BIOGEOCHEMICAL MODELING OF ACHANKOVIL RIVER, WESTERN GHATS, SOUTH INDIA

Dissertation submitted to Jawaharlal Nehru University
In partial fulfillment of the requirements
For the award of the Degree of

MASTER OF PHILOSOPHY

Submitted by

M. Bala Krishna Prasad

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New Delhi – 110 067
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CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled

"**Biogeochemical Modeling of Achankovil River, Western Ghats, South India**" has

been carried out in School of Environmental Sciences, Jawaharlal Nehru University, New

Delhi for partial fulfillment of the award of the degree of Master of Philosophy. This

work is original and has not been submitted in part or full for any degree or diploma in

any university.

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CHAPTER 1

INTRODUCTION

Rivers are the arteries of continents. They are the chief carriers of water, salt, organic matter and mineral particles (37%) from land to sea (Meybeck 1982). Continents on the other hand direct flow and composition of water in a number of ways. First, it is the height, the slope, and the direction of mountain chains in relation to the weather front, which determines the size and water potential of the catchment area. Second, rock type, climate and vegetation give characteristic imprints on the chemistry of the dissolved and particulate load of a river system. And, third, the impacts of humans on quality and distribution of water is felt in an ever-increasing fashion.

The transport of carbon and minerals by major rivers gives essential information on the rate of erosion of continents, the biogeochemical cycling of major and minor elements and nutrients upon the earth, and the contribution of terrestrial material to the ocean. Rivers transport a variety of material to the sea, and in some cases material respond rapidly to changes induced by natural causes or by human agency and may thereby be useful 'monitors' of events that take much longer than discharge (Meybeck 1982) that have been sporadic on major rivers. Some of the major rivers like Ganges, Mckong, Godavari, Cauvery etc., which are originating in Himalayas, contribute one-third of the global sediment transport to the world oceans (Milliman and Mede 1983).

In rivers, a particulate organic matter can originate from autochthonous production of phytoplankton and from allochthonus sources like soils, wastewater and atmosphere. In natural water systems, it represents a continuous size spectrum, beginning with free small molecules, macromolecules and aggregates and ending with organism. The fraction retained on a filter with a pore size of 0.5-$1.0\mu m$ is designed as particulate organic matter. The POM is subjected to different process in the water body. Their process such as minerilisation, desegregation and sedimentation determine its role and fate in the aquatic ecosystem. The average amount of POM transported by the world rivers in the range of 0.07-0.2×10^{15} g C Y^{-1} (Meybeck 1982). The POM could change the chemistry of water body. It could adsorb the nutrients from the water during reduction environments and releases to the environment during the oxidative conditions.

Role of minor rivers (with stream net in rural urban setting, monsoon climate with distinct seasonally and intensely framed catchment attracting large inputs of chemical fertilizers, soil amendments and pesticides) in transport of load have rarely been brought light (Douglas 1967). The rivers of Kerala (with exception of Thrivikranji 1989, Jose 1990) are a case in point. Nevertheless, these rivers are good systems to develop a model on them in respect of the material flux vis-à-vis its anthropogenic modifications. The transport of the nutrient fluxes carried by the river discharge can be calculated by various ways, these processes can be bettered studied by using various models. Environmental modeling can be classified into two basic categories. One is the modeling of individual components, e.g. the atmosphere and the hydrosphere. The other is the simulation of the entire environment as a dynamic system.

"Budget models" are simple mass balance calculations of variables (C, N, P, Si, S, etc). Within the defined geographic areas and over defined periods (Garden et al 1992). Usually budget models are built to aggregate the many small individual components of the system into smaller sets of pieces, which are similar to one another. Thus, all plant species in an ecosystem might be aggregated into "primary producers." Some grouping will occur for almost any model. As one applies a single model across a range of systems, the value of such groupings becomes readily apparent. For some purposes it may be adequate to group all organisms within an ecosystem into the "net biogeochemical" reactions" which occur within the system.

Basically a budget describes, the rate of delivery to the system (input), the rate of removal from the system (out put) and the rate of change of material mass within the system (storage). Some material may undergo internal transformations of state, which lead to appearance and disappearance of these materials. Such changes are some times referred to as 'internal sources or sinks'.

Budget in terms of a simple equation

$$dm / dt = \sum inputs - \sum outputs + \sum (sources-sinks)$$

Where

dm/dt represents the change of mass of any particular in the system with respect to time.

If dm/dt ratio becomes zero, which indicates that the system mass assumed to be at steady state. In some systems, the delivery of nutrients exceeds the assimilation rate, this would results eutrophication. However, some times the nutrients are deficient in the system, so the aquatic life with in the system has to depend on other source supply. This type system can also called as heterotropic system. The tropic nature and nutrient status of the water body can be studied by using the budget models.

Hence in this dissertation an attempt has been made to understand the biogeochemical behavior of the non-conservative nutrients and develop a biogeochemical budget model for small most homogeneous Achankovil River system. And an attempt has also been made to understand the climatic impact on biogeochemical process. This study is the first of its kind in the river system of Western Ghats.

LITERATURE REVIEW

Water is essential for life on earth and is always the talks of the town either due to too much of it or too little of it. The Indian subcontinent is one of the wettest places on earth, with an average of over 4000 km^3, that amounts to precipitation of about 110 cm, total river flow of about 1880 km^3, 7 millions hectares of various types of lakes, ponds, reservoirs and a potential renewable ground water sources of about 431 km^3. Riverine runoff provides a powerful geochemical flow playing important role in the planetary mass exchanging between worlds land and the ocean and is strongly affected by human activities. Natural, biological and geochemical activities in soils and bedrock, as well as anthropogenic activities, are responsible for the composition of river water, which eventually reaches estuaries and the ocean. Since 1910, an extensive research has been done so far on biogeochemistry of various fresh water systems across the globe by various researchers and scientists.

River transports dissolved material to the oceans in the form of suspended matter. The suspended matter contains a wide range of cations and anoins. Armstrong and Tibbilts (1968) had done work on N, P,and C chemistry of sea water. Later on, Meybeck (1981, 1982), Hu Ming- Hui and Stallard (1982), Millimam and Meade (1983), Sarin and Krishnaswami (1984), Ittekkot (1985), Saifulla (1986), Subramanian (1987), Hermer R (1989), Serlathan (1993), Rmesh R (1995), Ramanathan (1997) etc. have carried out nutrient studies of various river systems.

Recently people are working on modeling of biogeochemical processes. In this subject **LOICZ** has developed a software package called **CABARET (Computer Assisted Budget Analysis for Research, Education, and Training)** to calculate the material fluxes in and out of the system. In addition to CABART, so many packages developed so far, NURAMBO, MIKE series, and a large number scientists working on the biogeochemical modeling, David L Correl (2000), Desouza (1999), Paul W. Jewell (1994), Warnant (1994), Van Der Peijl (2000), Kuang-Yao Lee (2000).

1. Biogeochemistry:

In recent time, researchers have been concentrating on the nutrient fluxes coming and going out of the interested system. To study the mass balance mechanism, we should require the nutrient status and nutrient cycling in the system. Milliman and Meade (1983) estimated the annual suspended load of the world rivers to be about 13.5×10^9 t. the distribution of the sediment loads of different areas is very heterogeneous, and high sediment transport rates are concentrated in regions near the equater and in Arctic regions. Among the world rivers, the Huanghe delivers the height average concentration of sediment load (22000 mg/l) into the sea, followed by Nile (3700 mg/l), and the Ganges with (1700 mg/l). Important element in the biosphere is 'carbon'. Chief components of the carbon in the environment are CH_4, CO, CO_2 and organic matter (CH_2O). The CH_4 and CO that goes into the atmosphere and ultimately oxidizes to CO_2. CH_4 and CO are products of anoxic decomposition of organic matter; thus the main procedures of these are stagnant water systems as lakes and estuaries. Raymahashay (1986) formulated a methodology to estimate the percentage contribution of HCO_3^- in the surface water from different types of weathering. He showed that variation in the bicarbonate in the Indian rivers in primarily controlled by varying silicate fractions resulting from colonization reactions. Georg Iron (1991) and Jeffery E. Richey (1991) estimated Amazon river transports 3984×10^6 t of suspended material to the sea, DOC accounts for approximately 50% of the total organic matter transported by the Amazon. Approximately 80-90% of the DIC is bicarbonate. DIC ranged from 687 μ mol/l to 1228 μ mol/l. Telang, Pocklington, Naidu, et al (1991).

River input into the ocean is an important link in the biogeochemical cycling of carbon between its two major pools viz. land and ocean. The carbon compounds in these pools may be in the forms of biogeochemically inert metal complexed humic materials, polyphenols, and polysaccharides and rather unstable compounds such as polypeptides, fattyacids, and carbonates which get easily decomposed in the reverine environment (Degens 1982). The total amount of organic matter transported by rivers annually is extremely low (0.5×10^{15} g C a^{-1}) in comparison to the carbon pools linked by the rivers. The amount of carbon held within the soils of earth is about 1515×10^{15} g C (Schlesinger 1984) and ocean (dissolved and particulate together) 40600×10^{15} g C (JGOFS 1992).

Total organic carbon transported by the rivers to the oceans has been estimated to range from 0.03×10^{15} g C a^{-1} (Williams 1971) to 1×10^{15} g C a^{-1} (Richey et al 1980). Intermediate values have been proposed, for instance, by Garrel and Mackenzic (1971) 0.32×10^{15} g C a^{-1}, Duce and Duvrsma (1977) $0.1\text{-}0.15 \times 10^{15}$ g C a^{-1} Schleisnger and Melack(1981) 0.4×10^{15} g C a^{-1}, Sarmiento and Sundquist (1992) $0.3\text{-}0.5 \times 10^{15}$ g C a^{-1} and L.P.Gupta (1997) 3014×10^{6} ton PC a^{-1}. On a world average 0.5×10^{15} g C a^{-1} organic carbon is being transported is equally distributed between dissolved and particulate fraction of the riverine load (Spiczy and Ittekkot 1991).

The origin of N in river water is considerably more complex then it is for most other elements because N_2 exists in solution in several different forms and is intimately involved in biogeochemical cycling as an essential component of living tissue, both plant and animal. River out put of N is estimated to be 49-69 Tg N/yr. Because of denitrification and other gaseous emission process, this amounts to only about one fifth of the total N loss from the land.

This flux can be divided into different forms of nitrogen: (1). Natural dissolved inorganic nitrogen (DIN), consisting mainly of ammonium and nitrate with global riverine flux of 4.5 Tg N Y^{-1} (Meybeck 1982, 1993); (2). Dissolved organic nitrogen (DON), with a flux of 10 T g N Y^{-1} (Meybeck 1982, 1993) (3). Dissolved pollutive nitrogen, with a flux estimated to lie between 7 T g N Y^{-1} (Meybeck 1993) and 21 T g N Y^{-1} (Wollast 1993), and (4). Particulate nitrogen (PN), with a flux ranging from 27-33 T g N Y^{-1}. Total PN is both natural and anthropogenic in origin and represents undecomposed organic N derived from soil and natural activity along with NH^+_4 locked in K-containing silicate minerals.

Jeffery E. Richey (1991) stated that in Amazon nutrient distributions varied systematically overtime and space, Nitrate was the dominant form of combined N in the rivers, varying from 5-25μ mol/l. In general NO_3 concentrations observed at the lowest discharges. The global particulate nitrogen (PN) transport by rivers amounts to 33×10^{12} g N a^{-1}, more than 80% of which occurs in rivers having high suspended matter concentration e.g. Ganges, Mekong and Huangle (Ittekkot & Zhange 1989). Galloway et al (1995) estimated that coastal oceans receive about 41 m t N yr^{-1} via rivers, much of which is buried or denitrified in the coastal sediments it self. They predict that by the year

2020, two thirds of increase in anthropogenic N fixation will take place in Asia. More over, the nutrient budget calculations has done on small river systems in various parts of the world, Boyel et al (2002) estimated nitrate load in small Kennebec (333 kg km^2 yr^{-1}), Saw (389 kg km^2 yr^{-1}); rivers of US, Charles (644 kg km^2 yr^{-1}), Delaware (961 kg km^2 yr^{-1}) and Potomac (897 kg km^2 yr^{-1}). As much as 80% of PN transport is in Asian rivers with a large of suspended load (such as Ganges, Brahmaputra, Mekong and Haunch rivers), which are polluted from deforestation, nitrogen fertilizer application and sewage.

Phosphorus, unlike nitrogen, has no stable gaseous phase in the atmosphere. For this reason, in contrast to nitrogen, most phosphorus is lost from land by way of river run off, and a considerably smaller proportion, on average, of land input is provided by precipitation. The major ultimate source of phosphorus is weathering i.e. the removal of phosphorus from rocks. However, phosphorus in rocks and sediments is mainly in a relatively insoluble form as the calcium phosphate mineral, apatite. Even when released as soluble phosphate by weathering, phosphorus is usually quickly tied up in the soil on iron, aluminum and calcium as phosphates or by clay minerals (Devol et al 1990) to produce insoluble forms that are not accessible to biological systems. Because of the relative insolubility of phosphorus, it is often called as a limiting nutrient in biological systems; that is, it is in short supply.

The total amount of P (inorganic and organic) transported by rivers at present is approximately 20 Tg P yr^{-1} (Meybeck 1982,1993). Froelich et al (1982) estimated that the preagricultural river phosphorus flux due to weathering was about 10 Tg P yr^{-1} based on a preagricultural continental denudation rate of 10,000 Tg P yr^{-1} (Judson 1968, Greger 1970) and 0.1% P in the earth crust.

River	DOC 10^6 t y^{-1}	POC 10^6 t y^{-1}	P-PO$_4$ 10^3 t y^{-1}	PIP 10^3 t y^{-1}
Indus	3.83	1.3	36	-
Brahmaputra	1.93	1.5	72	516
Ganges	1.81	6.55	47	707
Godavari	-	-	15	141
Krishna	-	-	8.6	-
Cauveri	-	-	2	0.13
World Rivers				
Amazon	19.1	13	21.6	1485
Zaire	10.15	2.8	-	-
Niger	0.53	0.66	0.8	108.8
Meckong	-	-	3.8	690

Table: 1.1 Average annual fluxes of C and P in selected Indian and World Rivers.

Table: 1.1 shows the average annual P-PO$_4$ per year, in comparison to peninsular rivers such as Godavari, Krishna and Cauvery, which carryon an average of about 7 x 10^3 t P yr^{-1}. The high rate of discharge of the Himalayan rivers coupled with high elevation of these rivers are the primary influencing factor for the increased fluxes (Ramesh et al 1996). It can also be observed from the table that the P-PO$_4$ transports by Himalayan rivers are three orders of magnitude higher than that of the Amazon River. Most of the organic matter is liable in the river sediments of the Indian subcontinent (Subramanian & Ittekkot 1991, Gupta et al 1997) and is likely to release additional phosphorus into the river water. Therefore, the total DIP being exported out of South Asia to the Bay of Bengal is likely to be greater than 40µg/l (Subramanian 2000). Concentration of particulate phosphorus is always high in all Indian rivers. The flux of particulate organic and inorganic phosphorus from Indian rivers to the ocean is 0.2 and 1.5 million tones per year respectively (Ramesh et al 1995).

Chemical reactions in the river, which are intimately intertwined with life process, constitute major controls on the concentrations of the following constituents: Ca^{+2}, HCO$_3$, SO$_4$, H$_2$SiO$_4$, CO$_2$, O$_2$, NO$_3$ and PO$_4$ (Berger et al 1989, Wollast et al 1993).

Biological activity strongly affects many trace elements (Boyle et al 1977, Sclater et al 1976). The principal process can be recognized: (1). The synthesis of soft tissues or organic matter. (2). The bacterial decomposition of organic matter upon death, and (3). The secretion of skeletal hard parts.

Essentially all organic matter is ultimately formed in the surface water by photosyntesis in presence of light by photoplankton. Redfield (1958) had shown those average elemental components carbon, nitrogen and phosphorus can be represented by the molar ratio 106:16:1. This can be represented by the following photosynthetic equation:

$$\text{light}$$
$$106\ CO_2 + 16\ NO_3^- + HPO_4^{-2} + 122\ H_2O + 18\ H^+ \longrightarrow C_{106}H_{263}O_{110}N_{16}P + 138\ O_2$$
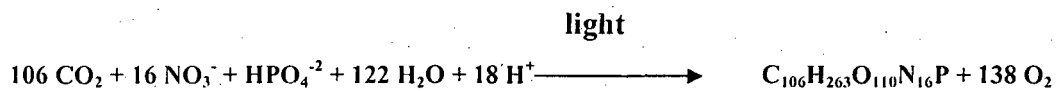
This reaction shows that photosynthesis requires not only CO_2 and light but also uptake of nutrients such as nitrate and phosphate. Highly varying nitrate and phosphate in surface waters is because of planktonic activity. The ratio between C: N: P is 106:16:1 can also called as Reidfield ratio.

BIOGEOCHEMICAL MODELING

An increasing curiosity about the fate of environment and its components has been initiated the modeling of environment, and its components. The pressure by the society for a better understanding of the environment and its components and an improved capacity for environmental prediction has been ever increasing.

Large number people have studied the biogeochemistry and biogeochemical process of different aquatic ecosystems (Meybeck (1982), Dovel A.H. (1990), Froenlich (1982), Subramanian (1997,1999,2000), Ramanathan (1996), Ramesh (1996). All of them had calculated the nutrient fluxes of the aquatic bodies viz. rivers & esturies and fate of the nutrients in the systems. Natural systems like rivers are very complex and dynamic in nature. The models predict the biological nature and availability of the nutrients. The models that are used for the study of the biogeochemical behavior of the nutrients are called biogeochemical model. There are so many models are in practice, box model is one of the widely used methods to study the behavior of non-conservative

nutrients like nitrate and phosphate. In box modeling one assumes that a proportion of the system is so well stirred that it is homogeneous in composition and can be treated as a uniform "box". In this case, input of a dissolved substance form streams, output by a surface outlet, precipitation and removal to bottom sediments and addition via dissolution or bacterial regeneration of the suspended and sedimented solids (Imbodenance Lerman 1978). Rates of these processes can be represented as:

$$\frac{\Delta M}{\Delta T} = Ci\, Fi - C\, Fo + Rd - Rp$$

Where

Fi = rate of water inflow from streams

Fo = rate of water outflow through outlet

m = total mass of dissolved substance in the system

Rp = rate of removal via sedimentation

Rd = rate of addition via dissoltion of solids

Ci = concentration of dissolved substance in the system

C = concentration of the nutrients in the system

T = time

This type of single box models is applicable to the lake systems, where as for riverine ecosystems the total area of the system has to divided into small boxes and scaling of each box is important for the estimation of the flux into and out of the system (Garden et al 2000).

An area of biogeochemical modeling research that is presently receiving great attention in India and various parts of the world. The physical, chemical and biological parameters of the water are affected by various factors. Nutrient flux calculations have been used for estimation of circulation and transport of the nutrients over a period of time spatially and temporally.

A model is any simplified description or abstraction of the process. There are various types of models from the simple box models to more complicated models which

describe specific process (e.g., primary production as a function of light, sediment transport as function of river flow, etc.). Many such process models may be further combined into an integrated system model (Gardon et al., 1996). However, in general, the more complex model structure, the less statically robust is the statistical output.

Generally models operate at the scale within which interactions among individual components with respect to the dynamic of the species (Malanson 1993). Some models are often specific to the ecosystem for which they have developed and usually their results cannot be extrapolated to other ecosystems or to a wider range of environmental conditions (White et al., 1993). The carbon flux into the biosphere represents the gross primary productivity (GPP) i.e. carbon fixed in the photosynthesis by organisms (Heimann et al., 1998). The net primary production (NPP) is the profit remaining from the photosynthesis of the organism, i.e. the GPP minus the respiration. The rate of respiration can be used for estimation of productivity of the system (Lieth & Whittaker 1975). The NPP is used for building up organic matter, part of which lost by water over a period of time (Larcher 1995). The net ecosystem production (NEP) represents the net exchange between the biosphere and atmosphere, a fraction of NPP can accumulate from one year to the next as NEP (Leith and Whittaker 1975).

Michael J. Vanni et al., (2001) estimated fluxes of dissolved and particulate nitrogen and phosphorus from three watersheds in US were quantified with a high resolution-sampling program over a five-year period. They estimated, over the five-year period, mean annual flux of soluble reactive phosphorus was 0.583 kg P ha^{-1} y^{-1} from smallest watershed and 0.295 kg P ha^{-1} y^{-1} from the intermediary watershed. Mean annual flux of nitrate was 20.53 kg N ha^{-1} y^{-1} in the smallest watershed and 44.77 kg N ha^{-1} y^{-1} in the intermediary watershed.

In addition to this, a large number of researchers have developed models on various aquatic ecosystems on various parameters (Evans and Gareen 1997, Doney et al., 1996, Flierl and Davis 1993) and studied impact of the mesoscale eddy field on the spatial and temporal scales of biological production and on overall productivity (Mc Gillicuddy et al., 1995, Smith et al., 1996, Dadou et al., 1996, Mc Gillicuddy and Robinson 1997). Hema Naik(C, N and P Budgets for Mahanadi Estuary, East Coast of India, 2000), S. N. de Sousa (The Mandovi Estuary, Goa 2001), J.I. Marshall Crossland,

C.J. Crossland and D.P. Swaney (Congo (Zaire) River Estuary, Democratic Republic of the Congo 2000), V. Wepener (Mhlathuze River Estuary, KwaZulu-Natal, South Africa 2001), X. Durrieu de Madron, L. Denis, F. Diaz, N. Garcia, C. Guieu (Gulf of Lions, France 2000), Inna Yurkova (Donuzlav estuary, Northwestern part of the Black Sea, Ukraine 2001), F. Muñoz-Arriola, J. Carriquiry-Beltran, E. Nieto-García and M. Hernandez-Ayon (Colorado River Delta 1999) and Shen Huan-Ting, Huang Qing-Hui, Liu Xin-Cheng (Nitrogen and Phosphorus budgets for the Changjiang (Yangtze) River 2000).

Paul W. Jewell (1994) developed a mass balance model of Ekman transport and nutrient fluxes in coastal upwelling zones. He developed a model using longshore transport, surface productivity and dissolved phosphorus. His observations were consistent with the conceptual model of surface and subsurface currents, which were moving towards the equator and continually being upgraded by the offshore flux of nutrients. Sybil P. Seitzinger (2002) developed a regression model (Riv R-N), that predicts the proportion of N removal from streams and reservoirs as an inverse function of the water displacement time of the water body. He observed that the proportion of N removal from all streams in the watersheds (37-76%) is considerably higher than the proportion of N input to an individual reach that is removed in that segment (> 20%) because of the cumulative effect of continued N removal along the entire flow path in down stream reaches. Richard B. Alexander et al., (2002) done a comparative study of models for estimating the riverine export of nitrogen export of N from large watersheds.

David C. Cornell et al., (2002) studied the microbial status of the Beaver Pond and its effect on the Maryland Coastal Plain. He observed in his study that over a period of time the biogeochemical parameters has been decreasing, this is due to the rapid growth of the aquatic flora and fauna within the system. Kuang Yao Lee (2002) used GLEF and ARC/INFO to study the hydrochemistry of the Choptank Rivers. He developed a model using ARC/INFO, his observations were used to assess the importance of hydrologic inputs and outputs relative to sediment burial, denitrificationn and nitrogen fixation.

In India, number of scientists have done work on biogeochemistry of major rivers, very few like S. Bajpayee, A.Verma, K.P. Thirivikramjai, Sabu Joseph have studied biogeochemical characteristics of small rivers which are flowing in Western Ghats.

The literature review points that the absence of Biogeochemical studies in Achankovil River basin. Hence, an attempt has been made in this study to produce a base line data on this study.

CHAPTER 2

STUDY AREA

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STUDY AREA

The Western Ghats comprise the mountain range that runs along the western coast of India, from the Vindhya-Satpura ranges in the north to the southern tip. The ecosystems of the Western Ghats are located mainly in the following regions: the tropical wet evergreen forests in Amboli and Radhanagari; the Montane evergreen forests in Mahabaleshwar and Bhimashanker; moist deciduous forests in Mulsi and the scrub forest in Mundunthurai.

There is a great variety of vegetation all along the Ghats: scrub jungles, grassland along the lower altitudes, dry and moist deciduous forests, and semi-evergreen and evergreen forests. There are two main centres of diversity, the Agashyamalai hills and the Silent Valley. The complex topography and the heavy rainfall have made certain areas inaccessible and have helped the region retain its diversity. There is an equal diversity of animal and bird life. There is only one bio-diversity reserve in the Western Ghats, the Nilgiri bio-diversity reserve, which helps in conserving endemic and endangered species. A few of the indigenous and exotic tree and plant species in the Western Ghats are the teak, jamun, cashew, hog plum, coral tree, jasmine, and crossandra.

There are a large number of rivers flowing through this mountain range. These are important for the bio-diversity of Western Ghats. Some of these are Periyar, Bharatphuzha, Kallada, Achankovil, Manimala, Pamba, Chalakudi, Muvattupuzha etc.

The present study mainly concentrated on three rivers Achankovil, Pamba and Manimala, which are covering mainly four districts of Kerala i.e. ALLEPY, PATHANAMTHITTA, and KOTTAM. The length of Achankovil, Pamba and Manimala are 128,176 and 90 km respectively

SOIL

The soil type of the study area is most predominantly lateritic, especially in the midlands. These are weathering product of rocks under the tropical humid conditions existing in the study area. It shows a developed A, B, & C profiles, which are deep to very deep. The B-horizon is well developed in most area and has abundant a ferruginnound quartz gravels. The other dominant soil type is Hapludolls-Tropudalfs-Tropeptic-Eutrothox (loam) type of soil, which is developed on the weathered crystalline rocks in the eastern part of study area. They are rich in organic matter.Tropofluvents - Eutropepts - Dystropepts (alluvium) type of soil is well developed along the river valleys and cut across the laterite cover . They are very fertilewith high holding capicity.Tropaqualps - Tropaquepts (brown hydromorphic) type of soil is present in parches in the areas of wetlands and are rich in organic matter and potash.Troporthents (grey onattukara) type of soil is found only in Alleppey and Quilon districts. It is grey in colour, course grained and acidic in nature.

TEMPERATURE

From last 10 year average data of temperature variation from Indian Meteorological Department, New Delhi, the day temperatures are more or less uniform over the plains throughout the year except during January, December and months of July when these temperature drop down by about 2 to 3° C. Both day and night temperature lower over the plateau and at high level stations than over the plain. Day temperatures of coastal places are less than those of interior places. March-April is hottest month with a mean maximum temperature range from 32°C to 37°C on different stations.

HUMIDITY

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

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

RAINFALL

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

ACHANKOVIL RIVER BASIN

Achankovil River is in south of Kerala with an area of 1484km^2 and annual average discharge of water about 1.5 km^{2}yr^1 bounded by hills on three sides on the south and north longitudes 8.75^0 and 9.5^0 and east longitudes

76.25° and 76.75° (fig 2.1). The land lies at a height of 20-120 meters above msl level. Side slope of the valley is moderate (50-180m). The area receives an annual rainfall of 289mm. The geology is crystalline rocks (pyroxene granulites, charnockitic gneiss, khondalites and associated calc-granulite bands). The basin displays dendritic to sub-dendritic and rarely rectangular and trellises drainage patterns. The river discharges into the Vembanad lake extends from Cochin (Kochi) to Alleppey (Alapuzha) for a distance of 83km and is the largest estuary in Kerala. Its width varies from a few hundred meters to 15km. It is elongated and oriented in NW-SE direction. Five major rivers, viz. Muvattupuzha, Meenachil, Manimala, Achankovil and Pamba discharges into this lake.

From last 10 year average data of temperature variation from Indian Meteorological Department, New Delhi, the day temperatures are more or less uniform over the plains throughout the year except during January, December and months of July when these temperature drop down by about 2 to 3° C. Both day and night temperature lower over the plateau and at high level stations than over the plain. Day temperatures of coastal places are less than those of the interior places. March-April is hottest month with a mean maximum temperature range from 32°C to 37°C on different stations.

PHYSIOGRAPHY: -

Physiographically, the State is divided into three divisions, viz., (I) The highland region in the east consisting of the forests of the Western Ghats and its slopes; (2) The midland region, and (3) the lowland region in the west coast. These three regions run nearly parallel to each other from one end of the State to the other. The topography of the highland region is mountainous with altitudes ranging from 400-2000m above the sea level. The midland (region) has a rolling or hilly topography roughening into slopes and gradually joining the mountains, the altitude varying from a few meters in the west to about 400 meters in the east. The narrow coastal belt of lowlands in the extreme west has a nearly level and flat topography. A series of natural
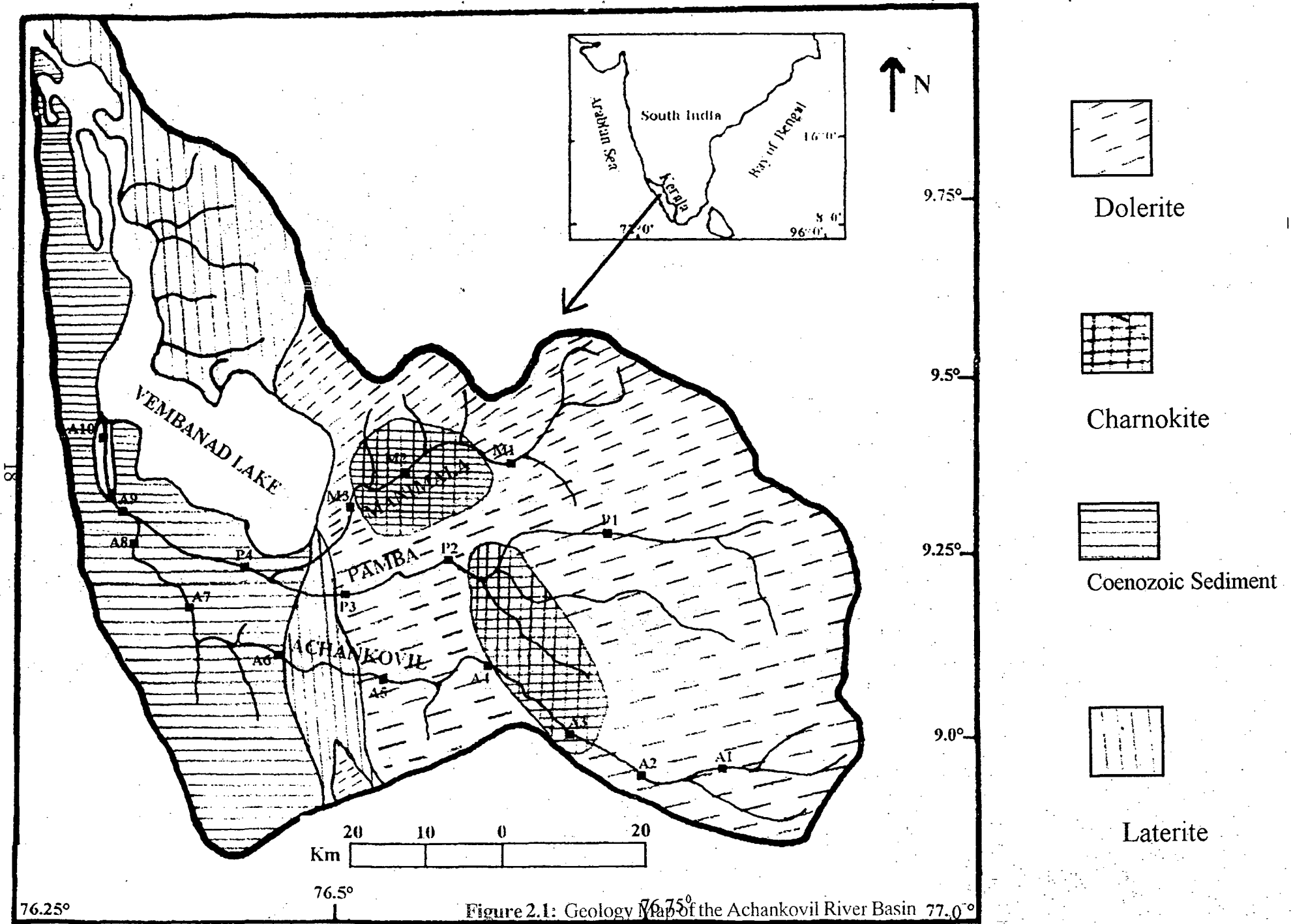
Figure 2.1: Geology Map of the Achankovil River Basin

Legend:
- Dolerite
- Charnokite
- Coenozoic Sediment
- Laterite

backwaters connected together by man-made canals is characteristic feature of this region. The entire face of the land is intercepted by a number of rivers, which originate in the mountains in the east and flow towards the backwaters for the sea in the west.

GEOLOGY

The main geological formations of the State belong to the Archean period except for the coastal tracts where the more recent sedimentary formations known as the Varkalai series exists and extend almost continuously from Varkalai in the south to Kasargod in the north (fig. 2.2). The sands alluvium, organic deposits and lacustrine beds of recent formations. According to the time scale, the geological formation of Kerala are given as follows:

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

VEGETATION

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

(i) The humid Temperate Zone of the high ranges (above 1,350 m).

(ii) The sub-tropical zone (750-1,350 m)

(iii) The monsoon forests (450-750 m).

(iv) The midland and coastal region (0-450 m).

Natural vegetation is now found that only in the first three zones which together constitute about 25 percent of the total area of the State.

Along the lower altitudes of the humid Temperate Zone trees of the Cypress and Eucalyptus species are seen. Shrubby forms are rare, but many perennial herbs and grasses are found. The tea shrub, Camellia sinensis, is cultivated extensively in this region. The climate of the sub-tropical zone is suitable for the growth of huge trees such as the teak (Tectona grandis), and the rosewood (Dalbergia latifolia). Saprophytic plants like orchids and fungi grow in the decaying organic matter of the forest floor. Extensive plantations of para rubber, (Alevea brasiliensis) and of cardamom (Elettaria cardamomum), as well as that of tea are found in this region. The chief characteristic of the monsoon forests is that the trees are mainly of the deciduous type so that leaf fall occurs at the beginning of the dry seasons. The whole of the midland and coastal regions is under human habitation and the vegetation consists

DRANAIGE

The Achankovil River originates at the place called Achankovil; it is in District Pathanamthitta of State Kerala. The total length of the river is about 128 km. It is the main water source for people of Pathanamthitta and Alleppy districts for drinking and agricultural purposes. It is flowing through the thick forests of Western Ghats and carries a lot of nutrients and organic load to near by areas. On this river so many dams and bridges are constructed e.g. Ambalakadav, Mavelikara. This river enters District Alleppey. At Viyyuvaram it confluence with Pamba and moves towards little northeast, finally meets with Vembanad lake.

CHAPTER 3

MATERIALS
&
METHODS

CHAPTER 3

MATERIALS AND METHODS

SAMPLING

Chemistry of water, collection of samples and the methods adopted for various authors (Chidambaram 2000) discussed the sampling techniques. The analytical techniques and the sample collection are important in order to obtain a good result and interpretation (APHA 1985, Ramanathan 1992, Ramesh 1996).

A total of 18 water samples were collected from three rivers for three seasons, 12 samples from Achankovil river, 3 from Pamba and 3 from Manimala in February-2002 (pre-monsoon), June-July-2002 (Monsoon) and October-2002 (Post-monsoon). The sampling locations are given in the table No: 3.1 and figure No: 3.1. Polyproplene was used for the water samples. All containers used for sampling were washed with 10% nitric acid solution followed by distilled water. 100 ml of the water samples were vacuum filtered using 0.45 μm Millipore membranes (the filter papers had been pre-weighed before filtration). 100ml of the water samples were filtered in the field and the filtrate acidified with phosphoric acid. Another sample of 100 ml was filtered but not acidified, while the third sample of 250ml was unfiltered but kept as the raw sample. All the three water samples and the suspended matter (filter paper) were brought to the laboratory and stored at 4^0 C in order to avoid any chemical alteration (APHA 1995).

3.1 FIELD MEASUREMENT

The pH, electrical conductivity (EC), dissolved oxygen (DO) and temperature measurements on the unfiltered water were carried out in the field using a field water analyzer kit.

Sample No.	Place of Location
AC 1	Konni
AC2	Aruvappalam
AC 3	Kumpazha
AC 4	Pathanamthitta
AC 5	Ambalakadau
AC 6	Thumpanom
AC 7	Pandalam
AC 8	Vettiyar
AC 9	Mavelikara
AC 10	Paippad
AC 11	Viyyuvaram 1
AC 12	Viyyuvaram 2
P 1	Vadaserikara
P 2	Ranni
P 3	Edathuva
M 1	Cheruvalla
M 2	Mallapally
M 3	Thiruvella

Table No: 3.1 Sampling Locations

3.1.1. pH

The pH was measured using water analyzer kit. The glass electrode was conditioned (4 MKCl as filling solution) and calibrated with buffer solutions of pH 4, 7 and 9.2. The temperature knob was set in accordance with the temperature of the water samples. The samples were stirred continuously in order to maintain homogeneity before noting the pH.

3.1.2. Electrical Conductivity (EC)

The conductivity was measured in micro-siemens/cm (μS/cm) using conductivity meter. The instrument was calibrated and set for 0.01 m KCl solution (1413μs/cm at 25^{0}C) (Todd 1980). water analyzer kit.
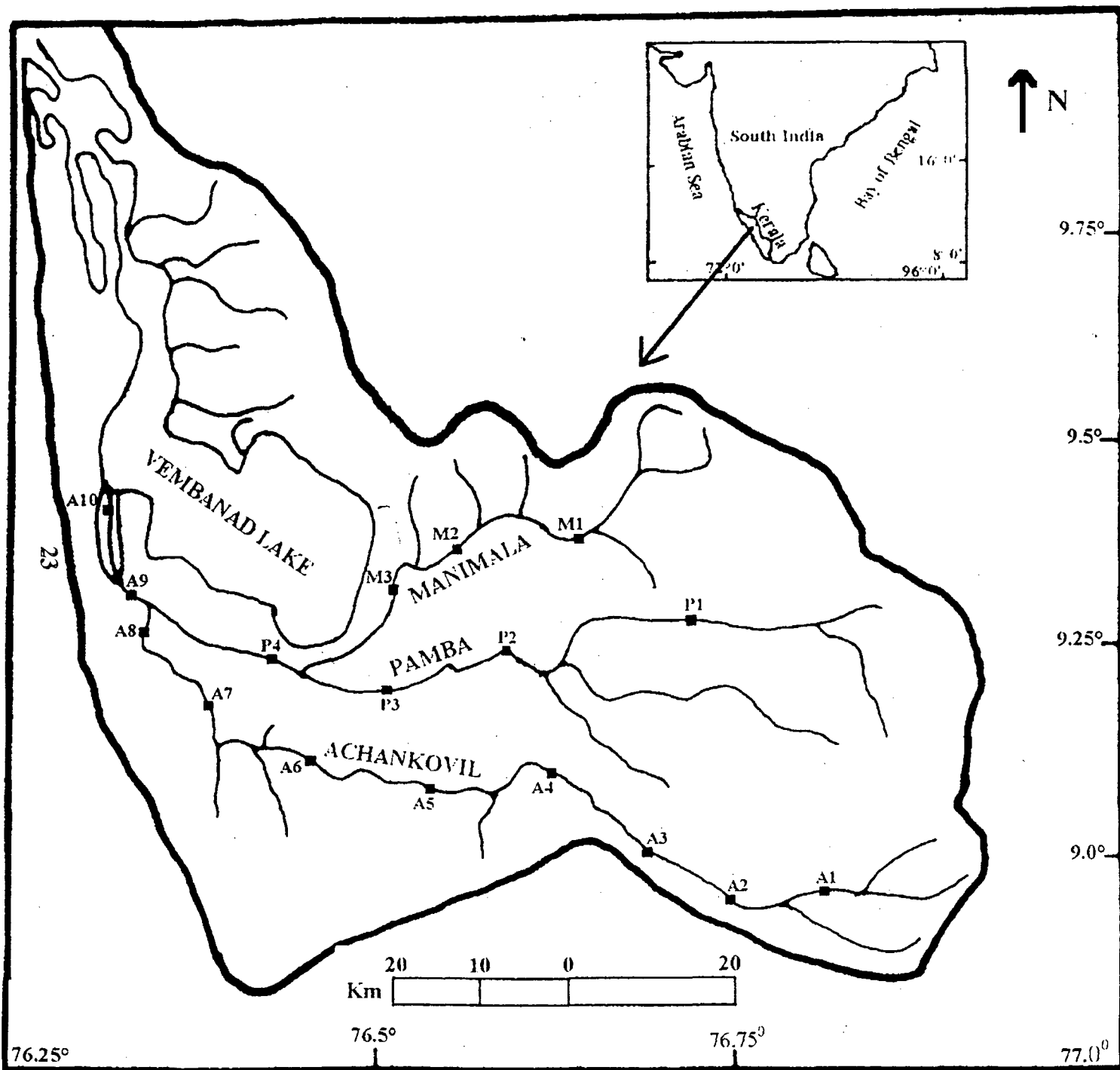
Figure 3.1: Sampling Locations of the Achankovil River system

3.1.3. Dissolved Oxygen

Dissolved oxygen was measured in milligrams per liter (mg/l) using water analyzer kit.

3.2 LABORATORY ANALYSIS

3.2.1 Bicarbonates

The bicarbonate content was determined following the potentiometric titration method (APHA, 1995). Bicarbonate standards ranging from 100-1000ppm was prepared from $NaHCO_3$. 50 ml of sample and a series of bicarbonate standards were titrated against 0.02 N HCL. The end point was noted at pH 4.5. A graph was plotted between bicarbonate standards and volume of acid consumed. The readings for samples were noted down from this graph.

3.2.2. Chloride

Chloride content was determined by 'Radelkis' chloride ion selective electrode, in combination with a double junction reference electrode (with inner junction 4M KCl and outer junction 1M KNO_3) (Coming 1981) and Consort P602 ion meter (Consort 1994). 25 ml of each sample and a series of chloride standards was mixed with equal volume of Ionic Strength Adjustment Buffer (ISAB). ISAB was prepared by dissolving 15.1g sodium bromate in 800 ml of distilled water and 75 ml concentrated HNO_3 was added and solution was stirred well before diluting to 1 liter by distilled water. The electrodes was conditioned and dipped into sample to note stable reading in mV. The instrument was calibrated with standard seawater after compensation for temperature had been done. The instrument directly recorded the concentration of chloride.

3.2.3. Flouride

Fluoride concentration was determined by 'Omega' fluoride ion selective electrode (Omega, 1993) in combination with a double junction reference electrode (with inner junction 4M KCl and outer junction 24 1M KNO_3) (Corning, 1981) and Consort

P602 ion meter (Consort, 1994). 25 ml of each sample and standard solution (0.1ppm –
10ppm, from NaF) was mixed with equal volume of Total Ionic Strength Adjustment
Buffer (TISAB) (prepared by mixing IM Sodium chloride, 0.25M Acetic acid, 0.75
Sodium acetate, and 0.001M Sodium citrate) (Corning, 1979). The instrument was
calibrated with standards, after compensation for temperature had been done. The
instrument directly recorded the concentration of fluoride.

3.2.4. Sulphate

The sulphate concentration was determined by turbidity method. Sulphate
standards of concentration ranging from 0.5 mg/l to 1.5 mg/l were prepared from Sodium
sulphate. 10 ml of each standard solution and samples were taken, and diluted to 100 ml
with distilled water. Then 20 ml of distilled samples and 5 ml of conditioning reagent
(mix 50 ml glycerol + 100 ml of 95% ethyl alcohol + 75 ml of NaCl) was added and
mixed well. The flask is constantly stirred with stirrer. Barium chloride is added while
stirring and turbidity developed was measured on spectrophotometer at 410 nm, after 5
min in both standards and sample. The standard curve by the absorbance values of
standard sulphate solution was plotted in the graph for specied ranges. Read the
concentration of sulphate in the sample is read from the calibration graph.

3.2.5. Phosphate

Phosphate was determined by the Ascorbic acid method (APHA, 1995)-
phosphate standards ranging from 0.01 – 0.5 ppm was prepared from KH_2PO_4. 40 ml of
each sample and standard solution was pipetted out in 50 ml volumetric flask and 5 ml of
molybdate antimony solution (prepared by dissolving 4.8g of ammonium molybdate and
0.1g potassium antimony tartrate in 400 ml 4N H_2SO_4 and making the total volume to
500 ml with the same acid) and 2 ml of ascorbic acid solution (2.0% w/v) was added and
mixed well. The mixture was diluted to 50 ml and optical density was measured at 880
nm using Cecil Spectrophotometer (model no. 954). A graph was plotted between
standard concentrations and optical density and sample concentration was recorded
directly from this graph.

3.2.6. Dissolved Silica

The dissolved silica content was determined by the molybdo silicate method (APHA, 1995). Silica standard was prepared, ranging from 5 to 20 ppm from natrium silicate (Na2SiO3). 20ml of each sample and standard was pipetted out in 50 ml volumetric flask and 10 ml of Ammonium molybdate solution (prepared by dissolving 2g ammonium molybdate in 10 ml of distilled water; 6 ml of concentrated HCl was added and final volume was raised to 100 ml by distilled water) and 15 ml of reducing reagent (preparing by mixing 100 ml metol sulphite solution, 60 ml 10% oxalic acid and 120 ml 25% sulphuric acid, and making the total volume 300 ml by adding distilled water) was added and mixed well. (Metol sulphite solution was prepared by dissolving 5g metol in 210 ml distilled water and 3o sodium sulphite was added and the volume was made upto 250 ml by adding distilled water). The samples was stirred properly, and kept for 3 hours to complete the reaction. The optical density was measured at 650 nm using Cecil Spectrophotometer-594. Graph between standard concentration and optical density was drawn and concentration of samples was recorded from it.

3.2.7. Cations

The cations in the sample were analysed using Metrohm Ion Chromatography with 709 IC Pump, 733 IC Seperator Centre and 732 IC Conductivity Detector. The column used was IC Cation Column Metrosep 1-2 (6.1010.000). The eluent used was 4 m mol/L tartaric acid, 1 m mol/L dipiclonic acid and conductivity approx. 700 mS/cm. The pH of the sample was maintained in the range of 2.5-3.5. The flow rate maintained during analysis was 1.0 ml/min.

CHAPTER 4

RESULTS
&
DISCUSSION

CHAPTER 4
RESULTS and DISCUSSION

4.1 BIOGEOCHEMISTRY:

Biogeochemistry is the study of biological controls on the chemistry of environment and geochemical regulations of ecological structure and function. Biogeochemistry is directly or indirectly influenced by various natural and anthropogenic activities. The uptake, storage and release of nutrients influence the natural water chemistry by the biological systems. In natural ecosystem, elements are taken up by the autotrophs from sources. These are repeated eating and being eaten by the higher tropic level biological systems and finally released into the system by the activity of the detrivores. In addition to this, natural processes can also mobilize the nutrients from the under ground stored reservoirs (parent rock) into the river system by weathering mechanism.

ION CHEMISTRY:

The chemical composition of the Achankovil river water for pre-monsoon, monsoon and post-monsoon are given in Table No: 4.1, 4.2 & 4.3. The Achankovil river water is neutral to mildly alkaline. The pH for pre-monsoon ranges between 6.92-7.4, 6.97-7.31 for monsoon 6.34-7.02 for post monsoon seasons. The pH for Pama and Manimala ranges from 6.87-7.56 and 6.91-7.62 respectively. The EC ranges between 43.5-53.5 µs/cm (pre-monsoon), 31-39.2 µs/cm (monsoon) and 31.1-41.3 µs/cm (post-monsoon). The EC values for Pamba and Manimala range between 25.3-45.1 and 27.7-52.1 respectively. In the up stream region, the river water is slightly acidic (pH 6.8) and has a lower EC (34.7 µs/cm) due to the influence of precipitation in the monsoon period. However, both pH and EC increase further down- stream of the river due to contributions from the weathering processes in the drainage basin and anthropogenic activities. EC is minimum during monsoon and post-monsoon and maximum in pre-monsoon. But there is no drastic change in EC may be due to the dominance of resistance rocks in the drainage basin. The influence of atmospheric precipitation on pH and EC is more pronounced in the river basin during monsoon and post-monsoon period. The increase in the ionic concentration in

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Table: 4.1: Water Chemistry of Achankovil River System - Premonsoon

Sample No.	pH	EC	ORP	DO	HCO$_3$	H$_4$SiO$_4$	NO$_3$	PO$_4$	SO$_4$	Cl	F	Na	K	Ca	Mg	TDS	TSM
AC 1	7.14	54	197	3.5	8.65	3.6	0.47	0.53	0.63	15.3	0.0456	2.49	0.35	2.93	0.98	35.97	0.011
AC 2	7.4	51	192	5.1	9.51	8.5	0.38	0.57	0.57	16.12	0.0487	3.34	0.11	3.59	1.75	44.48	0.063
AC 3	7.12	45.3	198	4.3	8.58	3.7	0.43	0.61	0.91	18.9	0.0469	3.38	0.13	3.78	1.78	42.25	0.02
AC 4	6.92	48.3	195	4.6	9.69	4.5	0.32	0.73	0.90	20.3	0.0425	2.98	0.103	3.18	1.53	44.27	0.054
AC 5	7.26	43.5	190	4.5	9.57	9.3	0.39	0.59	0.60	20.15	0.0478	3.02	0.104	3.34	1.72	48.84	0.094
AC 6	7.23	51.3	192	4.9	9.27	6	0.35	0.74	0.61	18.62	0.0421	2.71	0.098	3.17	1.46	43.08	0.057
AC 7	7.3	42.4	204	4.3	9.63	11.6	0.35	0.47	0.63	21.36	0.0436	4.4	0.509	3.1	1.47	53.56	0.044
AC 8	7.15	47.1	208	3.6	8.89	3.1	0.43	0.61	0.75	24.38	0.049	6.23	0.155	4.1	3.12	51.81	0.027
AC 9	7.01	50.3	198	4.6	8.98	9.1	0.41	0.41	0.56	21.39	0.0487	4.25	0.36	3.66	1.78	50.95	0.044
AC 10	7.2	48.3	194	5	9.26	2.5	0.35	0.76	0.55	23.68	0.0419	9.76	0.84	2.42	3.39	53.55	0.018
AC 11	7.25	53.5	218	4.4	8.83	2.9	0.47	0.41	0.61	24.52	0.0428	2.43	0.17	2.23	1.012	43.61	0.017
AC 12	7.12	48.4	195	4.9	8.23	3.6	0.43	0.37	0.62	23.5	0.0479	8.98	0.534	4.45	3.22	53.98	0.019
P 1	7.52	45.2	214	5.2	8.25	3.8	0.31	0.85	0.69	22.6	0.0432	1.47	0.62	1.3	0.525	40.47	0.016
P 2	7.09	33.7	208	4.8	8.45	4.1	0.50	0.46	0.56	23.5	0.0487	2.19	0.15	1.987	0.822	42.76	0.025
P 3	7.25	33.4	209	5.9	9.12	3.2	0.47	0.42	0.54	24.1	0.0429	3.14	0.098	2.55	1.317	45.00	0.023
M 1	7.05	45.1	215	5.1	9.62	3.5	0.25	0.37	0.49	21.6	0.0459	4.03	0.131	3.6	0.461	44.09	0.019
M 2	7.62	48.4	199	5.3	9.17	2.95	0.31	0.49	0.46	23.4	0.0483	5.28	0.208	2.23	0.861	45.39	0.022
M 3	7.15	52.1	218	5.9	9.03	3.6	0.49	0.40	0.66	23.5	0.0471	2.85	0.129	2.9	0.958	44.56	0.024

All are in mg/l except pH, ORP and EC (µ S/cm)

Table: 4.2 Water Chemistry of Achankovil River System - Monsoon

Sample No.	pH	EC	ORP	DO	HCO$_3$	H$_4$SiO$_4$	NO$_3$	PO$_4$	SO$_4$	Cl	F	Na	K	Ca	Mg	TDS	TSM
AC 1	7.25	34.7	198	8.7	16.35	6.6	0.27	0.66	0.754	22.1	0.0466	2.59	2.86	2.15	1.03	55.41	0.029
AC 2	7.14	36.6	187	8.7	15.29	5.2	0.28	0.61	0.73	18.3	0.0499	7.58	3.42	7.58	0.53	59.57	0.059
AC 3	6.97	34.9	196	8.9	16.91	7	0.43	0.57	0.658	15.2	0.0448	4.36	2.83	4.37	0.77	53.14	0.069
AC 4	7.29	34.5	183	8.6	15.86	4.8	0.32	0.61	0.569	22.4	0.0439	3.84	3.03	3.84	0.94	56.25	0.08
AC 5	7.31	38.7	195	8.5	14.98	5.5	0.39	0.61	0.61	21.3	0.0441	4.67	2.01	4.21	0.9	55.23	0.052
AC 6	6.98	31	187	8.6	16.38	4.4	0.35	0.63	0.553	25.6	0.044	3.93	2.37	3.94	0.84	59.04	0.088
AC 7	6.99	36.2	155	8.7	16.01	3.1	0.35	0.61	0.642	19.5	0.0445	2.95	2.02	3.91	0.26	49.40	0.028
AC 8	7.04	43.7	172	8.9	17.05	6	0.23	0.61	0.722	21.1	0.0446	2.19	2.39	1.19	0.84	52.37	0.032
AC 9	7.11	40.1	181	9.6	15.62	6	0.21	0.61	0.473	20.3	0.0454	1.35	2.53	1.32	0.77	49.23	0.024
AC 10	7.21	48.4	178	8.9	15.26	6.5	0.35	0.65	0.513	16.5	0.0435	1.26	1.03	1.2	0.55	43.85	0.024
AC 11	7.31	41.9	185	8.7	16.09	7.2	0.29	0.65	0.569	19.9	0.044	1.32	3.48	1.32	1.04	51.90	0.018
AC 12	7.13	39.2	189	8.6	16.29	8.2	0.28	0.65	0.788	19.6	0.0476	1.17	1.15	1.18	0.6	49.96	0.024
P 1	6.98	25.3	159	8.1	17.38	6.8	0.37	0.60	0.699	22.1	0.0436	1.37	1.2	1.38	0.69	52.63	0.015
P 2	7.56	33.7	178	7.9	16.59	7.4	0.45	0.52	0.622	21.6	0.044	1.05	1.3	1.05	0.79	51.42	0.021
P 3	7.26	34	164	8.6	16.64	8.2	0.31	0.62	0.899	22.6	0.0473	2.32	0.76	2.24	1.18	55.81	0.037
M 1	7.41	27.7	195	9.1	17.29	7.9	0.27	0.62	0.745	21.3	0.0479	5.52	0.89	4.53	0.52	59.63	0.032
M 2	7.15	30.2	184	8.4	16.83	7.5	0.32	0.66	0.847	24.1	0.0481	2.63	2.05	2.63	0.81	58.43	0.029
M 3	7.06	30.9	179	8.1	16.53	7.2	0.29	0.68	0.879	25.3	0.0474	1.07	1.17	1.01	0.79	54.97	0.036

All are in mg/l except pH, ORP and EC (μ S/cm)

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Table: 4.3: Water Chemistry of Achankovil River System - Postmonsoon

Sample No.	pH	EC	ORP	DO	HCO$_3$	H$_4$SiO$_4$	NO$_3$	PO$_4$	SO$_4$	Cl	F	Na	K	Ca	Mg	TDS	TSM
AC 1	7.02	40.2	207	8.7	15.14	8.7	0.2	0.56	0.70	25.0	0.0479	4.53	0.122	2.1	1.57	58.67	0.03
AC 2	6.92	34.5	204	8.5	14.58	9.5	0.19	0.62	0.67	30.0	0.048	2.58	0.114	2.3	1.04	61.64	0.14
AC 3	6.78	41.3	223	8.3	13.75	7.9	0.18	0.57	0.68	12.5	0.0481	2.37	1.256	2.3	1.72	43.28	0.13
AC 4	6.34	34.1	207	7.9	16.53	8.8	0.21	0.6	0.61	30.0	0.0466	2.73	0.99	2.69	1.18	64.38	0.1
AC 5	6.72	31.1	214	8.3	17.23	8.2	0.15	0.61	0.58	30.0	0.0475	2.53	1.121	2.13	1.9	64.50	0.09
AC 6	6.82	37.4	196	7.2	14.44	8.9	0.14	0.64	0.57	25.0	0.0477	3.25	1.037	2.31	1.76	58.09	0.1
AC 7	6.79	37.2	207	8.1	13.05	10.2	0.17	0.6	0.62	32.5	0.0476	2.46	0.971	1.98	1.67	64.26	0.09
AC 8	6.77	34	206	7.9	15.14	11.6	0.15	0.62	0.67	40.0	0.0473	2.74	0.184	3.07	1.06	75.28	0.09
AC 9	6.35	41.5	212	7.4	13.05	8.7	0.17	0.57	0.58	30.0	0.0472	5.03	0.211	3.44	1.31	63.11	0.11
AC 10	6.62	37	217	8.5	11.66	8.9	0.18	0.64	0.50	30.0	0.0482	2.66	0.96	2.67	0.99	59.20	0.09
AC 11	6.74	36.2	226	8.5	14.44	7.5	0.08	0.65	0.54	25.0	0.0476	5.43	0.21	3.39	2.83	60.11	0.12
AC 12	6.69	34.8	214	8.2	12.36	8.6	0.16	0.63	0.46	10.0	0.048	2.14	0.79	2.22	0.56	37.96	0.03
P 1	7.08	28	213	8.5	13.05	8.7	0.08	0.63	0.46	25.0	0.0476	1.86	0.72	1.69	0.77	53.01	0.03
P 2	6.96	24.9	211	7.8	17.23	8.4	0.05	0.62	0.48	32.5	0.0469	2.28	0.85	1.74	0.45	64.65	0.06
P 3	6.87	24	208	9.2	20.03	11.4	0.14	0.68	0.58	37.5	0.0473	2.87	0.81	1.93	0.76	76.74	0.08
M 1	6.91	36.4	216	7.6	17.93	9.8	0.18	0.62	0.54	27.5	0.0479	2.5	0.124	2.71	0.95	62.90	0.08
M 2	6.96	33.8	214	7.9	15.84	9.4	0.16	0.59	0.56	32.5	0.0481	2.51	0.121	1.11	0.35	63.19	0.01
M 3	7.02	33.7	241	8.2	14.44	9.7	0.15	0.62	0.52	32.5	0.0474	2.15	0.108	2.04	0.68	62.96	0.01

All are in mg/l except pH, ORP and EC (μ S/cm)

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premonsoon may be due to the partial evaporation effect during the low water level period aided by elevated temperature in the region.

Dissolved Oxygen in Achankovil water ranges between 3.9-4.9 ppm (pre-monsoon), 8.6-8.9 ppm (monsoon) and 7.2-8.9 ppm (post-monsoon). DO is very high in the monsoon and post-monsoon period. ORP trend also indicates the oxidation stock in the river and the abundance of DO in the water (table: 1, 2 and 3). High DO content in the river water is a result of rapid movement of surface water in the river system which enhances dissolution of oxygen in water (Dehadrai and Bhargava 1972).

The total suspended sediment load can be used to calculate the mechanical denudation rate for continents. Total suspended matter carried by the Achankovil water is ranges between 1.1-2 ppm(pre-monsoon), 1.8-8 ppm (monsoon) and 3-10 ppm (post-monsoon). TSM carried by Pamba and Manimala ranges between 0.016-0.03 and 0.01-0.036 ppm respectively. The TSM is very low here due to the dominance of resistant chornokites in the drainage basin. The relatively high amount of TSM value in Achankovil river basin in monsoon and post-monsoon period is may be due to heavy rainfall and large runoff.

Total Dissolved Solids (TDS) represents the total amount of solids (mg/l) which mainly derived from rock weathering and or by atmospheric inputs (Drever 1988, Leopold et al., 1964). In Achankovil river water TDS ranges between 35.97 ppm (pre-monsoon), 43.85-59.63 ppm (monsoon) and 43.85-59.63 ppn (post-monsoon). In Achankovil river watersystem the major anion contributor are in the this order $Cl>HCO_3>SO_4>NO_3$ and cation order are $Na>Ca>Mg>K$.

Almost all bicarbonate in river water is derived from the rock weathering. In Achankovil water, HCO_3 is major dissolved ion, its concentration ranges between 8.239.-9.69 ppm (pre-monsoon), 15.2-16.9 ppm (monsoon) and 11.6-17.2 ppm (post-monsoon). Bicarbonate in Pamba and Manimala ranges between 9.12-20.03 and 9.03-17.93 ppm respectively. High amount of HCO_3 in monsoon indicates the intense weathering processes take place in the drainage basin. The weathering derived HCO_3 comes from two sources, one is carbon from carbonate minerals and the other is from the result of reaction of CO_2 dissolved in water with carbonate and silicate minerals

(Rahmaysay 1986). The CO_2 is also derived almost entirely from rock weathering. Two weathering reactions are:

$$CO_2 + H_2O + CaCO_3 \longrightarrow Ca^{+2} + 2\,HCO_3^-$$

$$2CO2 + 11\,H_2O + 2\,NaAlSi_3O_8 \longrightarrow 2Na+ + 2\,HCO_3^- + Al_2Si_2O_5(OH)_4 + 4H_4SiO_4$$

As these reactions demonstrate, half of the bicarbonate resulting from carbonates weathering and a remaining from silicate weathering is derived from soil carbon dioxide. Reverse weathering demonstrates alkalinity (Von Damm & Edmong 1984), while the loss of sulfur (as sulfide) to either the sediments or atmosphere increases alkalinity (Kilhan & Cloke 1990).

Dissolved silica in river water comes from silicate weathering. Since, silicate minerals are plenty in the Achankovil river basin, derived silica is swamped by the ions from carbonate weathering here. Silica in Achankovil water ranges from 2.5-11.6 ppm (pre-monsoon), 3.1-8.2 ppm (monsoon) and 7.5-11.6 ppm (post-monsoon). Its concentration in Pamba and Manimala ranges between 3.2-8.2 ppm and 2.9-7.9 ppm respectively. The amount of dissolved silica is directly related to average temperature of the area (Meybeck 1980). Variations in the silica amount constant in the rocks here with higher average temperature in the area induced the higher silicate weathering from hard rocks. Hence, the amount of silica is higher than chloride and sulphate in the Achankovil river water which are of primarly atmospheric origin with minor contributions from the evaporite deposits found in the atmosphere and anthropogenic sources.

The majority of the world rivers have more than 50% HCO_3 and 10-30% Cl^- + SO_4 (Berner and Berner, 1996). Thus most large rivers are dominated by the sedimentary rock weathering and are mainly Ca^{2+} and HCO_3 waters derived from carbonate minerals.

Reeder & Stallard plotted the composition of Amazon waters on a ternary diagram with the three vertices represented by silicate rock weathering (Si), carbonate weathering (Cl+SO$_4$). He found that TDS increases from the Si vertex to the HCO_3 vertex and from HCO_3 vertex to Cl+SO$_4$ vertex. Figure: 4.1 for Achankovil river water shows that in pre-monsoon the ion concentration are falling more towards the bicarbonate vertex. In post-monsoon, the weathering rate values are falling closer to
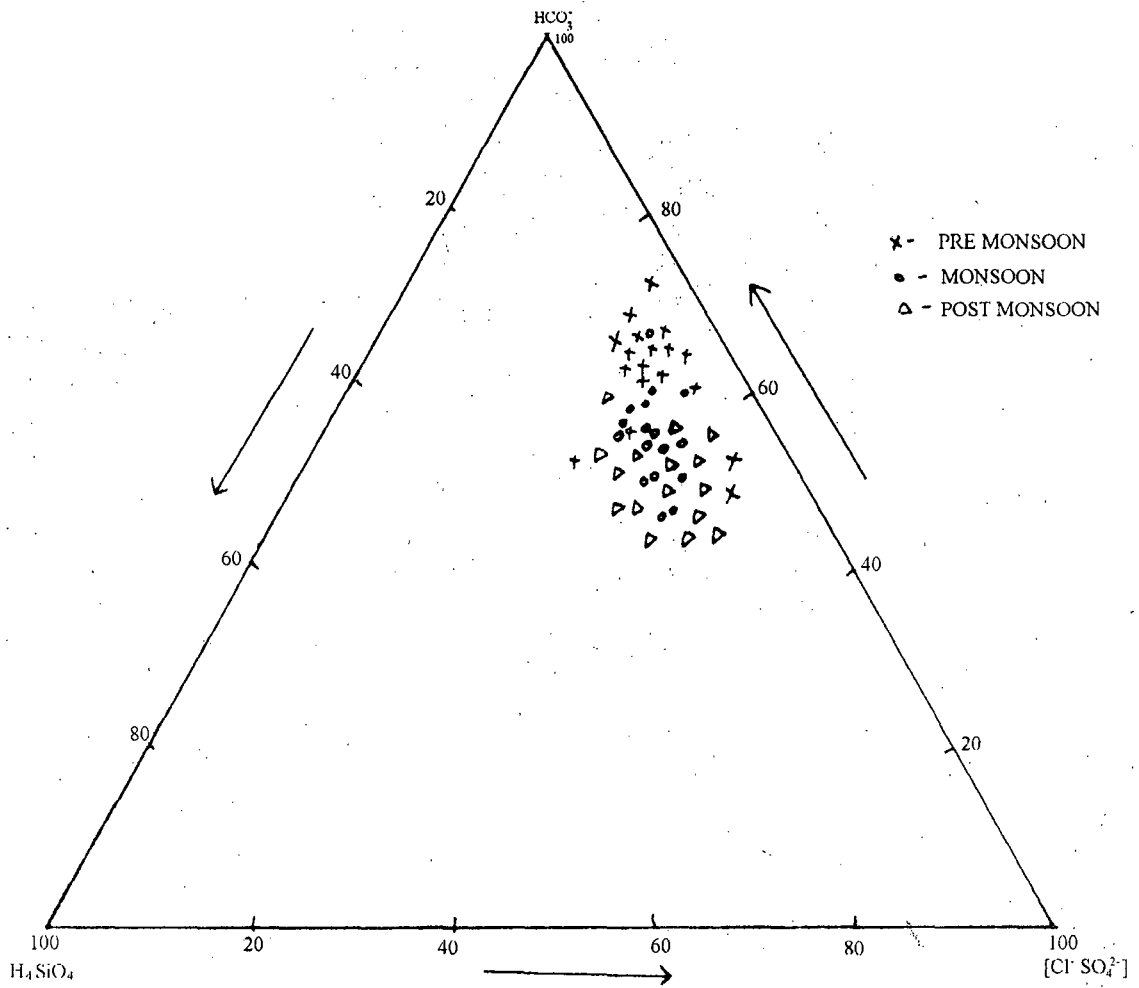
Figure 4.1: Triangular Plot showing the relative abundance of HCO_3, H_4SiO_4 and $(Cl+SO_4)$ in Achankovil river water system

HCO_3 vertex and in mouth with bicarbonate and $(Cl+SO_4)$. This suggests that pyroxene and feldspars in the rocks here are involved in the silicate weathering processes. In this figure the data cluster towards the alkalinity apex with secondary trend towards $(Cl+SO_4)$. This shows that drainage basin is experienced by the relatively high chemical weathering and atmospheric input. The amount of bicarbonate derived from the silicate and carbonate weathering of Achankovil River basin is given in table: 4.5.

There is a temporal variation in sulfate concentration, 0.55-0.9 ppm (pre-monsoon), 0.47-0.78 ppm (monsoon) and 0.45-0.69 ppm (post-monsoon). In Pamba and Manimala ranges between 0.48-0.89 ppm and 0.45-0.87 ppm respectively. This minor variation is indicates the low rock weathering rates in these three seasons. The rock weathering includes two major forms of sulphur in the sedimentary rocks: sulfite sulphur in pyrite and sulphate sulphur as gypsum and anhydride. The amount of sulfate from cyclic salt is very low (2%) in the coastal regions (Berner & Berner, 1992).

Chloride is extremely mobile and very soluble. In Achankovil river water, Cl concentration ranges between 15.3-24.5 ppm (pre-monsoon), 18.3-25.6 ppm (monsoon), and 10-40 ppm (post-monsoon). In Pamba and Manimala it ranges from 21.6-37.5 ppm and 21.3-32.5 ppm respectively. According to Fetch (1981), the maim sources of Cl in river water are (1). Sea salt (2). Dissolution during weathering of halite (NaCl) and (3) Pollution. The high amount of Cl in Achankovil river water is suggests that Cl has additional source from atmosphere and sea spray. Hence Cl is higher in monsoon as well. The F on the other hand is very low and it is ranges about 0.045 ppm. There is no variation from the up-stream to down-stream. Since there is no natural source of F here, so it is very less.

Sodium is a major component of seawater, it is a principal contributor to atmospheric cyclic salts, and therefore, should be prominent in river waters. This is one of the main reason for high amount of Na in river waters. In Achankovil river water, Na concentration ranges between 2.4-9.7 ppm (pre-monsoon), 1.17-4.6 ppm (monsoon) and 2.3-5.4 ppm (post-monsoon). In Pamba and Manimala its concentration ranges between 1.05-3.14 ppm and 1.07-5.28 ppm respectively. This is a major cation in this river system. A relatively high concentration of Na compared to

Table 4.5: Amount of Bicarbonate (HCO_3) derived from Silicate and Carbonate weathering

Sample No	$(HCO_3)_c$	$(HCO_3)_{Sl}$	$(HCO_3)_{tot}$
AC 1	0.14	0.01	0.15
AC 2	0.16	0.04	0.19
AC 3	0.14	0.06	0.20
AC 4	0.16	0.01	0.17
AC 5	0.16	0.02	0.17
AC 6	0.15	0.02	0.17
AC 7	0.16	0.07	0.22
AC 8	0.15	0.07	0.22
AC 9	0.15	0.25	0.40
AC 10	0.15	0.05	0.20
AC 11	0.14	0.27	0.42
AC 12	0.14	0.01	0.15
P 1	0.14	0.09	0.22
P 2	0.10	0.04	0.14
P 3	0.15	0.06	0.21
M 1	0.16	0.01	0.17
M 2	0.15	0.01	0.16
M 3	0.15	0.01	0.16

Ca, Mg, and K, is very characteristic of the peninsular Indian Rivers (Ramanathan et al 1994), since, granitic rocks chiefly cover the catchment areas of Indian rivers. The river basin of Achankovil is also dominated by Charnokite and sedimentary formation from varkali series, which contributes 'Na' mobility higher and hence keeps it ahead of other cations. Another possible source of Na in the river waters is from cation exchange of dissolved Ca^{+2} with Na^+ on detrial clay minerals during the weathering processes (Cerling et al., 1989).

Potassium in river water comes from the silicate weathering, particularly potassium feldspars and mica. The amount of K in the Achankovil river water is ranges between 0.11-0.53 ppm (pre-monsoon), 1-3.4 ppm (monsoon) and 0.11-1.2 ppm (post-monsoon). In Pamba and Manimala it ranges between 0.09-1.3 ppm and 0.12-2.05 ppm respectively.This shows that K is less dominant cation in river water chemistry. K is not completely dissolved and released ions as quickly as it is utilised by the biological systems. So that, potassium concentration is lower than remaining cations, Na, Mg and Ca. Holland (1978) estimated that on average only 50% of rock potassium released to solution during silicate weathering, it is a very biogenic element due to its utilization by grown vegetation.

Calcium and Magnesium are contributed to river almost entirely from rock weathering. However, their concentration is regulated by the precipitation of carbonate minerals which take place once saturation reaches with respect to the particular carbonate mineral is reached. In Achankovil River water Ca and Mg ranges between 1.3-4.5 ppm and 0.52-3.4 ppm (pre-monsoon), 1.18-3.94 ppm and 0.6-1.04 ppm (monsoon) and 1.69-3.44 ppm and 0.53-1.9 ppm (post-monsoon) respectively. Calcium and Magnisium in Pamba ranges between 1.05-2.55 ppm and 0.45-1.3 ppm and in Manimala 1.01-4.53 ppm and 0.35-0.95 ppm respectively.

The scatter for Total Cations vs (Ca+Mg) and (Na+K) and (Ca+Mg) vs Bicarbonate are used to study the weathering pattern and availability of ions in the river water system. The plot of (Ca+Mg) vs HCO_3 for Achankovil river water in figure: 4.2, 4.3, & 4.4 shows that most of the data fall below the equiline (1:1), although a few points approach this line. It suggests that an excess of alkalinity derived from silicate weathering other than from (Ca+Mg) carbonate weathering in monsoon and post-monsoon seasons. During pre-monsoon (Ca+Mg) an excess indicates additional source for the system. The excess of (Ca+Mg) over HCO_3 in some
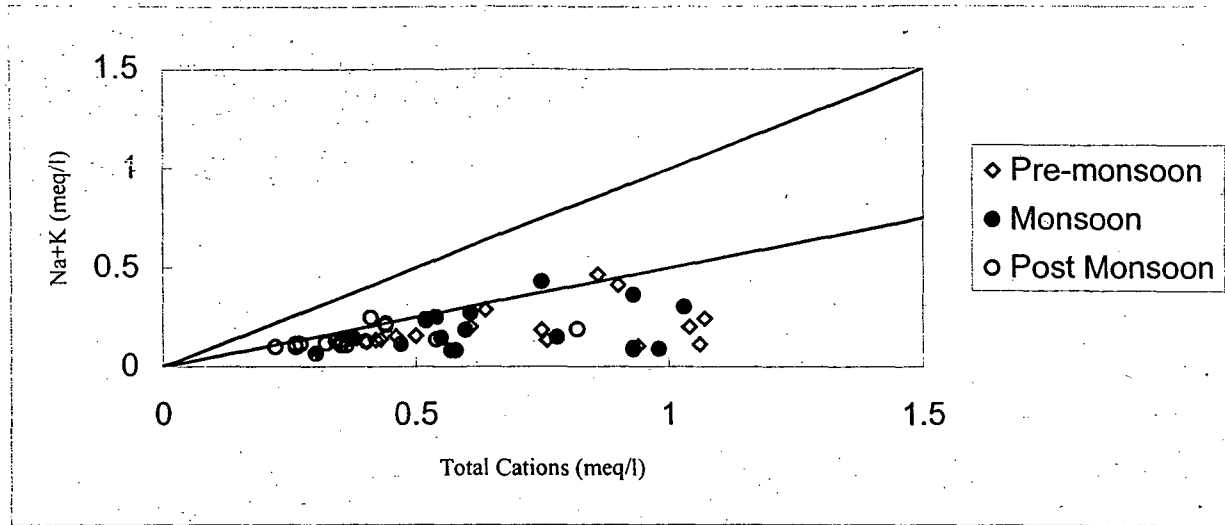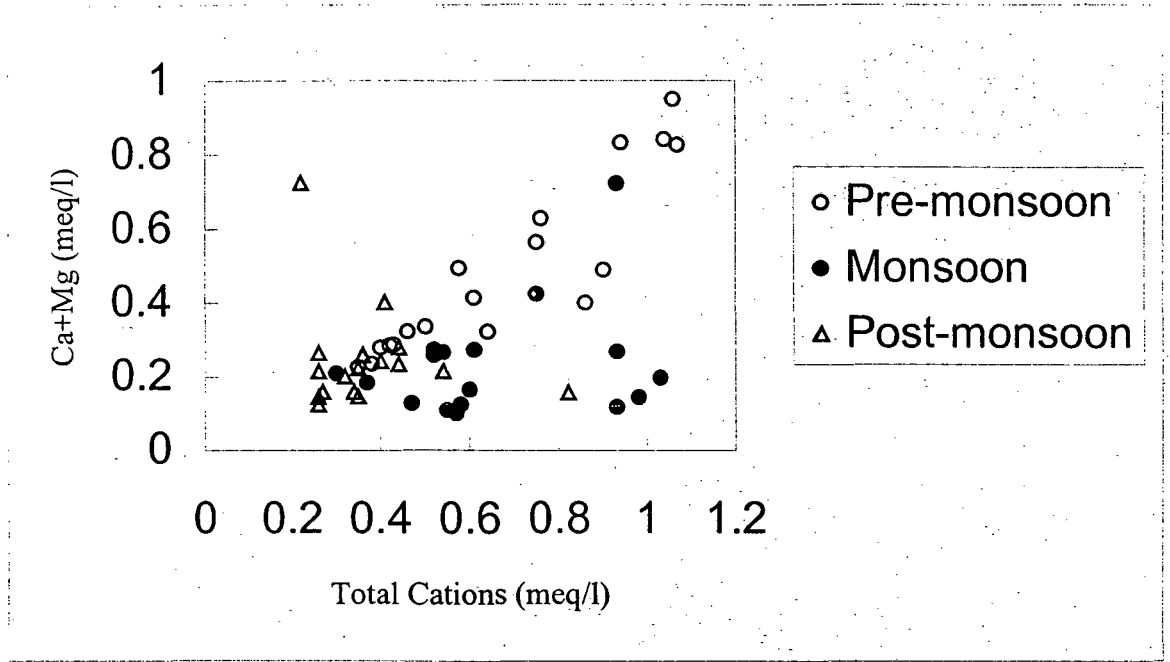
Figure 4.3: Total cations (meq/l) vs Na+K

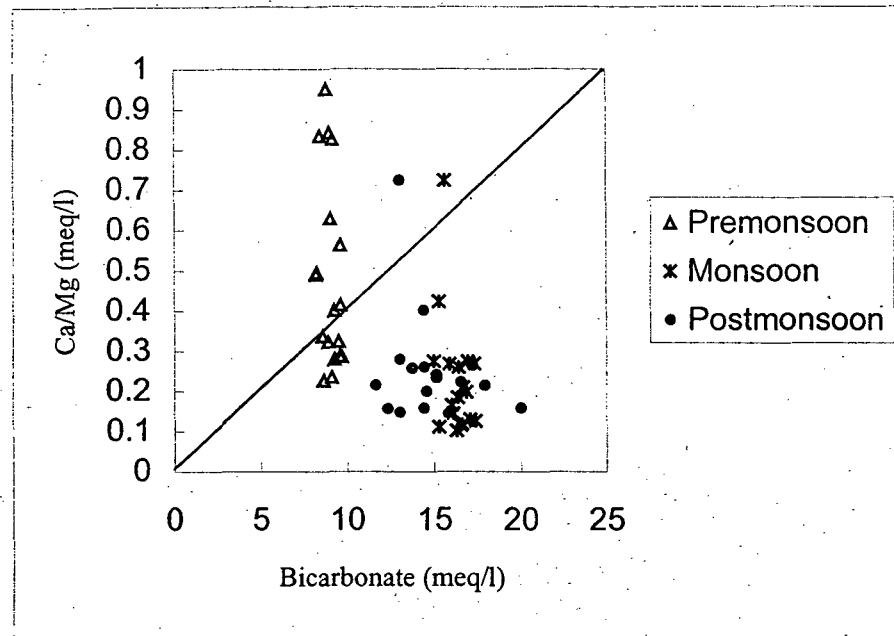Figure 4.3: Total cations (meq/l) vs Ca+Mg (meq/l)

Figure 4.4: Bicarbonate (meq/l) vs Ca+Mg (meq/l)

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samples reflects an extra source of Ca and Mg. It might have been balanced by Cl and SO_4 or supplied by silicate weathering (Zhange and others 1995). Further, Total cations vs (Ca+Mg) shows that the most data lie far below the theoreotical line (1:1) and 30% in the line (figure: 4.2), explains an increasing contribution of alkalies to the major cations ions. Significantly, the increase in alkalies corresponds to a simultaneous increase in Cl + SO_4 suggesting a common source for these ions (Datta and Tyagi 1996). The Achankovil river water have a lower ratio of (Na+K) vs Total Cations (figure: 4.3) depicting the contribution of cations via carbonate weathering, and some extent via silicate weathering (Sarin et al., 1989)

According to the classification of Gibbs (1970), the major natural mechanism controlling world surface water chemistry are (1). Anthropogenic precipitation (2). Rock weathering and (3). Evaporation and fractional crystallization. A boomerang shaped diagram will result when the ratio of two major cations, Na+Ca plotted as Na/(Na+Ca) vs TDS (figure: 4.5). This figure shows that all values are lie in the beginning of the rock dominance zone immediately after precipitation zone. This shows that precipitation weekly controls the weathering of the rocks. intermediate region where more than one mechanism controls the chemistry of the water. This shows that the availability of ions in the river water is mainly due to the weathering of the parent rock. The dissolution of various rock forming minerals in water is a primary factor controlling the chemistry of the water in Achankovil river basin. However, some samples fall outside this zone indicates an additional source to this ion. thus, Gibbs assumption that at low to moderate levels of TDS, Na is primarily supplied by the precipitation may not be valid, since they can be a significant weathering product of silicate rocks here.

The correlation analysis of Achankovil river water is given in table: 4.4. In this water system, there is good to excellent correlation is obtained between EC with other dissolved ions. The higher amount of bicarbonate in this river system shows good correlation with Ca and Mg. It indicates that both are having the same source to this river system.
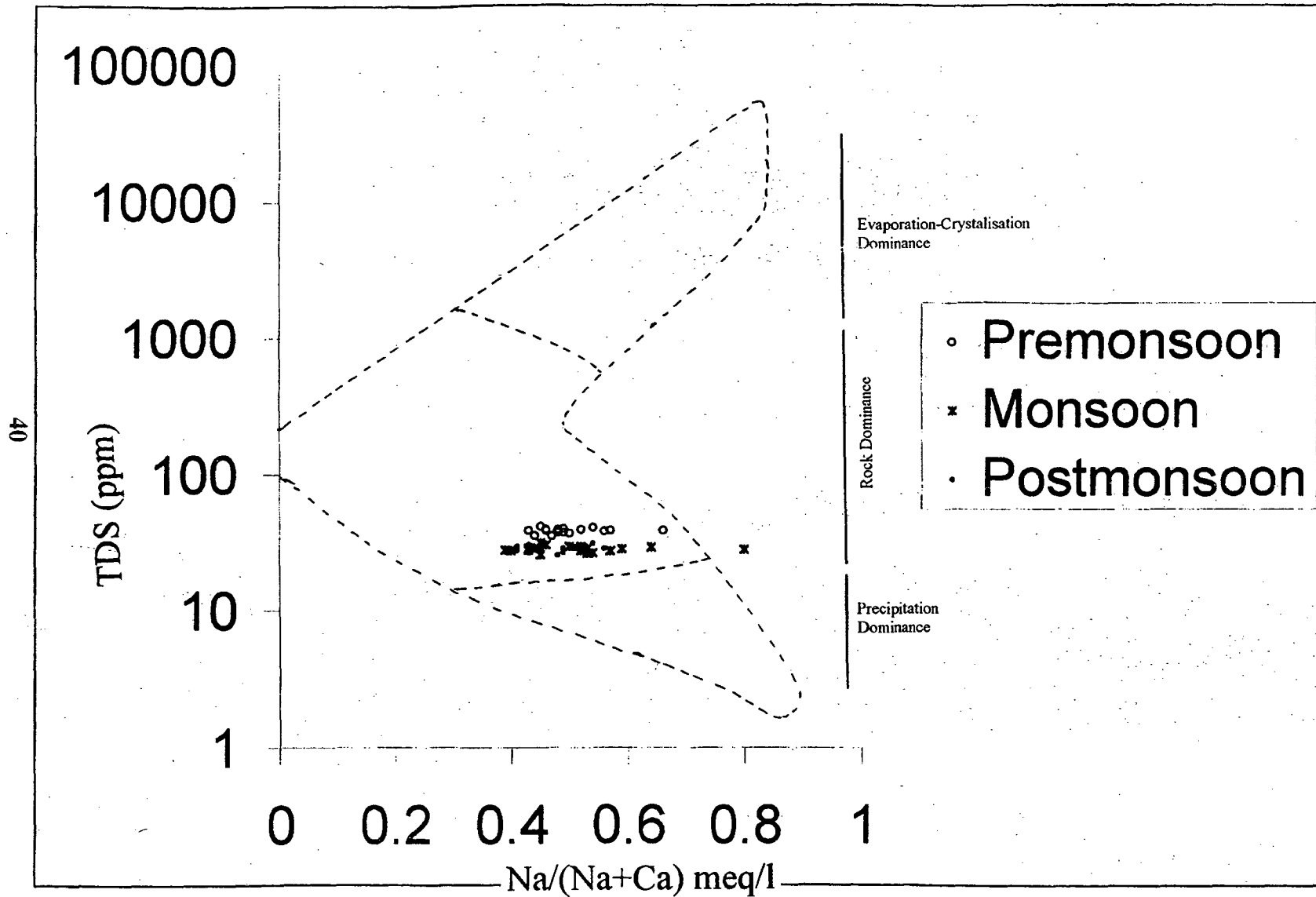
Figure 4.5: Variation of the weight ratio Na (Na+Ca) as a function of TDS in the Achankovil river water system

Table 4.4: Average Correlation Matrix for Achankovil River system (n=18)

	pH	EC	HCO$_3$	H$_4$SiO$_4$	NO$_3$	PO$_4$	SO$_4$	Cl	F	Na	K	Ca	Mg	TDS
pH	1.00													
EC	-0.41	1.00												
HCO3	0.18	0.65	1.00											
H4SiO4	0.03	0.20	0.14	1.00										
NO3	0.08	-0.09	-0.03	-0.10	1.00									
PO4	-0.08	0.09	-0.24	0.44	0.17	1.00								
SO4	0.07	0.05	0.23	-0.05	0.35	0.01	1.00							
Cl	-0.02	0.37	0.49	0.24	-0.27	0.01	-0.13	1.00						
F	0.18	0.16	0.27	0.62	0.26	-0.76	0.31	0.03	1.00					
Na	0.12	0.62	0.23	0.13	-0.23	0.00	-0.11	0.32	0.11	1.00				
K	0.40	0.50	0.42	-0.19	0.26	0.29	0.15	0.49	-0.34	0.22	1.00			
Ca	0.28	0.32	0.07	0.35	0.08	0.07	0.24	0.38	0.20	0.65	0.40	1.00		
Mg	0.41	0.68	0.43	0.13	0.24	0.20	0.02	0.27	-0.22	0.51	0.57	0.27	1.00	
TDS	0.12	0.23	0.59	0.50	0.30	0.09	0.02	0.84	0.22	0.11	0.31	0.14	-0.07	1

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WATER –MINERAL EQUILIBRIA

River water derives its composition from weathering of parent rock and suspended sediments. The released minerals are actively under go reaction with water and reach chemical equilibrium with certain mineral assembles, principally clay minerals, will coexist in the sediment phase provided the chemistry of water does not change. All these have been takes place at STP conditions. Garrel & Christ (1967), Berner (1971), Garrel and Meckenge (1971), Subramanian (1979), Ramanathan (1994) and several others have predicted the presence of theoretically calculated the mineral equilibrium for various aquatic systems across the globe.

CARBONATE SYSTEM

Carpenter (1962) has developed a diagram that shows metastable and stable equilibria among the calcium and magnesium carbonates (figure: 4.6). The early mineral assembles are those would be deduced from mineral assembles (dashed lines), these phases eventually equilibrate to give phase relations (solid lines). The phase diagram shows that river water is found to be equilibrium with the dolamite. Subramanian (1982) on Indian rivers, Ramesh (1989) on Krishna, Chakrapani (1990) on Mahanadi, Ramanathan (1992) on Cauvery has observed the same.

SILICATE SYSTEM

Achankovil water chemistry can be represented in phase diagram of K_2O-Na_2O-MgO-CaO-Al_2O_3-SiO_2-H_2O components. The composition of river water has been plotted in mineral stability diagram (figure: 4.7.a, 4.7.b, 4.7.c & 4.7.d.). The main observations are the water is equilibrium with Kaolinite/Albite in Na-aluminosilicate system, Kaolinite in K and Ca- Aluminosilicate system and Chlorite in Mg- Aluminosilicate system in presence of Dolomite.

NUTRIENTS

The two major nutrients in the river water that are nitrogen and phosphorus. These nutrients are highly reactive and essential for biological world. Once these nutrients are released into the system, the biological bodies readily assimilate these in the river system. So, these can be called as non-conservative nutrients.
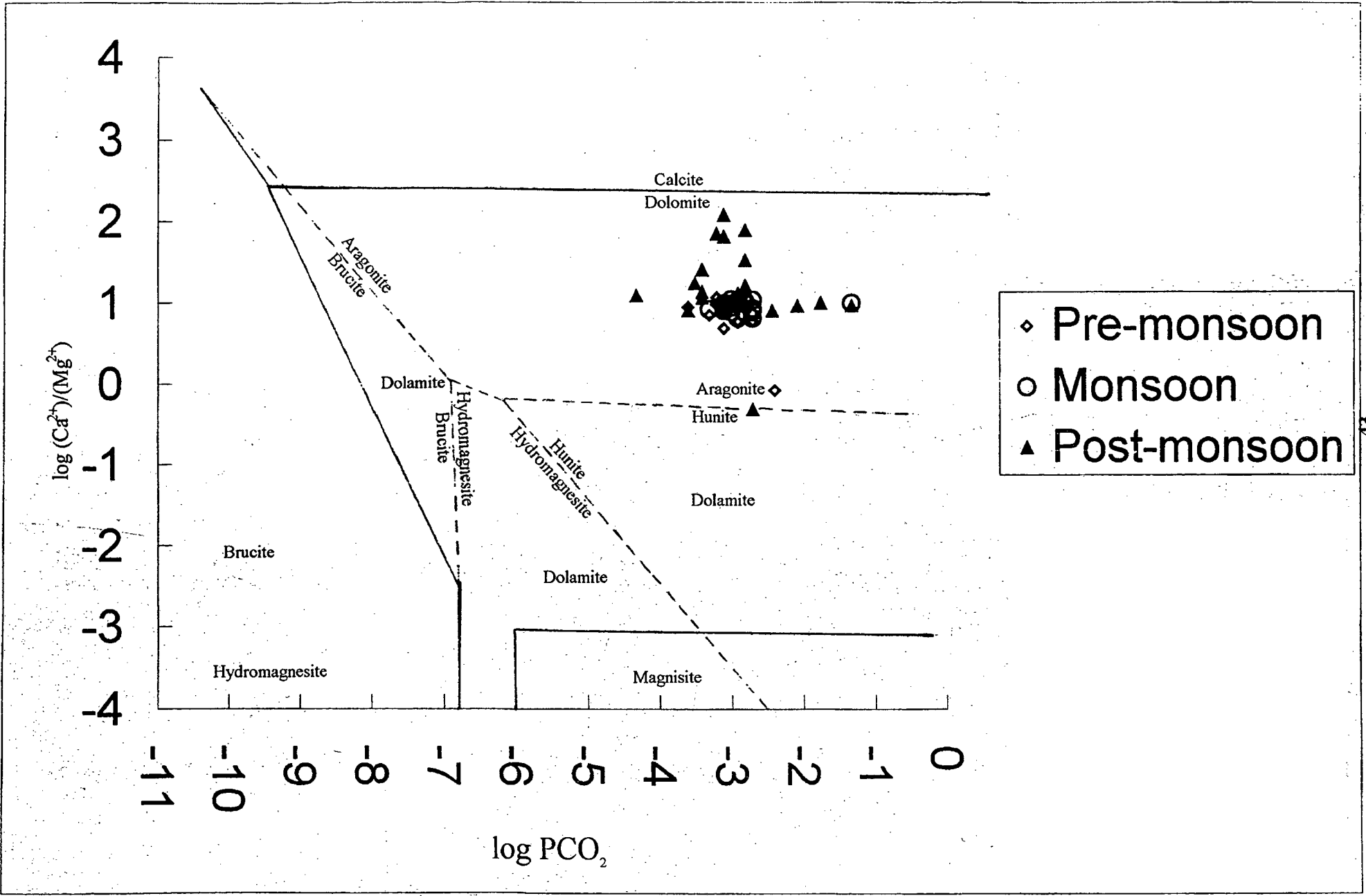
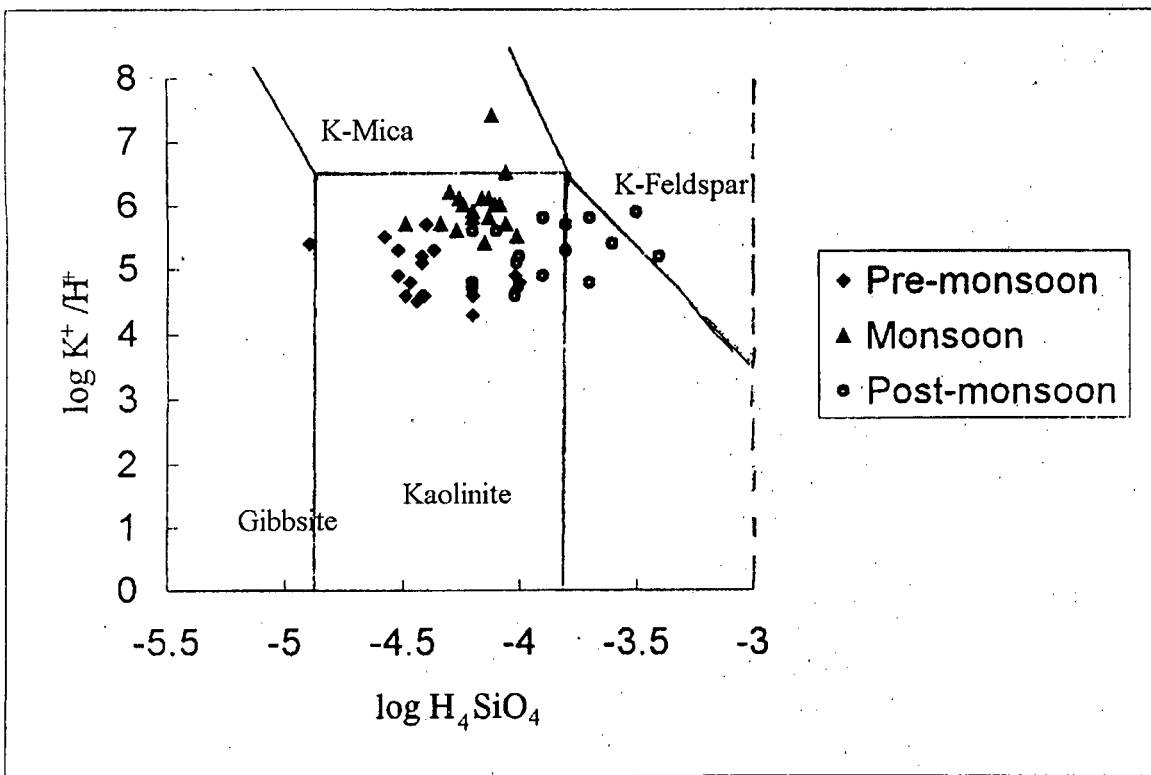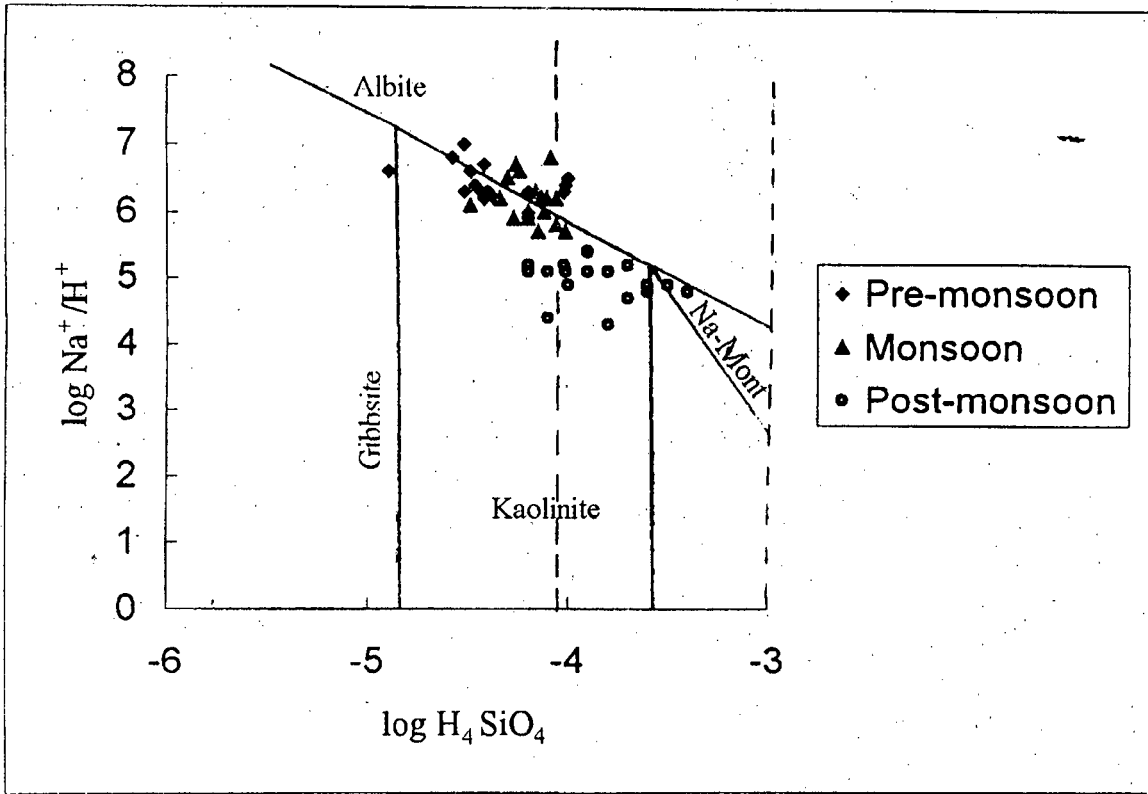**Figure 4.6:** Stability Diagram for Carbonate system

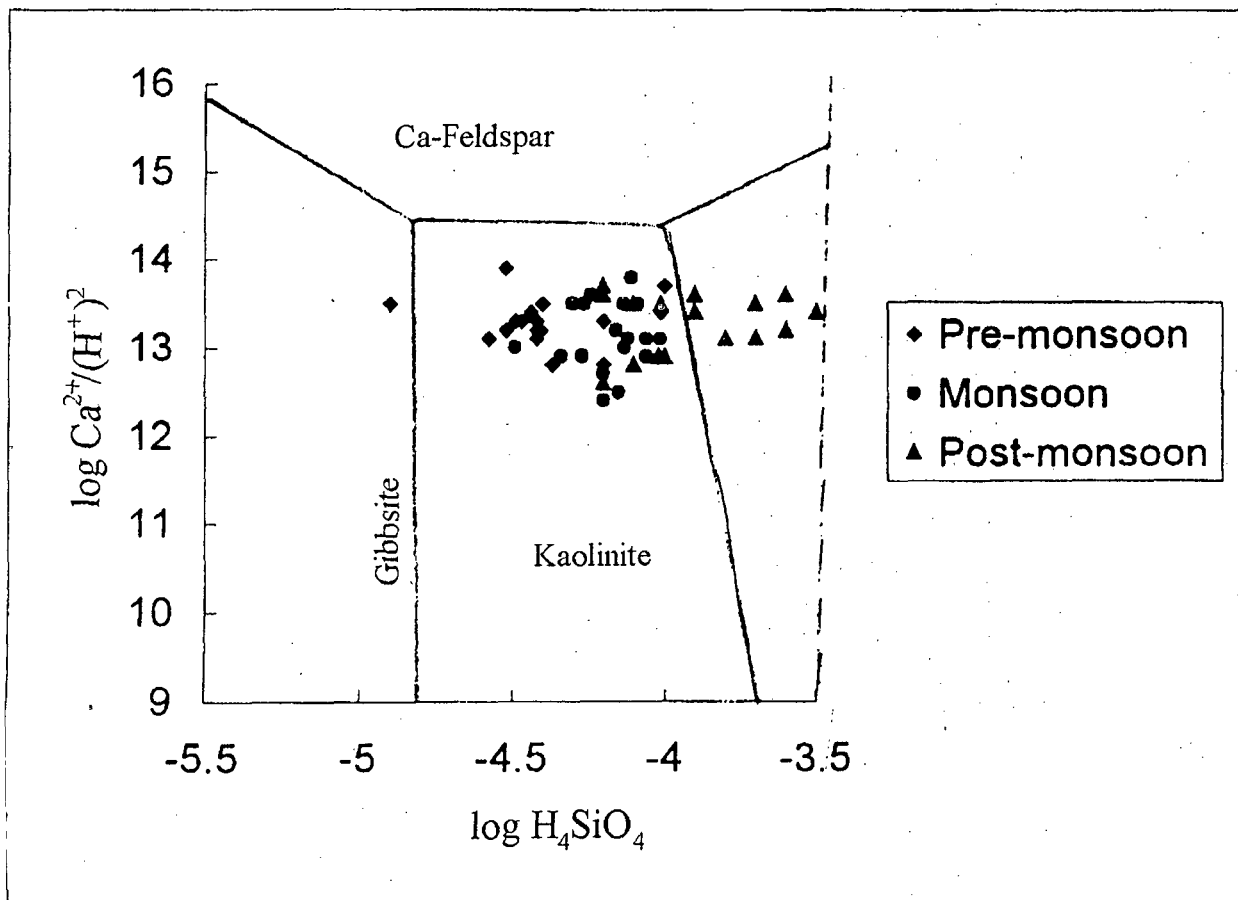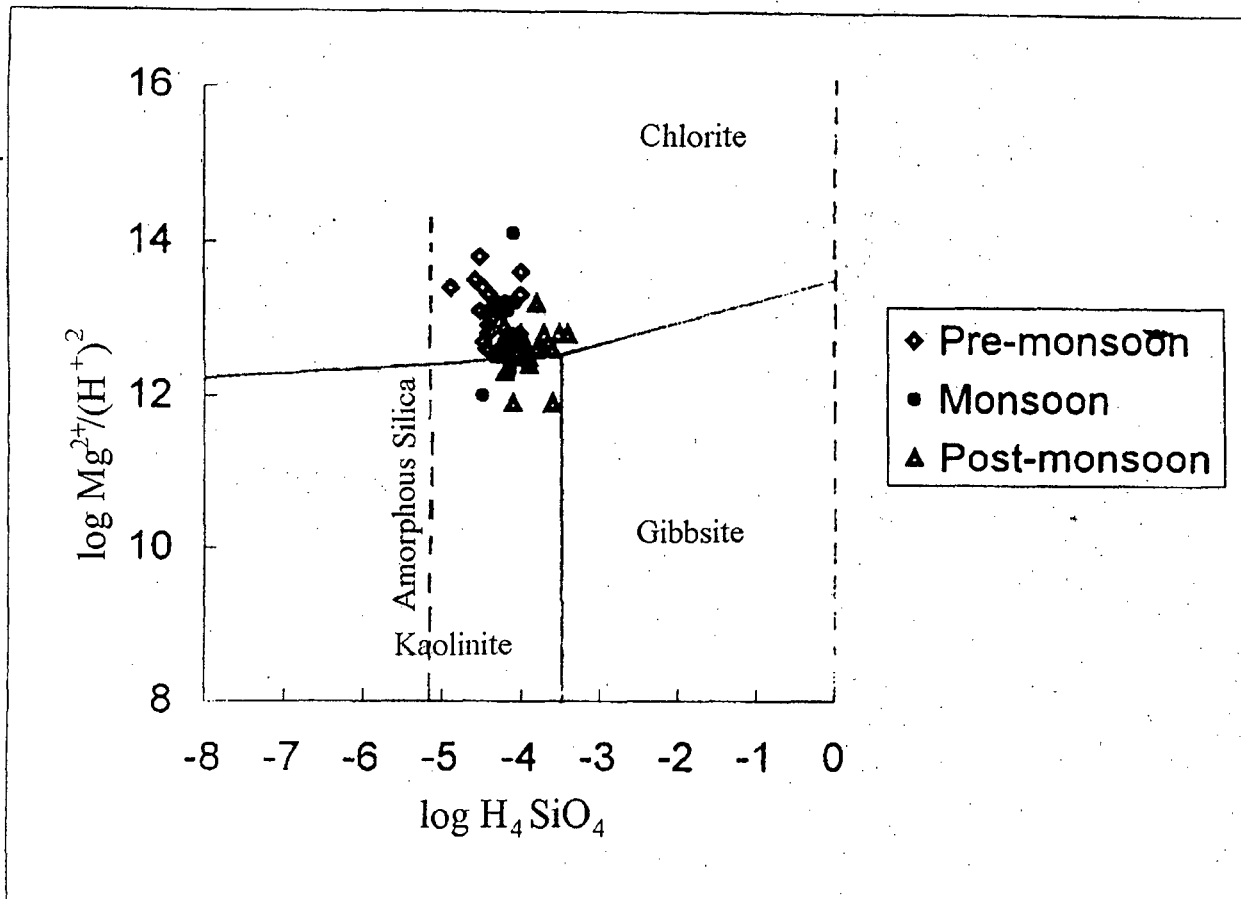**Figure 4.7 a and 4.7 b:** Silicate Stability Diagrams

Figure 4.7 c and 4.7 d: Silicate Stability Diagrams

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The origin of nitrate in the river water is considerably more complex than most other elements because nitrogen exists in many forms (Gaillardet et al 1995). In Achankovil river water nitrate concentration ranges between 0.23-0.4 ppm (pre-monsoon), 0.21-0.43 ppm (monsoon) and 0.08-0.21 ppm (post-monsoon). In pamba and Manimala nitrate ranges between 0.05-0.49 ppm and 0.15-0.49 ppm respectively. The variation in the nitrate concentration is mainly due to river runoff and dilution. In the study period, in monsoon and post-monsoon, nitrate showing negative correlation with DO. This indicates that biological systems are very active in uptake of the nutrients for its cellular growth i.e. biological nitrogen fixation taking place at the expense of dissolved oxygen. The decrease is the trend of in nitrate concentration from upstream to down stream is observed. Taking into accounts that sedimentation and biological up takes of nitrate in the Achankovil river system may be dominant from upstream to down stream. Generally intensive farming applications in the catchment area of the river increases nitrate concentration. Chemical fertilizers containing Na+K are widely used in the cultivation, which may contribute nitrate and potassium in the river (Zhange et al 1995).

Phosphate concentration varies between 0.36-0.75 ppm (pre-monsoon), 0.6-0.66 ppm (monsoon) and 0.57-0.65 ppm (post-monsoon). Phosphate concentration in Pamba and Manimala ranges between 0.52-0.85 ppm and 0.36-0.67 ppm respectively. Slight variations were found in monsoon and non-monsoon periods. This is due to weathering processes induced by SW and NE monsoons and this period coincides with crop cultivation time and agricultural runoff is rich in agricultural waste and higher turbidity. The turbidity restricts most of the dissolved phosphate remains un-consumed which is responsible for high concentration of dissolved phoaphate in the river water (Berner and Berner 1996).

Dissolved phosphate shown good correlation with major dissolved ions (table: 4.4), which suggest that inorganic source of phosphate in river water. Domination of inorganic process in regulation of phosphate levels in turbid rivers is well-documented (Lebo 1991, Fox 1993). The major aquatic supply of phosphate is the weathering of the parent rock (Fox 1993). Thus limit of weathering saturation plays in restricting phosphate in river water (Schuiling et al 1988, Vaithianantham et al 1998, Subramanian 1980, 1984).

4.2 BIOGEOCHEMICAL MODELING

A model is any simplified description or abstraction of a process. In science, models are tools that help us conceptualize, integrate, and generalize knowledge. Natural systems such as ecosystems are usually very complex, and models vary greatly in the degree of simplification away from that complexity. "Budget models" are simple mass balance calculations of specific variables (such as water, salt, sediment, CNP, etc.,) within defined geographic areas and over defined periods. Usually budget models are built to aggregate the many small individual pieces of a system into smaller sets of pieces, which are similar to one another. Thus, all plant species in an ecosystem might be aggregated into "primary producers." Some grouping will occur for almost any model. As one applies a single model across a range of systems, the value of such groupings becomes readily apparent. For some purposes it may be adequate to group all organisms within an ecosystem into the "net biogeochemical reactions" which occur within the system.

One can proceed from these simple, highly aggregated, models to more complicated models which describe specific processes (e.g., primary production as a function of light; sediment transport as a function of river flow, etc.). Many such process models may be further combined into an integrated system model. However, in general, the more complex the model structure, the less statistically robust is the statistical output.

SCALING OF A SYSTEM

One of the important considerations in picking a system to budget is the issue of scale: What are the spatial boundaries of the system to be budgeted. There is some interesting trade off here. The reason to develop these materials is to calculate fluxes of carbon, nitrogen, and phosphorus (CNP) which do not simply follow the flow of water through the system. These fluxes are said to be "non-conservative" with respect to the water and salt balances. In general, large systems are more likely to show non-conservative fluxes of CNP than are small systems. However, the larger the system, the less the ability to resolve what components of the system account for these non-conservative changes. Thus, it is fairly easy to obtain a budget for non-conservative CNP fluxes for the whole ocean. As long as we assume that the masses of CNP in system water are not changing, all of those materials added to the system

must either be transferred to the sediments or transferred to the atmosphere. However, this scale of analysis does not tell us where, within the entire system, the reactions occur to remove these materials from the water. For smaller systems such as individual bays and estuaries, there are likely to be hydrographic fluxes, which add and remove materials. These hydrographic fluxes complicate the calculation of non-conservative fluxes. Whatever non-conservative fluxes are calculated to occur, however, can be attributed to processes within those bays and estuaries. As the scale gets smaller—perhaps individual system areas within the bay—hydrographic fluxes are likely to become so dominant that non-conservative fluxes cannot be calculated.

We find it useful to approach the issue of scale from two points of view: The first and simplest point of view is that it "makes sense" to work with physiographically defined units. Whole estuaries are examples of such units; sometimes there are obvious breaks such as individual basins within an estuary. Relatively enclosed bays may be physiographically obvious units to budget; bays, which are little more than slight coastal indentations may not be. Individual shelf seas are physiographically relatively easily defined and should be amenable to budgeting; stretches of open shelf may be more challenging. In general, it makes sense to budget a whole system first, and then consider the possibility of budgeting smaller portions of the system.

The second point of view for approaching budgets is that if water exchange is to be estimated by a salt and water balances there must be a difference in salinity between the system and the next system water with which the system changes. Such a salinity difference is fundamental to using the salt and water budget. Alternative methods of estimating nonconservative material fluxes include measurement of water composition of an isolated water mass over time (for example, in some sort of incubation chamber); following a water mass through time with dyes, again, measuring water composition changes; either direct physical observations or numerical models of water flow to calculate water residence time. These methods are discussed in Gorden et al (1996) and elsewhere. The boundaries considered for Achankovil river system for biogeochemical modeling are given in table 4.6.

Table 4.6: Details of the model set up for the Achankovil river system

Box No.	Boundaries	Depth (mts)	Area (10^6 m^2)	Volume (10^6 m^2)
AC 1	Between 120 km and 72 km from the mouth	6.5	5.45	29.7
AC 2	Between 72 km and 42 km from the mouth	7	5.09	35.63
AC 3	Between 0 km and 42 km from the mouth	8.5	6.3	53.55
Pamba	Between 17 km and 75 km from the mouth	6.2	7.2	57.89
Manimala	Between 15 km and 80 km from the mouth	6.8	6.5	63.21

DEFINITIONS OF KEY TERMS IN BUDGETING CALCULATIONS

In the steady-state case, the difference between in-puts and out-puts is zero and the hydrographic fluxes as described above. For the non-steady state case, see (Gordon et al., 1996). The notation DY is used for the non-conservative flux, where Y represents any material of interest. Within the context of most LOICZ calculations, the Y's most frequently examined are dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN). If available, dissolved organic P and N (DOP, DON) are also examined.

While ignoring the salinity of water sources other than as specified above is unlikely to cause significant errors in the water and salt budgets, this is not true for the nutrient budgets. Failure to account for significant fluxes of nutrients via runoff, waste load, etc. is likely to introduce spurious results for the non-conservative fluxes. Large (positive or negative) nonconservative fluxes that fall outside the rules of thumb given on the modeling web page (http://data.ecology.su.se/MNODE/Methods/rot/thumb.htm) may arise from failing to account for all significant fluxes.

The initial units follow from the hydrographic fluxes and are therefore most conveniently reported as moles/time. Because the data are used for comparisons among systems, it is usually useful to divide the initial units by system area, yielding mol length $^{-2}$ time^{-1}. Various budget flux variables are given in the table 4.7.

Table: 4.7

Variable	Definition (units)	Comments
V_Q	Runoff flow volume (length^3 time^{-1})	Sum of gauged or estimated stream flow into budgeted portion of system. Always a positive or 0 value; usually the dominant source of fresh water. Usually can be ignored in salt budget. May or may not be important in the material budgets, but should be considered.
V_G	Groundwater flow volume (length^3 time^{-1})	Sum of measured or estimated groundwater flow into budgeted portion of system. Always a positive or 0 value; usually a secondary source of fresh water and usually can be ignored in the water budget; may be important in the other material budgets.
V_O	Other flow volume (length^3 time^{-1})	Sum of other water discharges (particularly waste discharge) into budgeted portion of system. Always a positive or 0 value; usually a secondary source of fresh water and usually can be ignored in the water and salt budgets. If there is any inflow of V_O, it should not be ignored in the other material budgets.
V_P	Precipitation volume (length^3 time^{-1})	Obtained as precipitation (length time^{-1}) multiplied by surface area of system (length^2). Always a positive or 0 value. Can often be ignored in budgets, for both water and other materials.
V_E	Evaporation volume (length^3 time^{-1})	Obtained as evaporation (length time^{-1}) multiplied by surface area of system (length^2). Always a negative or 0 value. Can often be ignored in budgets, for both water and other materials.
V_{Q^*}	Net freshwater inflow volume (length^3 time^{-1})	An often useful generic term that includes the sum of V_Q, V_G, V_O, V_P, V_E. Will be positive, 0, or negative (in the case where V_E numerically dominates over the other terms).
V_R	Residual flow volume (length^3 time^{-1})	In single-box systems, this has a value that is equal in value and negative in sign to V_Q^*. In multiple-box systems, it is important to keep track of the sign of V_R; flow **from** one box will be negative and represent positive flow **to** the next box.

V_x	Horizontal exchange volume (length^3 time^{-1})	In single-layer systems, this represents horizontal mixing between the budgeted system or box and the adjacent ocean, or between two adjacent boxes. V_x is always 0 or positive; any calculation generating a negative value contains some underlying error that must be addressed (e.g., bad algebra, violation of steady-state assumption, incorrect numerical values for salinity or other conservative tracer, incorrect values for contributors to V_{Q*}).
V_s	Surface flow volume (length^3 time^{-1})	In two-layer systems assumed to have "estuarine circulation," this is the outflow from the surface layer to the ocean or adjacent box. It is the sum of V_R and V_d (defined below) in a two-layer, single-box system. It will have a negative or 0 value.
V_d	Deep flow volume (length^3 time^{-1})	In two-layer systems assumed to have "estuarine circulation," this is the inflow from the ocean or adjacent box to the box of interest. It is the difference between V_d and V_R in a two-box, single-layer system. It will have a positive or 0 value. In effect, V_d in a two-layer system is equivalent to V_x in a single layer system.
V_{ent}	Vertical entrainment flow volume (length^3 time^{-1})	In two-layer systems assumed to have "estuarine circulation," this is the flow of water from the deep to the surface layer. It is equal to V_d in a two-box, single-layer system. It is negative with respect to the deep layer and positive with respect to the surface layer.
V_z	Vertical exchange volume (length^3 time^{-1})	In two-layer systems, this represents vertical mixing between the surface and deep boxes. Like V_x, V_z is always 0 or positive; any calculation generating a negative value contains some underlying error that must be addressed.
T	Exchange time (time)	System volume divided by the sum of V_x plus the absolute value of V_R (in a single layer, single box system); or system volume divided by the absolute value of V_s in a single-box, two-layer system. For exact derivations in multiple-box systems, see Gordon et al (1996).
$t_{hydraul}$	Hydraulic residence time or fill time (time)	System volume divided by the absolute value of V_Q*

Biogeochemical modeling of water systems calls for determination of the water budget as a useful element. This includes the river inflows, ground water seepage, amount of fresh water, actual concentration of nutrients in spatially and temporally, precipitation and evapo-transpiration. In order to establish budgetary calculations, data for all dissolved nutrients, N and P for Feb 2002(Premonsoon) June-July 2002 (monsoon) and Oct 2002 (post-monsoon) along with water discharge during these periods are calculated.

Cabaret (**C**omputer **A**ssisted **B**udget **A**nalysis for **R**esearch, **E**ducation, and **T**raining) is a stand-alone program for computer platforms running MS-Windows developed to assist the user to create nutrient budgets for aquatic ecosystems. The interactive program leads the user through a series of screens in which characteristics of the system are entered. First, the analyst may specify the geographic location, general description, and the number of seasons appropriate to understand the system behavior. Number of 'seasons' may vary from 1 to 12 (e.g. if monthly data are available). Next, geometry and topology of the coastal ecosystem are specified. For example, spatially extended systems in series with multiple layers may be specified. After the number of 'boxes' and seasons are selected, the user is prompted for the information needed to characterize water flows, salinity and nutrient fluxes following the standard LOICZ methodology.

The multi-box, single –layer model used (Craig et al 2002 and Gullaya et al 2000) for the estimation of the net fluxes of N and P. Evaporation and precipitation data were collected from IMD and discharge were calculated in the field. Remaining related data was collected from local sources in the study area. Table No: 4.8 gives the amount of Dissolved Inorganic Phosphate (DIP) and Dissolved Inorganic Nitrate (DIN) for three study seasons for budgeting modeling the Achankovil river system.

Figure: 4.8 & 4.9 illustrates the dissolved inorganic N and P for the Achankovil river system for pre-monsoon. Overall the input from the other minor rivers (Manimala and Pamba) are very small in comparison to the main river especially in the premonsoon period. The DIN supply the other river seems to be very significant in comparison to the DIP. The input by this river to lake and ultimately to the coastal regions is dominated by DIN. DIP constitutes 50% of the DIN load. The DIP and DIN are only added to the system and are not removed from the system. In this period the residual flow ($V_R DIP_R$) of DIP (4784.9×10^6 mol/yr) is very low than

Table 4.8: DIN and DIP concentrations used in the budget for Achankovil River.

Box No.	Pre-monsoon		Monsoon		Post-monsoon	
	DIN m mol m^{-3}	DIP m mol m^{-3}	DIN m mol m^{-3}	DIP m mol m^{-3}	DIN m mol m^{-3}	DIP m mol m^{-3}
AC 1	32.14	18.38	23.37	19.8	13.57	18.81
AC 2	48.3	20.4	26.26	20.29	11.96	19.75
AC 3	38.7	19.13	18.76	20.22	10.92	20
PAMBA	19.07	24.58	20.35	20.29	8.35	20.32
MANIMALA	20.7	18.58	25.23	20.77	11.66	20.64

the monsoon period (41773.9 X 10^6 mol/yr). This may be due to release of release of phosphate in the monsoon period by the weathering of the parent rock. In case of DIN it is lower that, it may be due to the low biological activity in the river system in the monsoon period, due to lower temperature conditions. Horizontal exchange volume is high, this may be due to the flush out of the nitrate from the AC 3 to the next system (Vembanad Lake).

Where as in monsoon (June-July 02) the input of DIP and DIN from the minor rivers (Manimala and Pamba) are considerably important for DIP and DIN modeling studies.The residual flow volume of DIN from Manimala and Pamba to the main symtem (AC 3) is about 91900.64 X 10^6 mol/yr.The horizontal exchange volume between Pamba box and AC 3 is 47626.7 X 10^6 mol/yr. The horizontal exchange volume between the box AC 3 and the recipient box i.e. the Vembanad Lake is around 31468.47 X 10^6 mol/yr. The runoff flow to the AC 1 box system is 16.23 X 10^6 mol/yr. This value is high in monsoon period. The DIP supply these rivers to the box AC 3 is 96554.4 X 10^6 mol/yr. The horizontal mixing volume of DIP between the Pamba box and AC 3 is 14976.9 X 10^6 mol/yr. This value is high among three seasons, this may be due to the high erosion of the phosphate rock in the monsoon period by higher discharge of the water. The residual flow volume between the AC 3 and the lake is 13725.4 X 10^6 mol/yr (Fig: 4.10 & 4.11).

In post monsoon period the situation somewhat interesting (fig: 4.12 and 4.13). In DIN budget model the runoff flow volume is 4.74 X 10^6 mol/yr. The horizontal exchange volume between the river system and the lake is 4348.7 X 10^6 mol/yr. This lower amount may be due to the sedimentation of DIN with in the system. And the post-monsoon period is also a rainy season influenced by NE monsoons. So, somewhat monsoon conditions would correlate with the post-monsoon flux values. The same trend is also observed in case of residual flow volume. Pamba and Manimala contributing high amount of DIN to the Achnkovil river system. In DIP budget the residual flow volume is higher than the horizontal exchange volume, this may be due to the activity of biological systems. The contribution of DIP by Pamba and Manimala is also found to be considerably important.
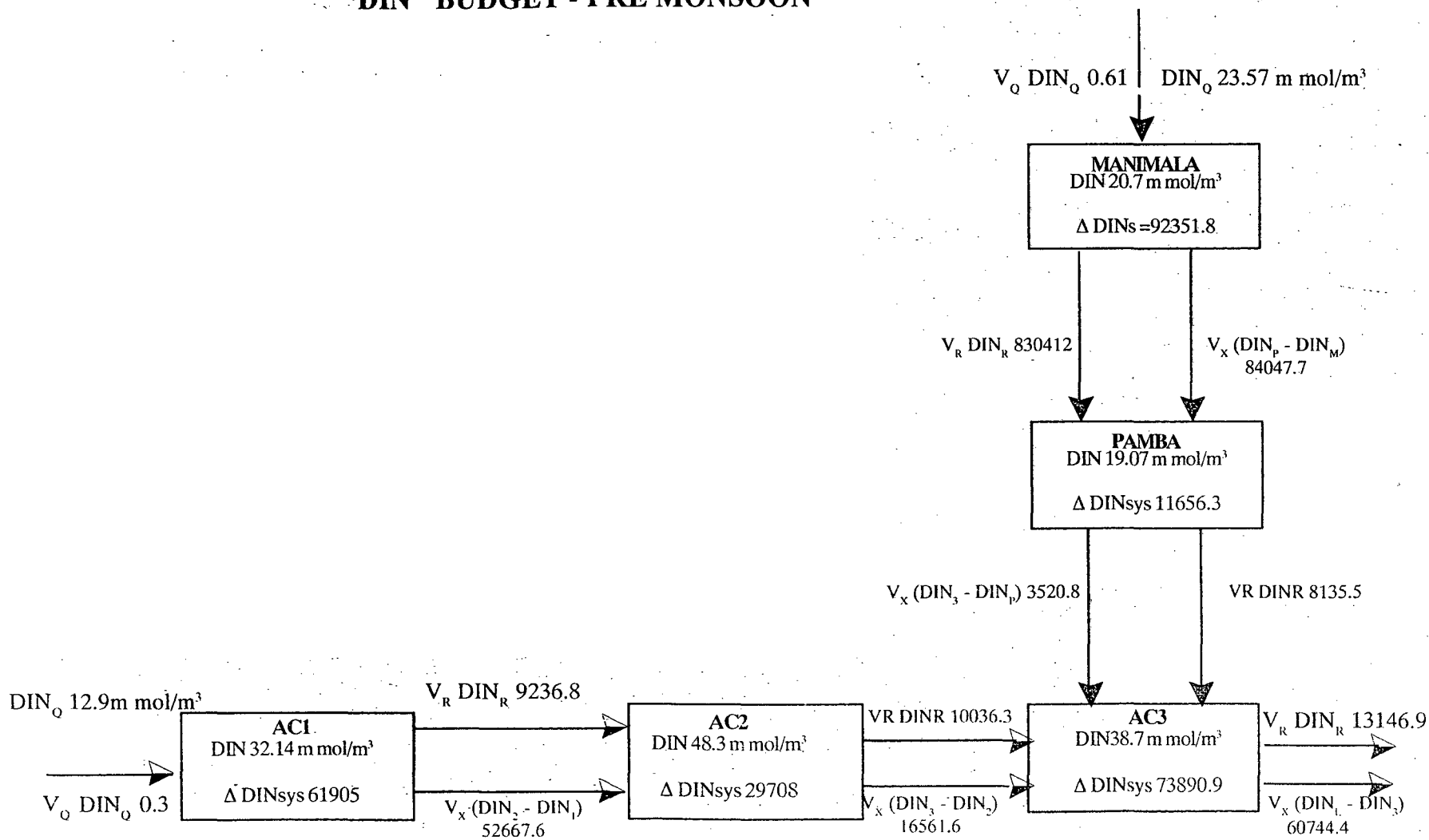
DIN BUDGET - PRE MONSOON

V_Q DIN_Q 0.61 | DIN_Q 23.57 m mol/m³

MANIMALA
DIN 20.7 m mol/m³

Δ DINs =92351.8

V_R DIN_R 830412

V_X (DIN_P - DIN_M)
84047.7

PAMBA
DIN 19.07 m mol/m³

Δ DINsys 11656.3

V_X (DIN_3 - DIN_P) 3520.8

VR DINR 8135.5

DIN_Q 12.9m mol/m³

V_R DIN_R 9236.8

AC1
DIN 32.14 m mol/m³

Δ DINsys 61905

V_Q DIN_Q 0.3

V_X (DIN_2 - DIN_1)
52667.6

AC2
DIN 48.3 m mol/m³

Δ DINsys 29708

VR DINR 10036.3

V_X (DIN_3 - DIN_2)
16561.6

AC3
DIN 38.7 m mol/m³

Δ DINsys 73890.9

V_R DIN_R 13146.9

V_X (DIN_L - DIN_3)
60744.4

Figure: 4.8

All flux values are in 10⁶ mol/yr

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DIP BUDGET - PRE MONSOON

V_Q DIP_Q
0.42

DIP_Q 16.3m mol/m³

MANIMALA
DIP 18.58 m mol/m³

Δ DIPsys 34027.3

V_R DIP_R
6011.4

V_X
$(DIP_3 - DIP_2)$ 28015.9

PAMBA
DIP 24.58 m mol/m³

Δ DIPsys 20713.6

V_R DIP_R
8941.6

V_X
$(DIP_3 - DIP_P)$ 11772

DIP_Q 12.9m mol/m³

V_Q DIP_Q 0.3

V_R DIP_R 6562

AC 1
DIP 18.38 m mol/m³

Δ DIPsys 8171.1

V_X
$(DIP_2 - DIP_1)$ 8105.13

V_R DIP_R 4559.02

AC 2
DIP 20.4 m mol/m³

Δ DIPsys 6743.16

V_X
$(DIP_3 - DIP_2)$ 2184.14

V_R DIP_R 4784.9

AC 3
DIP 19.13 m mol/m³

Δ DIPsys 13394.5

V_X
$(DIP_L - DIP_3)$ 8609.8

Figure: 4.9

All flux values are in 10⁶ mol/yr

DIN   BUDGET - MONSOON

DIN_Q 26.07 m mol/m³ V_Q DIN_Q 78.13

MANIMALA
DIN 25.23 m mol/m³

Δ DINs 226398

$V_X (DIN_P - DIN_M)$
151666

V_R DIN_R
74737.05

PAMBA

DIN 20.35 m mol/m³

Δ DINsys 44273.9

$V_X (DIN_3 - DIN_P)$
47626.7

V_R DIN_R
91900.64

DIN_Q 19.1m mol/m³

V_Q DIN_Q 16.23

AC 1
DIN 23.37 m mol/m³

Δ DINsys 38599.5

V_R DIN_R 26150.2

$V_X (DIN_2 - DIN_1)$
12433.14

AC 2
DIN 26.26 m mol/m³

Δ DINsys 168703.9

V_R DIN_R
19999.23

$V_X (DIN_3 - DIN_2)$
148704.75

V_R DIN_R
19999.23

AC 3
DIN 18.76 m mol/m³

Δ DINsys 73242.3

V_R DIN_R 41773.9

$V_X (DIN_L - DIN_3)$
31468.47

Figure: 4.10

All flux values are in 10^6 mol/yr

DIP BUDGET - MONSOON

V_Q DIP_Q 26.07 | DIP_Q 78013 m mol/m³

MANIMALA

DIP 20.77 m mol/m³

Δ DINsys 66864.6

V_R DIP_R 68108.15

V_x (DIP_P - DIP_M) 1243.16

PAMBA

DIP 20.29 m mol/m³

Δ DIPsys 81577.5

V_R DIP_R 96554.4

V_x (DIP_3 - DIP_P) 14976.9

DIP_Q 21.42m mol/m³

V_Q DIP_Q 18.23

AC 1

DIP 19.8 m mol/m³

Δ DIPsys 22030.5

V_R DIP_R 21361.37

V_x (DIP_2 - DIP_1) 650.95

AC 2

DIP 20.29 m mol/m³

Δ DIPsys 10125.4

V_R DIP_R 17858.04

V_x (DIP_3 - DIP_2) 7732.64

AC 3

DIP 20.22 m mol/m³

Δ DIPsys 40966.5

V_R DIP_R 40455.45

V_x (DIP_L - DIP_3) 511.08

Figure: 4.11

All flux values are in 10⁶ mol/yr

DIN BUDGET - POST MONSOON

DIN_Q 12.84 m mol/m³ V_Q DIN_Q 4.87

MANIMALA

DIN 11.66 m mol/m³

Δ DINsys 30286.9

$V_R DIN_R$
5279.2

$V_X (DIN_P - DIN_M)$
25002.9

PAMBA

DIN 8.35 m mol/m³

Δ DIPsys 27401

$V_R DIN_R$
5287.9

$V_X (DIN_3 - DIN_P)$
22113.6

DIN_Q
14.28
m mol/m³

$V_Q DIN_Q$
4.74

AC 1

DIN 13.57 m mol/m³

Δ DINsys 3788.57

$V_R DIN_R$
7218.97

AC 2

DIN 11.96 m mol/m³

Δ DINsys 7860

$V_R DIN_R$
8956.1

AC 3

DIN 10.92 m mol/m³

Δ DINsys 3510.86

$V_R DIN_R$
7859.56

$V_X (DIN_2 - DIN_1)$
3435.14

$V_X (DIN_3 - DIN_2)$
1096.06

$V_X (DIN_L - DIN_3)$
4348.7

Figure: 4.12   **All flux values are in 10⁶ mol/yr**

DIP BUDGET - POST MONSOON

$DIP_Q 20$ | $V_Q DIP_Q$
7.6

MANIMALA

DIP 20.64 m mol/m³

Δ DIPsys 9610.8

$V_R DIP_R$
10811.8

$V_X (DIP_P - DIP_M)$
1208.6

PAMBA

DIP 20.32 m mol/m³

Δ DIPsys 11549.64

$V_R DIP_R$
10544.48

$V_X (DIP_3 - DIP_P)$
1005.16

$V_R DIP_R$
10907.66

$V_R DIP_R$
14941.84

$V_R DIP_R$
13725.4

$DIP_Q 18.06$

$V_Q DIP_Q$
5.99

AC 1

DIP 18.81 m mol/m³

Δ DIPsys 12919.26

AC 2

DIP 19.75 m mol/m³

Δ DIPsys 17986.46

AC 3

DIP 20 m mol/m³

Δ DIPsys 9445.73

$V_X (DIP_2 - DIP_1)$
2005.61

$V_X (DIP_3 - DIP_2)$
3044.92

$V_X (DIP_1 - DIP_3)$
4279.67

Figure: 4.13

All flux values are in 10⁶ mol/yr

NET METABOLISM and PRODUCTIVITY

Non-conservative fluxes in the steady state these are obtained as the difference between nutrient concentration and the hydrographic fluxes. For the non-steady state case, (Gordan et al 1996). The difference between primary production and respiration (p-r), is net ecosystem metabolism (NEM): This is derived as –(C: P) part X DIP, where (C: P) part is the molar composition ratio of locally reacting organic matter. The assumption behind this calculations that net system production or oxidation of organic matter is the primary non-conservative uptake (flux from the system, so – ve) and release (+) pathway for DIP within the system.

Nutrient is very much essential for the biological productivity. In the inland aquatic systems N, P act as limiting nutrients. (Redfield 1963) .So the ratio of the dissolved N and P has been used to assess the nutrient status of the water body. If the N: P ratio is <16:1 then the river waters are N limiting but if the ratio is > 16:1 they are P limiting. The N : P ratio of these river indicates that they are mostly N limiting, 55-70% in post monsoon, 50-70% in monsoon and 60-70 % in premonsoon (Figs 4.14, 4.15 & 4.16) . In general in the Achankovil River the P and N are almost act as limiting nutrients and are considerably loaded by the human influence.

CLIMATE IMPACT

Climate change will have a profound effect on the future distribution, productivity and health of this ecosystem. Because warming is expected to be particularly large at high latitudes, climate change could have substantial impact on net ecosystem processes (Dixen et al., 1996, IPCC 1996, Karnkina 1997).

The impact of climate change on biogeochemical parameters of aquatic systems usually is estimated by studying scenarios for change in climatic variations over the study period. Considerable effort has been made on developing improved hydrological models for estimating the effects of climate change on aquatic systems. Improved models have been developed to be of general applicability with no locally calibrated parameters. In estimating impacts on water recharge and quality, however translation of climate into response is well understood and additional uncertainty is introduced. In this area, there has been a reduction in uncertainty, since the
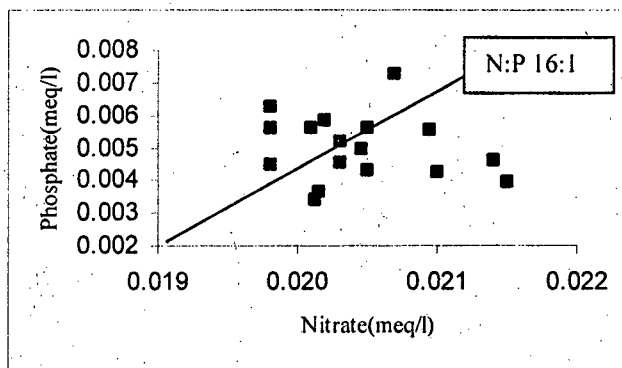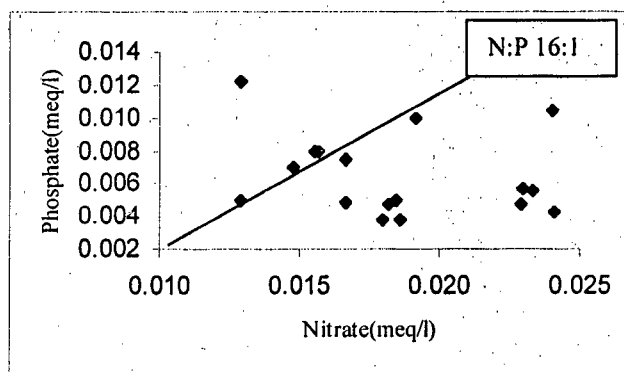
Figure 4.14: N/P Ratio- Premonsoon

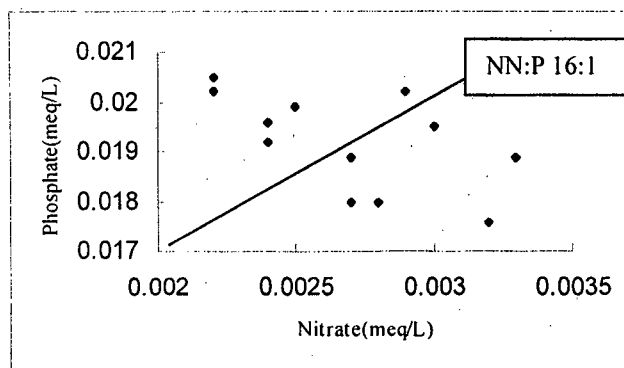**Figure 4.15:** N/P Ratio Monsoon

Figure 14.16: N/P Ratio Post- Monsoon

biogeochemical models have been improved and in recent years with more studies conducted on aquatic systems.

The local climate of Achankovil River basin has been explained in Figures: 4.17 & 4.18. From these graphs it is clear that, there is wide variations in temperature and rainfall among three different seasons. These variations are mainly due to variations in temperature, rainfall and discharge in pre-monsoon, monsoon and post-monsoon periods. The study area gets maximum amount of rainfall in by SW monsoons (June-mid Sep), which accounts approximately about 73% of annual rainfall. However NE monsoons (Oct-mid Jan) also gives some amount approximately of rainfall 10-23%. This is the main reason for high discharge in monsoon and post monsoon periods. In summer period, due to high temperature, atmosphere pressure automatically increases along with temperature, which partially increases evaporation rate than other seasons and decreases the discharge from the river to the ocean (even though this region is highly humid). The discharge variations in the study period are shown in figure: 4.19.

In monsoon, due to high rainfall, moist climate and high discharge, weathering is higher, hence phosphate is released from weathered rocks to the system highly, uniform distribution with the basin discharge (Figure: 4.20). In pre-monsoon due to high temperature and high biological activity, the phosphate distribution is irregular, and the fluctuations are may be due to contributions from the anthropogenic sources. As in monsoon, similar trends have been observed in post-monsoon. Similarly nitrate which is not having any natural lithospheric source here, its concentration is very low in monsoon period and post-monsoon, due to low biological activity, temperature and moist climate (figure: 4.21). And in these periods, high rainfall and discharge diluted nitrate with in the river system. The nutrient status over the study period is related with DO, is shown in figure: 4.22. In dry pre-monsoon period, temperature is relatively high with low moisture content, which increases the biological activity with in the river system, and hence nitrate concentration is irregularly distributed. Whenever the changes in temperature and biological activity are more, irregular trend in nitrate concentration is observed.
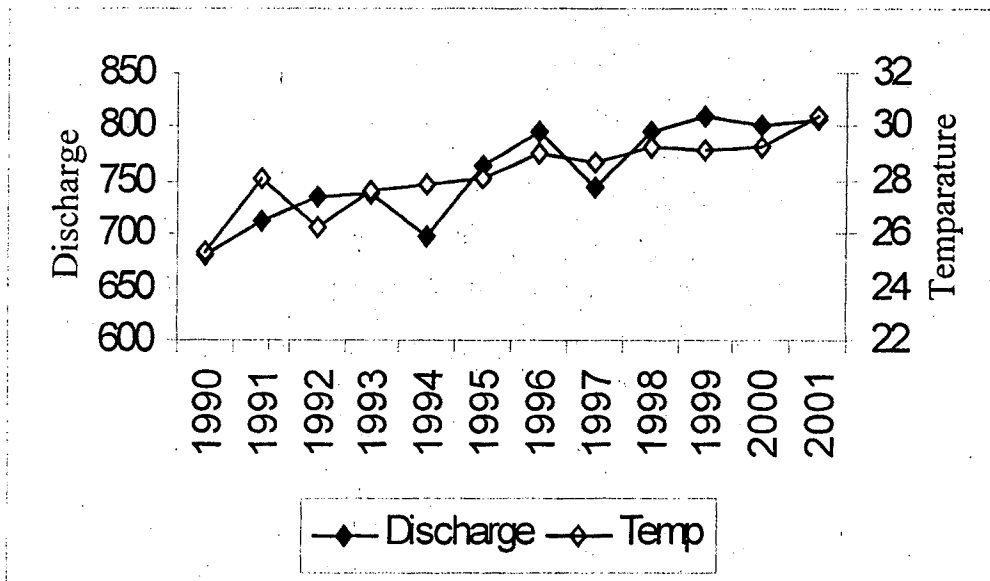
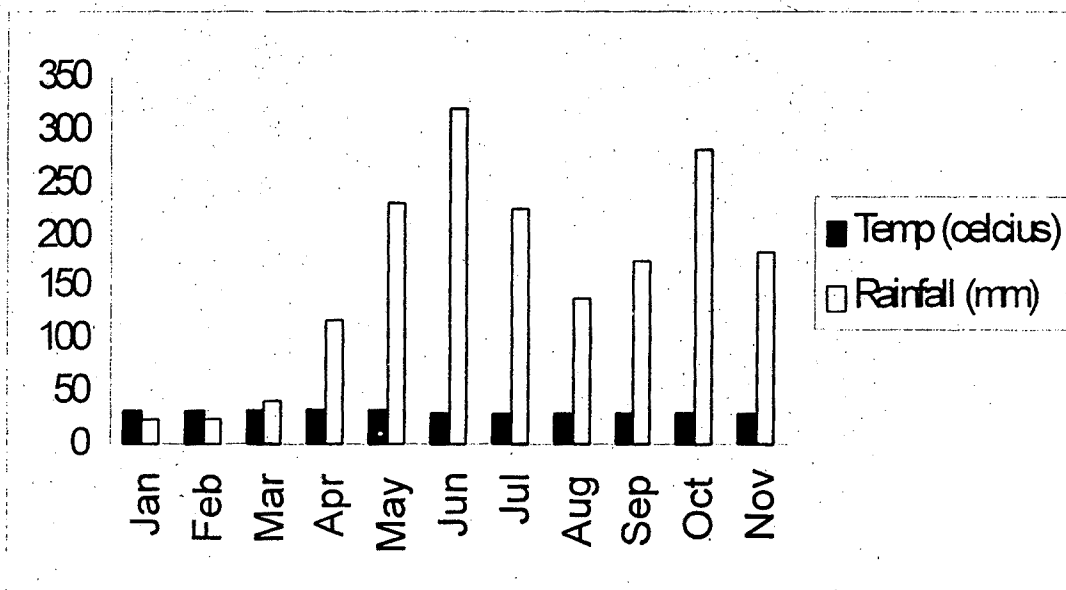**Figure 4.17:** Year vs Discharge (m^3/sec) and Temperature(^{o}C).

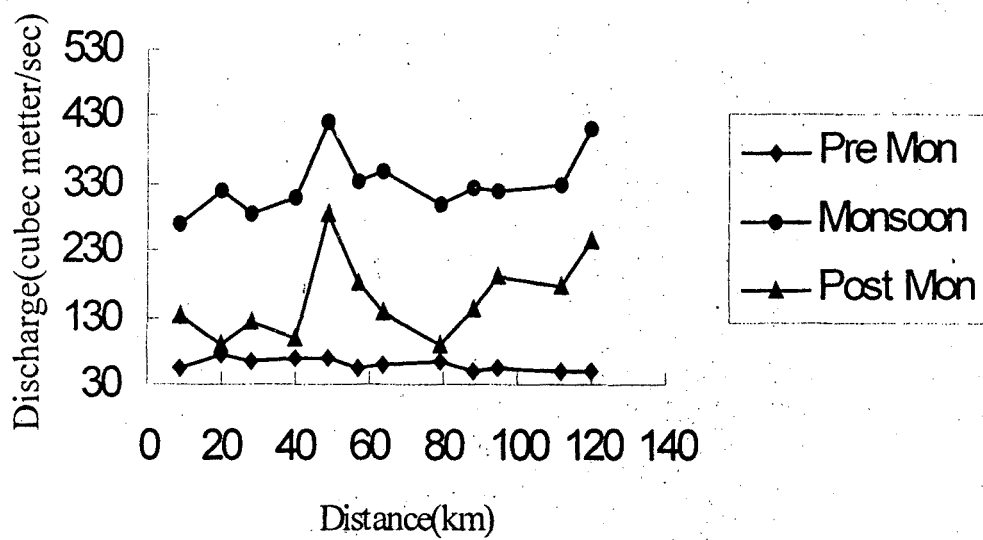**Figure 4.18:** Temperature and Rainfall variation in 2002.
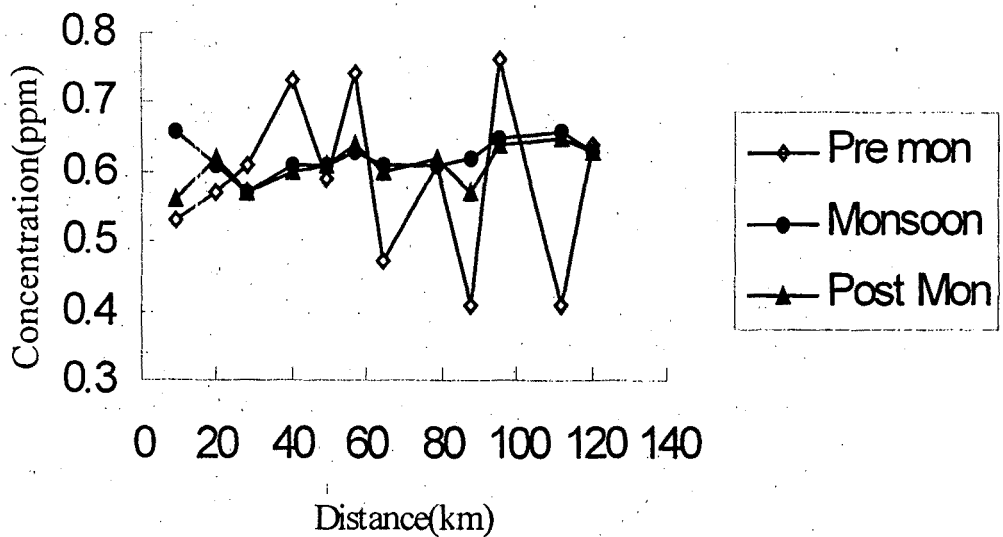
Figure 4.19: Distance vs Discharge

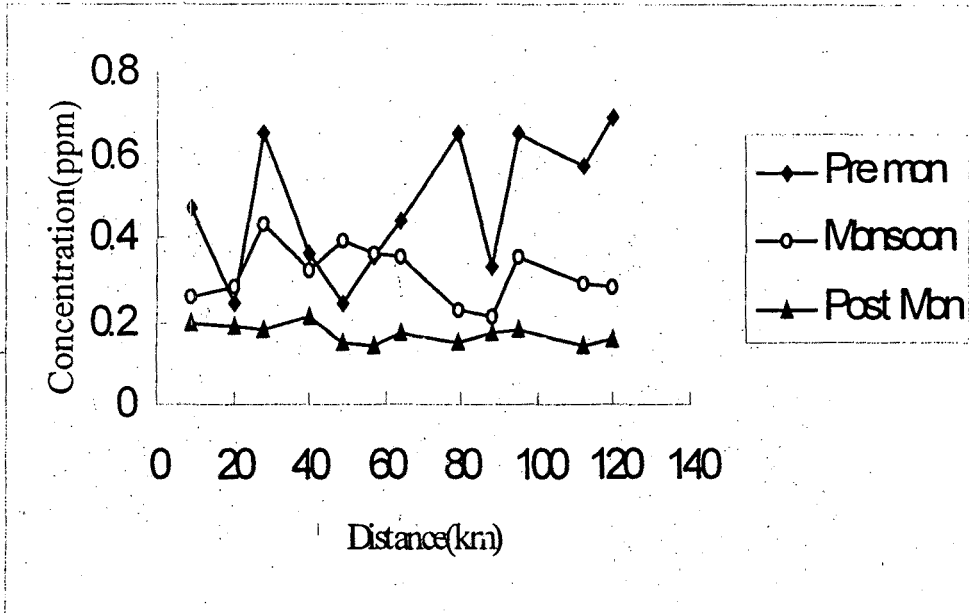**Figure 4.20:** Distance vs Phosphate

Figure 4.21: Distance vs Nitrate
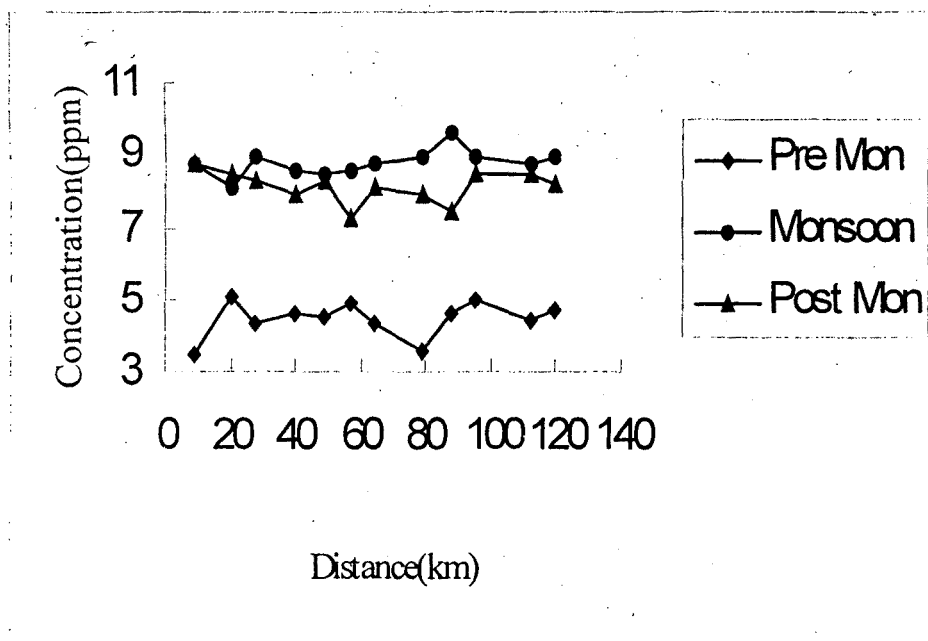

Figure 4.22: Distance vs Dissolved Oxygen

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SUMMARY
&
CONCLUSION

SUMMARY & CONCLUSIONS

The rivers are one of the major dynamic ecosystems in the biosphere. It transfers nutrients and particulate load from the continents to the adjacent oceans. The bio-geochemistry of the river is impacted by natural and anthropogenic impacts. The modeling of the biogeochemical parameters gives a conceptual idea about the behavior and fate of the nutrients in the river ecosystems.

The salient features of the present study are given below: bicarbonate is the main anion and sodium is the main cation. The abundance of the dissolved ions in the Achan kovil river water is as follows: $Cl>HCO_3>SO_4>NO_3$ (anions) and $Na>Ca>Mg>K$ (cations). Rock weathering is the most important mechanism controlling the water chemistry. The low amount of $(Ca+Mg)/(Na+K)$ and $(HCO_3)c/(HCO_3)si$ ratios indicates that water chemistry is controlled largely by the silicate weathering and partly by carbonate weathering. In pre-monsoon higher concentration of nitrate and lower concentration of phosphate is observed. This is due to the biological activity in the river system. The seasonal and spatial variations in TDS are attributed to lithological and climatic control over the ionic concentration. The higher concentration of Na, K, Cl, and sulphate in monsoon period indicates the contribution from the dissolution of suspended matter.

The river system in the upstream to downstream acts as sources for the DIP and DIN. Within the river system they behave in contrast to each other due to the differential weathering of the drainage rock, microclimatic changes and the runoff from the human sources. So the system seems to be a source and may be sink at the end (lakes region) for these two nutrients in a given short period with rapid changes. In general here the river input of DIN and DIP is higher than agricultural runoff. This will support and compensate decomposition with in the system. It shows that here de-nitrification is found to be higher than nitrogen fixation. So these rivers are apparently the net producers of organic material. Hence their concentrations in two seasons were not varied too much and it also indicates the rivers higher current assimilative capacity. Stoichiometric calculations of the non-conservative fluxes to derive net system metabolism may not reliable because of the very short water exchange time with in the river system.

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Since there is no longtime data on nutrient variations with regard to climate is not available. This study considered to the nutrient variations with respect to the climate changes over the period of study. This will be the base line data for long term study of nutrient distribution and climatic impacts.

For simulation of future climatic impact on any ecosystem requires a long-term study. The long-term study would enable us to derive more sophisticated budget calculations to understand the ecosystem dynamics and biogeochemical behavior of the nutrients within the ecosystem in relation to global climatic changes.

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