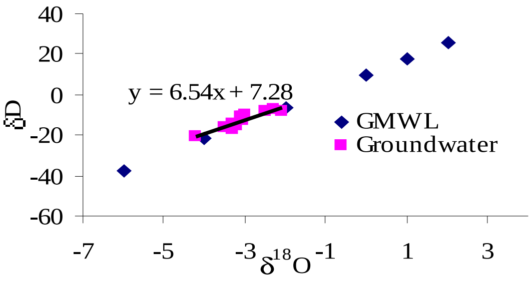


Figure 8.9 δ^{18}O-δ^{2}H plot for groundwater samples

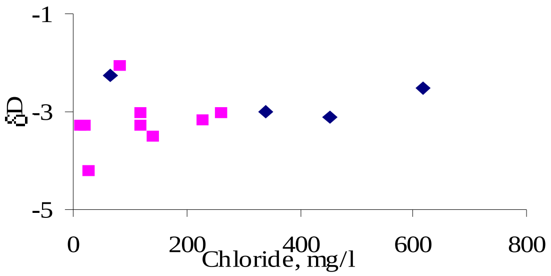


Figure 8.10 A plot δ^{18}O versus Chloride concentration for groundwater

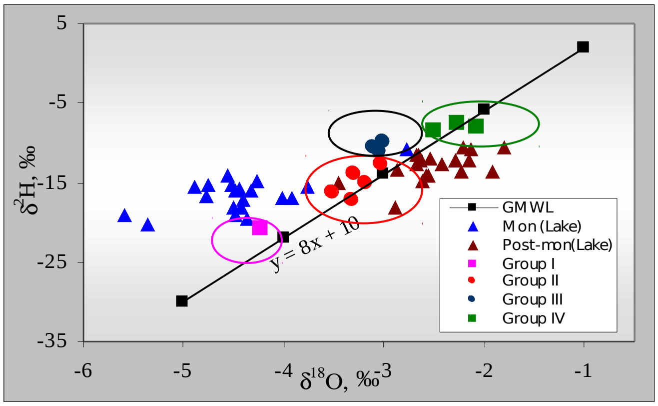
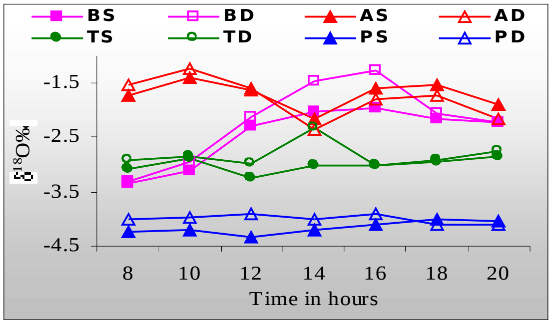


Figure 8.11 *X-Y* plot of $\delta^{18}O$ and $\delta^{2}H$ of surface water and subsurface samples showing different groups

8.3.4 Tidal impact and change in delta values

A set of 56 samples including surface and bottom water, from different stations of cochin estuary were collected to study the impact of tidal waves on δ values. The results of the analysis are given in table 3 and its variation is shown in the Figure 8.12&8.13. The respective delta values of each station were plotted as meteoric waterline (Figure 8.14).

The spatial variation of $\delta^{18}O$ and $\delta^{2}H$ showed most enriched value at the station Aroorkutty. The station Pathalam has recorded most depleted delta values for both oxygen and hydrogen. Boat Jetty, through which sea water enters into the lake, has lesser value of delta compared to Aroorkutty which is away from the estuary. The temporal variation in isotope ratio is different in different stations. Boat Jetty has a larger variation with enrichment in delta from morning 8am to evening 4pm. After 4pm the delta value decreases till 8pm. Temporal variation of delta values at Aroorkutty has two times enrichment and depletion. The other two stations, Thanneermukkom and Pathalam, have virtually uniform distribution through out the day.



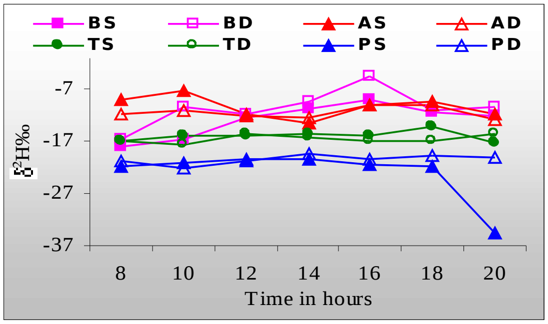


Figure 8.12&8.13 Variation of $\delta^{18}O$ and $\delta^{2}H$ along the estuary

The enrichment and depletion at Boat Jetty is a function of tidal change, which was confirmed from the salinity data. The highest enriched value at Aroorkutty was due to both mixing of saline water and evaporation effect. Highly depleted delta value at Pathalam contributed from precipitation at higher altitudes, were the river Periyar originates. The data further indicate no mixing of estuary to the region Pathalam, at the time of sampling.

Comparison of the delta values at bottom and surface of the water body showed station wise difference in their behavior. Evaporation effect at stations Thanneermukkom and Aroorkutty made the delta values to enrich in surface sample. Higher impact of salinity at the bottom made Boat Jetty to enrich delta values in bottom samples. Higher flow at Pathalam contributed the surface water depleted in isotope ratio.

The variation of $\delta^{18}O$ with chloride is shown in the Figure 8.14. The plot showed two clusters corresponding to Thanneermukkom and Pathalam, which is further away from the other two stations. But in the meteoric water line only the station Pathalam has different characteristics from the other three stations (Figure 8.15). It shows that, even though the ionic concentration at Thanneermukkom is comparatively low, the local meteoric water line clearly explains the mixing of saline water to this region.

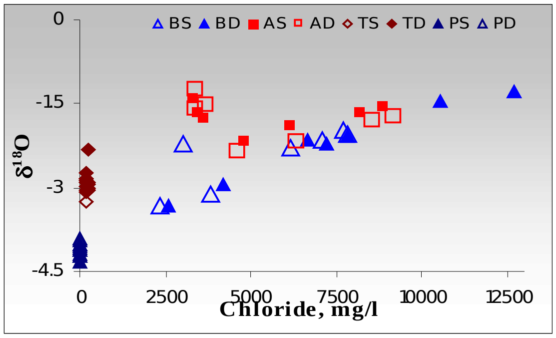


Figure 8.14 $\delta^{18}O$ versus Cl^{-} plot for different stations of the estuary

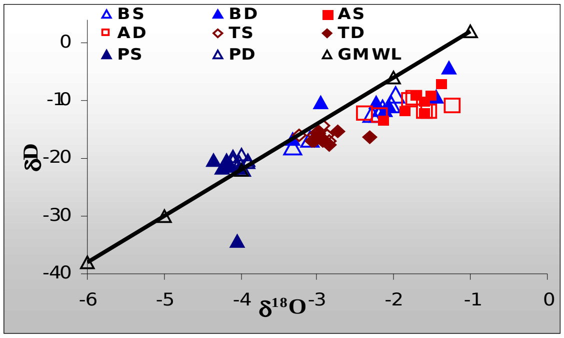


Figure 8.15 X-Y Plot of $\delta^{18}O$-$\delta^{2}H$ in different stations of the estuary

8.3.5 δ^{34}S of sulphates

Dissolved sulphate of water samples from five stations of Vembanad lake were analysed for δ^{34}S. Sulfur isotope ratios of dissolved sulfate ranged from +10.5‰ to +23.9‰. The highest value was observed for the sample collected from Komalapuram. The sample collected from Thanneermukkom has a value of 19.09‰. A plot of sulphate concentration versus δ^{34}S for the samples indicated that sulphate is predominantly derived from marine origin. Increasing δ^{34}S values and simultaneously decreasing sulfate concentrations (Figure 8.16) indicated that bacterial (dissimilatory) sulfate reduction is an important process for the natural attenuation. The low sulphate with low δ^{34}S indicated mixing of sulphate of marine source with some other sources.

8.2.6 Cesium-137 (^{137}Cs)

The ^{137}Cs profiles of the sediment core collected from centre of the lake closely parallel to its weapon fall-out record pattern, as reported by other studies (Livingston and Cambray 1978), revealed a major peak in 1963-64. The variation of ^{137}Cs activities is due to varying sedimentation rates, sediment composition, organic matter content and different histories of deposition. The activity of cesium in each slices of the sediment core is plotted against the depth in Figure 8.17. The sedimentation rate of the lake is calculated from the activity profile and was found to be 0.51cm/year. The sedimentation rate determined for Vembanad lake is in agreement with the similar studies reported for other lakes (Bhishm Kumar et al. 2007). This indicated that Vembanad Lake is getting silted at a fast rate.

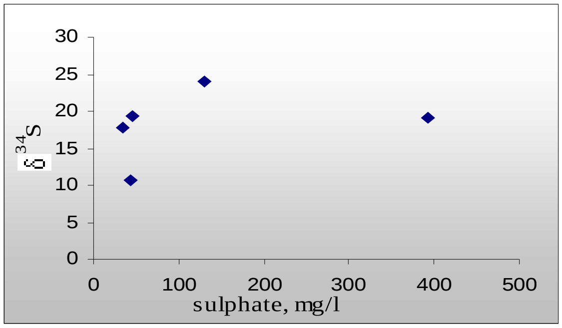


Figure 8.16 Variation δ^{34}S with sulphate concentration

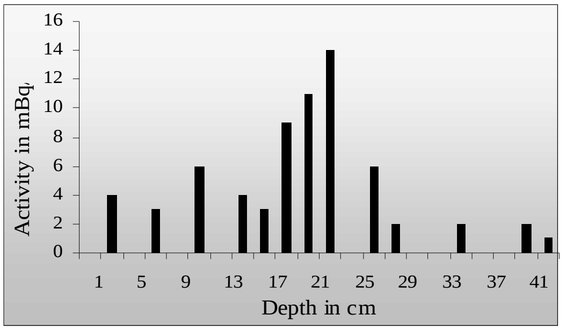


Figure 8.17 Depth versus ^{137}Cs activity in the sediment core

8.2.7 Summary

The precipitation samples of the area follows the equation $\delta D = 5.32\delta^{18}O+9.0$ with a slope of 5.33. The lake water has the most enriched values of δ^{18}O and δ^{2}H in the pre-monsoon season. The stable isotopes (δ^{18}O and δ^{2}H) of the lake water suggested that, in the Vembanad wetland system, the δ^{18}O is an indicator of salinity mixing and δ^{2}H indicates the evaporation effect. The variation of δ^{18}O with chloride indicated complete mixing of lake in monsoon season. The slope of the best fit line to all ground water data in δ^{18}O-δD plot is 6.5 with a d-excess of 7.3‰. The surface water groundwater interconnection study identified that most of the shallow groundwater sources are directly connected with the lake. There is no interconnection between the lake and a ground water source which is very near to the lake. The tidal study confirmed the direct impact of tide on the change in delta value of samples in the estuary. The δ^{34}S value of the dissolved sulphate indicated its contribution from marine origin. The sedimentation rate of the system is very high.

Table 8.1 Stable isotope values of the lake water in different seasons

SI No	Sample ID	Pre-monsoon		Monsoon		Post-monsoon	
		δD (‰)	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{18}O$ (‰)
1	1/VL	-10.11	-2.30	-15.41	-4.52	-15.23	-3.45
2	2/VL	-11.90	-2.01	-19.19	-5.60	-12.64	-2.67
3	3/VL	-11.73	-1.70	-20.21	-5.36	-11.52	-2.68
4	4/VL	-9.21	-0.84	-19.60	-4.36	-12.19	-2.63
5	5/VL	-7.23	-0.91	-19.22	-4.49	-12.05	-2.55
6	6/VL	-3.62	0.22	-18.09	-4.43	-12.26	-2.28
7	7/VL	-3.29	0.30	-16.96	-4.01	-14.93	-2.61
8	8/VL	-4.03	0.06	-18.28	-4.51	-12.67	-2.43
9	9/VL	-3.11	3.34	-16.04	-4.49	-10.54	-2.21
10	10/VL	9.47	2.26	-14.90	-4.28	-10.67	-1.80
11	11/VL	6.50	2.11	-14.26	-4.57	-12.16	-2.28
12	12/VL	17.00	-0.26	-15.87	-4.44	-13.63	-2.23
13	13/VL	4.85	-0.56	-15.71	-4.90	-12.30	-2.15
14	14/VL	3.26	-0.51	-16.90	-3.93	-10.91	-2.14
15	15/VL	0.24	-1.52	-15.50	-3.77	-13.79	-1.92
16	16/VL	-4.20	-2.20	-16.05	-4.33	-13.43	-2.87
17	17/VL	-6.84	-1.76	-16.83	-4.77	-11.45	-2.65
18	18/VL	-8.45	-2.06	-15.35	-4.76	-14.24	-2.57
19	19/VL	-1.68	-0.71	-17.21	-4.40	-18.27	-2.90
20	20/VL	0.90	-0.26	-10.81	-2.77	-14.27	-2.56
Maximum		17.00	3.34	-10.81	-2.77	-10.54	-1.80
Minimum		-11.90	-2.30	-20.21	-5.60	-18.27	-3.45
Mean		-2.16	-0.47	-16.62	-4.43	-12.96	-2.48

Table 8.2 Stable isotope values of the groundwater and precipitation in Vembanad region

Groundwater			Precipitation					
Sample ID	δD‰)	δ^{18}O(‰)	Sample ID	δD(‰)	δ^{18}O(‰)	Sample ID	δD(‰)	δ^{18}O(‰)
1VG	-12.79	-3.03	Nov	-30.88	-7.40	II/My	-4.10	-3.80
2VG	-14.03	-3.30	I/Fb	-14.01	-0.20	II/Jn	-9.44	-3.81
3VG	-20.87	-4.23	I/Mc	1.85	-1.36	II/JY	-10.50	-4.12
4VG	-11.11	-3.05	I/Ap	-13.56	-3.00	II/At	-10.20	-3.72
5VG	-15.18	-3.18	I/My	2.30	-1.12	II/Sr	-8.88	-3.11
6VG	-10.71	-3.11	I/Jn	-6.66	-3.32	III/Fb	11.62	-0.26
7VG	-9.84	-3.01	I/Jy	-12.97	-4.32	IIIAp	-16.81	-4.72
8VG	-16.19	-3.52	I/At	-9.65	-4.09	III/My	-27.07	-5.38
9VG	-8.09	-2.07	II/Fb	4.97	-1.31	III/Jn	-11.90	-4.08
10VG	-17.24	-3.31	II/Mc	16.24	-0.33	IIIR/Jy	-23.62	-5.09
11VG	-7.65	-2.27	II/Ap	-5.75	-3.98	III/At	-11.02	-3.47
12VG	-8.59	-2.51						
13VG	-14.03	-3.29						
Maximum	-7.65	-2.07	Maximum	16.24	-0.20	Maximum	16.24	-0.20
Minimum	-20.87	-4.23	Minimum	-30.88	-7.40	Minimum	-30.88	-7.40
Mean	-12.79	-3.07	Mean	-8.64	-3.27	Mean	-8.64	-3.27

Table 8.3 Stable isotope values of the lake water in different seasons

ID	δD(‰)	δ^{18}O(‰)	ID	δD(‰)	δ^{18}O(‰)	ID	δD(‰)	δ^{18}O(‰)	ID	δD(‰)	δ^{18}O(‰)
Boat jetty, Ernakulam			Thanneermukkom			Aroorkutty, Bridge			Pathalam, estuary side		
1BS	-17.95	-3.33	1TS	-16.84	-3.07	1AS	-8.90	-1.73	1PS	-21.62	-4.24
2BS	-16.56	-3.10	2TS	-15.87	-2.87	2AS	-7.11	-1.39	2PS	-21.17	-4.21
3BS	-12.29	-2.29	3TS	-15.86	-3.25	3AS	-11.86	-1.63	3PS	-20.33	-4.34
4BS	-10.57	-2.03	4TS	-15.59	-3.00	4AS	-13.31	-2.14	4PS	-20.24	-4.20
5BS	-9.00	-1.97	5TS	-15.92	-3.03	5AS	-10.03	-1.61	5PS	-21.26	-4.12
6BS	-11.42	-2.15	6TS	-14.24	-2.94	6AS	-9.16	-1.54	6PS	-21.82	-4.02
7BS	-12.21	-2.21	7TS	-17.14	-2.84	7AS	-11.65	-1.88	7PS	-34.49	-4.04
1BD	-16.70	-3.32	1TB	-16.92	-2.91	1AD	-11.90	-1.53	1PD	-20.60	-4.01
2BD	-10.23	-2.95	2TB	-17.53	-2.84	2AD	-11.08	-1.23	2PD	-21.95	-3.96
3BD	-11.60	-2.13	3TB	-15.42	-2.98	3AD	-12.14	-1.59	3PD	-20.69	-3.92
4BD	-9.27	-1.46	4TB	-16.37	-2.33	4AD	-12.25	-2.37	4PD	-19.27	-4.00
5BD	-4.32	-1.27	5TB	-16.84	-3.03	5AD	-9.92	-1.80	5PD	-20.38	-3.90
6BD	-10.99	-2.07	6TB	-17.00	-2.92	6AD	-9.83	-1.73	6PD	-19.69	-4.11
7BD	-10.42	-2.23	7TB	-15.48	-2.74	7AD	-12.81	-2.17	7PD	-20.19	-4.10
Max	-4.32	-1.27	Max	-14.24	-2.33	Max	-7.11	-1.23	Max	-19.27	-3.90
Min	-17.95	-3.33	Min	-17.53	-3.25	Min	-13.31	-2.37	Min	-34.49	-4.34
Mean	-11.68	-2.32	Mean	-16.22	-2.91	Mean	-10.85	-1.74	Mean	-21.69	-4.08

9.0 Conclusions and Recommendations

9.1 Conclusions

The salient findings of the study on **"Water Quality Assessment and Isotope Studies of Vembanad Wetland System"** are reported in the following sections.

Physico-chemical analysis of the water samples collected during different seasons gave an insight into the pollution level of Vembanad wetland system. The water quality is seriously impaired by many organic and inorganic pollutants of different origin. The seasonal variation in water quality showed more pollution in pre-monsoon season. Spatial variation indicated more inorganic ions in the northern side due to salinity intrusion and more organic components in southern region due to different anthropogenic activities. There is a gradual decrease in conductivity values from the Thanneermukkom bund towards the upstream. Most of the cations follow same order as conductivity values. Increased load of sewage input from Alappuzha town and the coir retting activities in many regions of the wetland resulted in low dissolved oxygen values at many stations. Biological oxygen demand was also high in some sites of southern region. High nutrient level caused hypereutrophic stage in many parts of the system. The high concentration of phosphorus increased the amount of algal growth, making the situation hypereutrophic. The ratio of nitrate plus ammonia to soluble reactive phosphorus indicated phosphorous limited algal growth. The microbiological pollution level was so high that no stations in the monsoon season were free of coliform bacteria. The level of oil and grease in the system was very high. Abnormal high chlorophyll-*a* concentration suggested excessive nutrients possibly from anthropogenic sources in the water column. The water quality assessment based on irrigation quality revealed unsuitable condition for irrigation during pre-monsoon season. The tidal study conducted indicated direct input of ions from the Cochin estuary to the southern side of the wetland system, which causes excessive threat to the paddy fields. The abundant sodium in the pre-monsoon and post-monsoon season promoted cation exchange with positive values for the chloro-alkaline indices whereas the negative values in monsoon indicated no cation exchange. The variation of weight ratio of major ions as a function of total dissolved solids placed the Vembanad Lake in the region of precipitation and rock dominance in monsoon season and saline water dominance in pre-monsoon and post-monsoon season. The chemical classification of water samples based on Wilcox and USSL diagram were made. Based on permeability index the waters were categorized as good for irrigation with 75% or more of maximum permeability. Based on residual sodium carbonate there is no threat to the agriculture.

The ionic composition of most of the groundwater samples were sodium-calcium-chloride-bicarbonate type. The relative proportion of the cations indicated that, 47% of the sample exceeded alkali group compared to alkaline earths and for anions 70% of the samples predominated for strong acids such as chloride and sulphate. Based on Indices of Base Exchange, 38% of samples showed the presence of ion exchange reactions in the aquifer. Gibbs index value suggested 77% samples of rock dominance and 13% of evaporative enrichment in the aquifer. As a general water quality parameter, 77% of the groundwater samples were hard. High correlation coefficient of chloride with sodium might be due to weathering of sodium chloride rocks. The high correlation of sulphate with calcium indicated more contribution from gypsum. A few water samples reported problems due to fluoride contamination. More than 50% of the samples have problems due to iron contamination. Coliform contamination is severe in the groundwater as coliform forming units were present in 100% of the samples.

The geochemical analysis of core sediments from southern and northern regions of the Vembanad wetland system revealed that, irreparable ecological damage is being happened to the system. The analysis of textural class revealed sand dominated sediments with sandy loam in eastern side, silty loam in middle portion and completely loam in the western side of the Vembanad Lake. The percentage of organic carbon ranged from 1.84% to 11.84%. Decay process by heterotrophic organism caused a gradual decrease of organic carbon from surface to bottom. The variation of C/N ratios indicated higher contribution of terrestrial sources towards organic matter. The concentration levels of exchangeable cations in both sides of the wetland were very high. Determination of nutrient concentration indicated hypereutrophic stage of lake with vertical increase in the rate of deposition of nitrate, sulphate, and phosphate. Fractionation studies indicated different sources which are contributing phosphorous to the wetland system. The source of ortho-phosphorous to the system could be agricultural runoff and organic-phosphorous would be municipal effluents. The amount of phosphorous in sediments is so high that even if the source of phosphorous to the system is banned, it contributes phosphorous to the water column to maintain the hypereutrophic stage for a long period of time. The concentrations of pesticides were very high.

Heavy metal pollution of the wetland system was determined by dividing the wetland as a whole into two parts, one in fresh water region and other in industrial belt of the wetland system. The impact of anthropogenic heavy metal pollution on Vembanad wetland system was evaluated using sediment quality guidelines, pollution load index, sum of toxic units, with ERL/ERM and TEL/PEL values of EPA guidelines and degree of contamination. The contamination in the estuarine region is more severe than the fresh water region according to different quality guidelines. The results indicated that sediments in Vembanad Lake were polluted in moderate rate for copper, moderate to high rate for zinc and nickel, and non polluted to moderate rate for lead. Core sediments in Cochin estuary were polluted in heavy rate for all metals. The degree of contamination is severe at all the stations of Cochin side. Down-core variations of elements indicated an increase of heavy metals probably during the past few centuries. The ERM levels indicated a probable effect range with in which adverse biological effects frequently occur. The above results confirmed that the Cochin estuary is facing serious environmental degradation especially due to heavy metal contamination and it act as the main source of heavy metals towards the fresh water region of the wetland system.

The study using aquatic macrophytes to find out the load of accumulation of different heavy metals reported higher concentration levels in the roots of *Alternanthera pheloxeroide.* The minimum concentrations of trace elements were detected in *Sacciolepis interrepta* and *Pistia stratiotes.* All the macrophytes showed higher concentration of manganese and zinc compared to that present in bottom sediments. Comparison of the heavy metals with the background concentration present in sediment showed more chromium and mercury in *Alternanthera pheloxeroides.* The concentration factor calculated showed the suitability of different macrophytes as biomonitor for specific heavy metal in the study area. *Eichornia crassipes* is the suitable biomonitor for iron, *Alternanthera pheloxeroides* for manganese, nickel, lead, mercury and chromium and *Salvinia molesta* for copper, cadmium and zinc. Above all *Alternanthera pheloxeroides* is the best hyper accumulator, which can be used for phytoremediation of the aquatic eco-system.

Isotope study was conducted in the Vembanad wetland system to understand various hydrological processes occurring in the system. It revealed a number of important findings. The monthly stable isotopic ratio of the precipitation ranged from -30.88‰ to +16.24‰ for $\delta^{2}H$ and from -7.4‰ to -0.26‰ for $\delta^{18}O$ during the observation period, and showed seasonal variation with lower values in winter and higher values in summer. The precipitation samples of the area follows the equation $\delta D = 5.32\delta^{18}O+9.0$ with a slope of 5.33. The lake water has the most enriched values of $\delta^{18}O$ and $\delta^{2}H$ in the pre-monsoon season. The stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) of the lake water suggested that, in the Vembanad wetland system, $\delta^{18}O$ variation is used as an indicator of salinity mixing and $\delta^{2}H$ variation indicates the evaporation effect. The variation of $\delta^{18}O$ with chloride indicated complete mixing of lake in monsoon season. The slope of the best fit line to all groundwater data in $\delta^{18}O$-δD plot is 6.5 with a d-excess of 7.3‰. The surface water groundwater interconnection study identified that most of the shallow groundwater sources are directly connected with the lake. There is no interconnection between the lake and a groundwater source which is very near to the lake. The tidal study confirmed the direct impact of tide on the change in delta value of samples in the estuary. The $\delta^{34}S$ value of the dissolved sulphate indicated its contribution from marine origin. The sedimentation rate of the lake calculated from the activity profile was found to be 0.51cm/year, which is in agreement with similar studies reported in other lakes in India.

9.2 Recommendations

The study of “**Water Quality Assessment and Isotope Studies of Vembanad Wetland System**” has put serious attention of researchers for the conservation, management and restoration of the Vembanad wetland system. To maintain the natural quality of the system, the present study endorses following recommendations and policy guidelines.

1. Pollution prevention

    - ✓ Regulate the use of plastics
    - ✓ Control of non-point source pollution
    - ✓ Prevent oil spillage from house boats
    - ✓ Restrict dewatering from agricultural areas
    - ✓ Manage solid waste properly.

2. Capacity building:

    - ✓ Environment education by establishing eco-schools, training and awareness program.

3. Scientific operation of Thanneermukkom bund.
4. Declaring buffer zone of wetlands as protected area devoid of any developmental activities and implementation of national and state water policies with amendments to protect and preserve water bodies.
5. Conservation and restoration of mangrove ecosystem.
6. Research needs:

    - ✓ Regular monitoring of water quality and developing a database for risk evaluation.
    - ✓ Regular monitoring of sediment quality and develop a suitable sediment quality guidelines appropriate to Kerala conditions.

✓

- ✓ Regular monitoring of water samples of different source for isotopic variations and use of ^{15}N and ^{34}S for pollution research
- ✓ Preventing the siltation through appropriate land use and land cover approach and monitoring of sedimentation using radioisotopes.
- ✓ Biological studies and eutrophication research to ensure clean water.

The present study emphasizes the researchers for further studies to develop a suitable sediment quality guideline appropriate to the conditions of Kerala with support from different branches of science. More attention should be given for the speciation of heavy metals which will give a clear idea of how much threat was imposed to the aquatic life. In our future research we will incorporate the above findings.

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