Chemistry of Water and Sediments in the Western Ghat Rivers of Kerala

Dissertation submitted to the Jawaharlal Nehru University
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Master of Philosophy

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CERTIFICATE

This is to certify that the work embodied in this dissertation entitled **"Chemistry of Water and Sediments in the Western Ghat Rivers of Kerala"** has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted in part or full for any other degree or diploma of any university.

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DEDICATED TO
MY PARENTS

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"A teacher affects eternity; he can never tell where his influence stops."
- Henry Adams

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(Sujit Kumar Bajpayee)

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CHAPTER - 1
INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction:

Rivers represent the evolution of civilization all over the world. All the major cultures have used the riverine fresh water environment as the focal point of their habitat. Ancient societies, because of their life style, recognized the importance of viewing the rivers as source of life and thus to be looked upon with reverence. This was the key to the then existing sustainable development. Afterall the quantity of water in the riverine segment of the hydrological cycle has not changed. But there has been progressive change in the quality of the river sector in recent times in response to disequilibrium between development and nature's inability to accommodate small scale variabilities in the given time scale. One of the component of global change thus involves freshwater - particularly rivers.

Rivers contain a tiny fraction of the world's freshwaters. Rivers and lakes with a total mass of 0.3×10^{20} g make up only about 0.002 % (Figure:1.1) of total mass of hydrosphere (Drever, 1982). Yet they are a vital component of the hydrological cycle, annually transporting 32-37 km^3/yr of water to the world's ocean. Most of the precipitation that falls within a river basin returns directly to the atmosphere by evaporation and plant transpiration. Some water may reach stream channels by overland flow, but this is usually a small fraction, except in very intense storms or in areas of little vegetation cover and compacted soils.

Rivers transport an enormous amount of sediment to the oceans, some 15-20 billion tonnes annually. The rivers of South Asia and Oceania carry
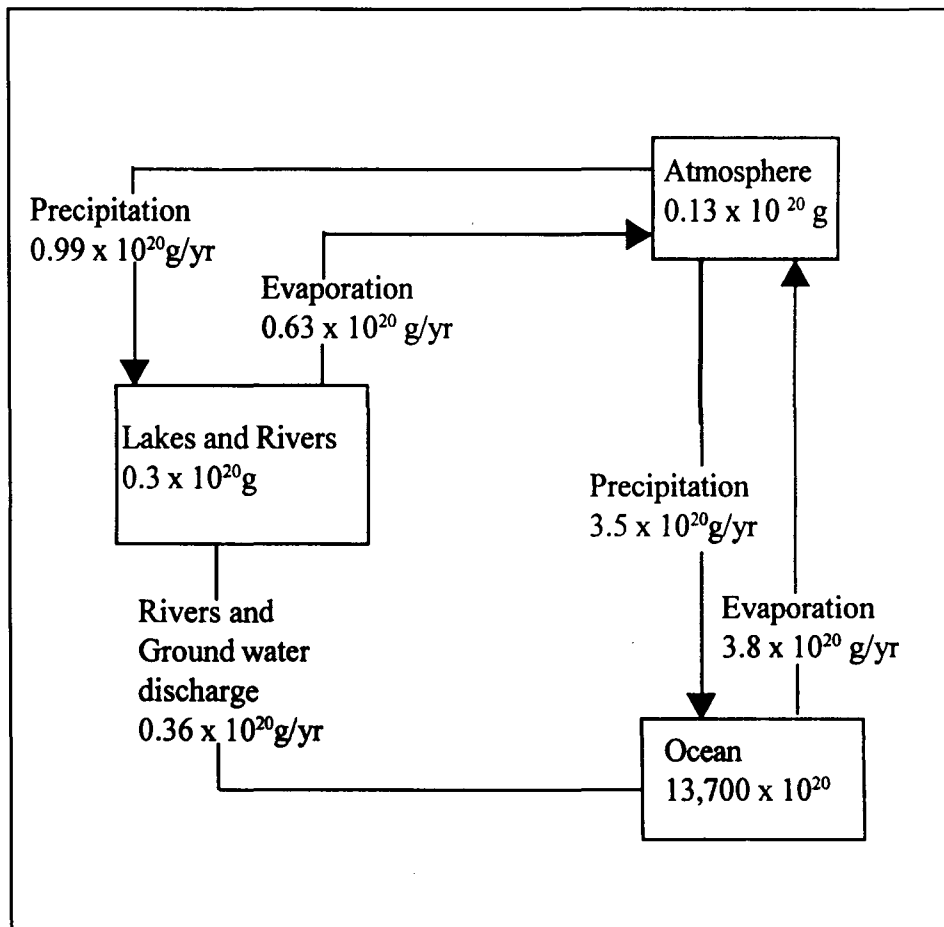
Figure 1.1 : Schematic diagram of the hydrologic cycle (Drever, 1982)

Atmosphere
0.13×10^{20} g

Precipitation
0.99×10^{20} g/yr

Evaporation
0.63×10^{20} g/yr

Lakes and Rivers
0.3×10^{20} g

Precipitation
3.5×10^{20} g/yr

Rivers and
Ground water
discharge
0.36×10^{20} g/yr

Evaporation
3.8×10^{20} g/yr

Ocean
$13,700 \times 10^{20}$

the greatest sediment loads. Worldwide, differences in lithology, landuse, precipitation and steepness of slope are more important than are difference in discharge in determining pattern of sediment export. Most particulate material is carried in suspension and the minimum particle size that can be eroded and transported increases with current velocity. A lesser amount of material is transported by skipping rolling along the bottom, termed the bed load.

Many factors influence the composition of river water, causing variation from place to place. Rain is one source of chemical inputs to rivers, and a stream flowing through a region of relatively insoluble rocks can be chemically very similar to rain water and its composition. Ultimately all of the constituents of the river water originate from dissolution of the earth's rocks. The dissolving of the rocks is commonly the major determinant of river water chemistry locally as well, but this varies with geology and with the magnitude of input via other pathways including rainwater, volcanic activity and pollution. Materials are concentrated by evaporation and altered by chemical and biological interactions within the stream, unlike sea water, which is quite constant everywhere and can be approximated with an artificial standard, river water varies considerably in its chemical composition.

The dissolved load of a river represent chemical processes in the catchment area while the sediment load reflect the physical processes of weathering and erosion. In spite of extensive data base available, so far the

relationship between the chemical process and the physical process in a river is not well understood (Walling, 1992).

Rivers are the representative of the present day geochemical processes involving constant mobility of materials such as water, sediments and dissloved salts to the ocean. Rock weathering and subsequent transport by flowing river water to the ocean is one of the most important phenomena that controls the morphology of the Earth surface. This acts through two complimentary processes: the chemical weathering partially dissolves rocks and minerals and transports erosion products in a soluble form; fracturing of rocks provides fine grained material that can be more easily transported by river waters. Chemical and mechanical erosion processes enhance each other in that crushed rock provides chemically reactive surfaces and weathered rocks are easily fractured. Global erosion will depend *a priori* on many factors, such as lithology, climate, relief, tectonics and vegetative cover. As silicate rock weathering consumes atmospheric CO_2, riverine erosion is likely to have an important effect on long-term climate evolution (e.g. Berner,1992).

The two fundamental processes of erosion - mechanical and chemical, result in suspended and dissloved load in the rivers, which represent quantitatively the most important input materials to the ocean (Holland, 1978). Rivers transport of materials gives essential information both on the processes affecting the continental surface (weathering, plant production, pollution, etc.) and on the amount and nature of material carried to water bodies such as lakes, sea, and oceans (Garrels & Maackenzie,

1971; Garrels et al., 1975). Annual estimated transport of water to ocean by the rivers is 37000 km^3. The annual estimated sediment transport to ocean by the rivers is $15-16X10^{12}$ (Milliman and Meade, 1983; Walling & Webb, 1983). The lesser mobile components like SiO_2, Al, Fe, Ti and K are mainly exported by mechanical erosion processes, whereas highly mobile components like Ca, Mg, Na and HCO_3 are removed from the basin primarily by chemical erosion (Probst, 1986).

The sediments carried by rivers are responsible for the transportation of various kinds of metals as they are either structurally attached to the lattice or they are just adsorbed on the surface of the soil.

Most of the work done on chemical and mechanical erosion in rivers are confined to major rivers which are multilithologic and understanding the mechanism of erosion becomes difficult in this case. So studying the rivers which are monolithologic will be great help to understand the otherwise complex mechanism of chemical and physical erosion. This study aims at studying the chemistry of water and sediments of eleven such small and monolithologic rivers of Kerala in order to understand the factors responsible for dissolved and particulate load in the river.

1.2   River Water Chemistry:

Lot of work has been published since sixties on river water chemistry. Livingstone's (1963) study on chemical composition of inland waters of the world is one of the pioneering and the most quoted work. But the work on

the water chemistry has been limited to large and medium size rivers. The important work on major rivers have been done by Gibbs (1967, 1971), Stallard & Edmond (1981, 1983) on Amazon; Negrel et al., 1993; Dupre et al., 1996; Gaillardet et al, 1995; Allegre et al., 1996; Gaillardet et al., 1997 on Amazon and Congo; Brunskill (1975) on Mackenzie; Hu Ming et al, (1982) on Chinese Rivers.

In India the work on river geochemistry was started by Raymahashay (1970) followed by Abbas & Subramanian (1984), Sarin & Krishnaswami (1984), Ittekkot & Arain (1986), Sarin et al (1989), Datta & Subramanian (1997) on Ganges - Brahmaputra river system.

1.3   Bed Sediment Chemistry

By now it is well proven fact that study of bed sediment chemistry is very important for calculation of individual elemental fluxes and their mass balance studies. Sediment chemistry of major rivers have been reported by Garrel and Mackenzie (1971), Turekian and Scott (1967) and Martin and Meybeck (1979).

97% of the mass transport of metals from continents to ocean is associated with sediments (Gibbs, 1977). Martin and Meybeck (1979) made a comparative study review of the particulate transport of elements by world's major rivers. The relative importance of the particulate forms in increasing sequence Al, Mn, Co, Zn, Ni, Cu, Cd has also been found by Yeats and Bewers (1982) from St. Lawrence river in Canada. Metal

pollution has been studied by analysing sediments in a number of rivers (Fristner and Wittman, 1979; Knutson et.al.; Barole et.al. 1988; Campbell et.al., 1988 and Kremling and Pohl, 1989).

In India, Naidu et.al. (1967); Rao and Rao (1973); Sarin et. al., (1979), Kalesha et. al., (1980) have studied the geochemistry of sediments on Eastern Continental Shelf and Slope. Individual river basins have been studied by Sarin et.al., 1989 (Ganges-Brahmaputra river system); Ramesh & Subramanian,1989 (Krishna); Bhiksham and Subramanian, 1989 (Godavari); Chakrapani and Subramanian, 1990 (Mahanadi); Paul and Pillai, 1978 (Periyar); Gupta and Subramanian, 1994 (Gomti); Ramanathan et. al., 1994 (Cauvery); Gupta and Subramanian, 1997 (Godavari); Datta and Subramanian, 1997 (Ganges-Brahmputra system). Subramanian et. al. (1985) made a comparative study on chemistry of river sediments from the Indian sub continent. Despite the diverse geology of individual river basins, the chemical composition of sediments varied only for those elements which are mobile (Ca, Mg, Fe etc.).

Partial analysis of sediments from Narmada and Tapti estuary has been reported by Sarin et. al. (1979) and Barole et. al. (1982). Various workers have studied the water chemistry, sediment chemistry and nutrient distribution in some of the rivers of Kerala, Periyar (Sarala et.al.; 1991), Vembanad Lake (Padamlal & Saralathan; 1991), Ashtamudi Lake (Damodaran & Sajan; 1983), Cochin Estuary (Joseph & Kurup; 1990), Padamlal and Saralathan (1991) studied the interstitial and overlying water for P, Fe and salinity. He observed opposite trend in concentration of P and

Fe in the interstitial water to the that in sediment. Damodaran and Sajan; 1983 after studying the carbonate content in the sediments in the Ashtamudi Lake, west coast of India observed striking difference in the distribution pattern of carbonate in different part of the lake and it was attributed to the type of sediments, the rate of sedimentation and the biogenic productivity in the area. Anirudhan et.al. (1994) studied the roles of relief and climate on composition of detrital sediments of Bharatpuzha river basin, Kerala. Rajendran et.al. (1996) studied the heavy mineral and geochemical composition in lower Bharatpuzha sediments, Kerala. He observed the increase of heavy minerals towards finer sizes with opaques, hornblende and pyroxenes responsible for more than 90% variablity. The order of abundance of heavy metal was found to be Fe>Mn>Ni>Cr>Zn>Pb>Cu>Cd with bulk samples showing the least content. He also observed that enrichment factor values of Cu, Zn, Cr and Mn are close to crustal abundance.

1.4 Clay Mineralogy of the sediments

Over the years a number of papers have described the distribution and abundance of clay minerals within ocean basins (Griffin and Goldberg, 1963; Subba rao, 1964; Naidu and Mowatt, 1983. The mineralogical contribution contribution of rivers also has been taken care of due course (Gibbs, 1967; Subramanian, 1980; 1988; 1994). They have observed that clay mineralogy is controlled by size segregation and, hence, most of the studies centre around 2μ size fraction.

In general the principal clay minerals are illite, montmorillonite, chlorite, kaolinite and their mixed layer derivatives.

Chlorite may be characterised as the high latitude clay mineral, as it is found in the most abundance in polar regions of the world. They are not confined to the clay fraction but occur throughout the silt range (2μ - 62μ).

Illites are mainly detrital. Illite concentration clearly delineate the extent and the amount of contribution of TSM to marine sediments (Griffin et. al., 1968).

Kaolinite abundance shows the intensity of weathering regime. The high kaolinite abundance in recent marine sediments are confined, in general, to the equatorial sediments and kaolinite may be considered as low latitude clay mineral.

The clay plays a diverse role in the natural water. The sorption of silica by clay minerals (Siever and Woodford, 1973); calcium-magnesium exchange in montmorillonite and vermiculite (Levy and Shainberg, 1972) and selective sorption and fixation of cations by clay minerals (Sawhney, 1972) have been studied in detail.

CHAPTER - 2
STUDY AREA

2.1 Introduction

All the rivers in the study area can be classified as small rivers depending on the size of the catchment area (Rao, 1979). Periyar river has the largest basin area of 5284 Km^2. among all. Lengthwise also Periyar stands top. Bharatpuzha and Chaliyar comes second and third respectively both basin areawise and river lengthwise. The study area lies between the latitude $8.5°N$ - $11.5°N$ and $76°E$ - $77°E$. except for few, all the river basins are confined within the Kerala state, India.

2.2 Climatic Features
2.2.1 Rainfall

The study area falls in the tropical kind of climate. According to another bioclimatic classification done by J. Pascal, the study area falls in Alleppey-Mangalore regime. In this regime the mean temperature is more than $23°C$ and rainfall is 2000-5000 mm. The area receives two monsoons, namely the SW (June-September) and the NE (October-December) monsoon. The SW monsoon contributes to 60% of the total rainfall. Based on an analysis of rainfall data from about 80 stations during the period 1901-1980 (excluding the period monsoon steadily increases from south to north. The NE monsoon yields less rainfall, with the maximum (>100 cm) recorded in Neriyamangalam. The general trend of rainfall over the study area is given in figure 2.1.
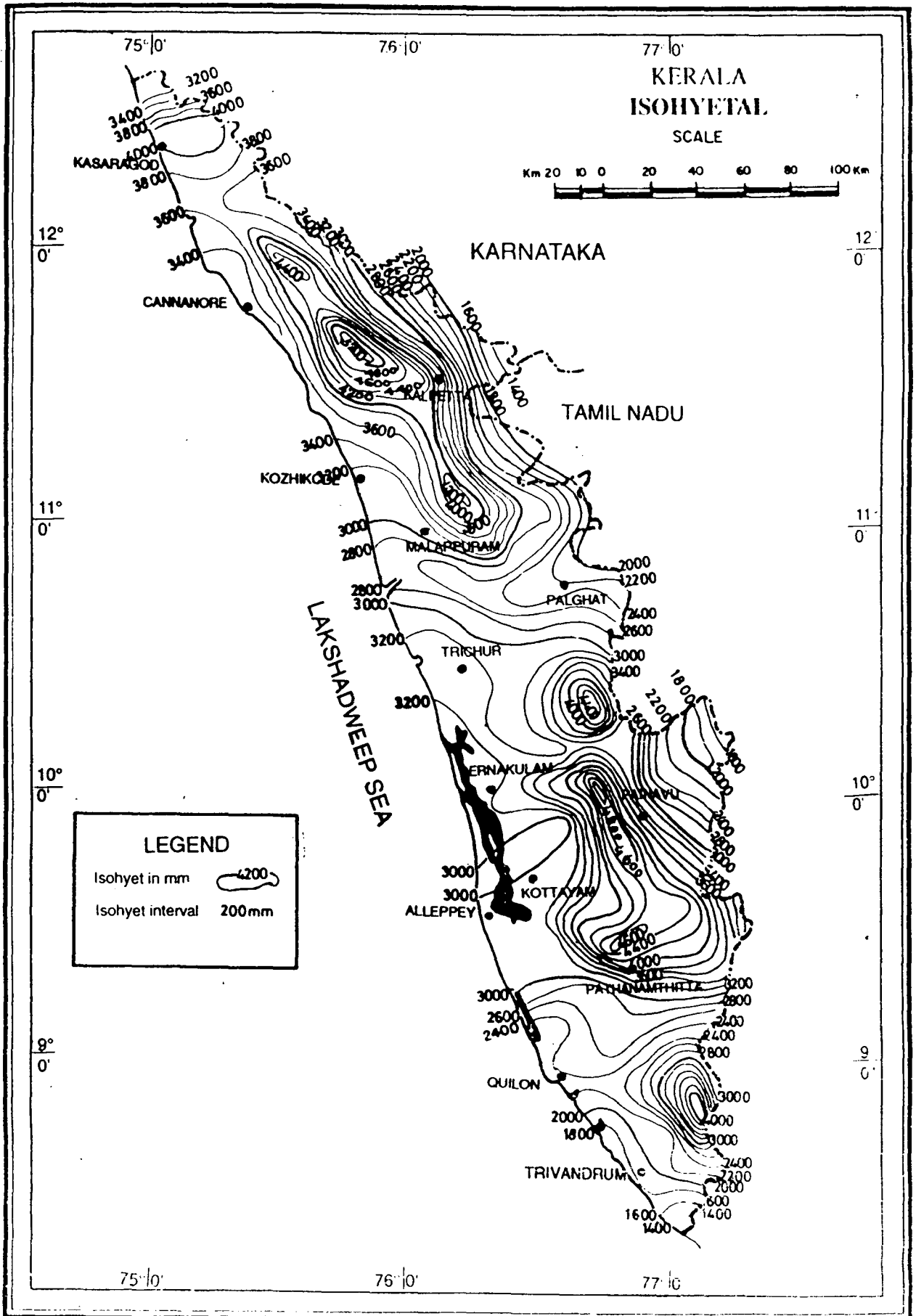
Figure 2.1 : Rainfall Map for the Study Area

2.2.2 Temperature

According to a temperature record from 16 stations for the period 1931-1979, the maximum temperature (>32°C) reaches during March-May and the lowest temperature(<27°C) is experienced in the months of December and January (Figure 2.2).

The seasonal and diurnal variations of temperature are not uniform and it depends on the distance from the sea. The seasonal and diurnal variations in temperature for the stations located near the coast are nearly in the same range (5°C-7°C). But in the high ranges, which are typically sub-tropical, the diurnal variation is very high (>15°C in some months).

The difference between the mean temperature of the hottest and the coldest months is 2.8-5.3°C throughout the study area and the mean temperature of the hottest month is in the range of 23-30.9°C in the study area which falls under Allepey-Mangalore bioclimatic zone (Pascal, 1982).

2.2.3 Humidity

Annual mean relative humidity varies from 79-84% in the morning and 73-77% in the evening along the coastal areas. During the period from January to March, afternoon humidity reduces to 60-63%, with variation from 35% in the interior to 71% in the coastal areas.
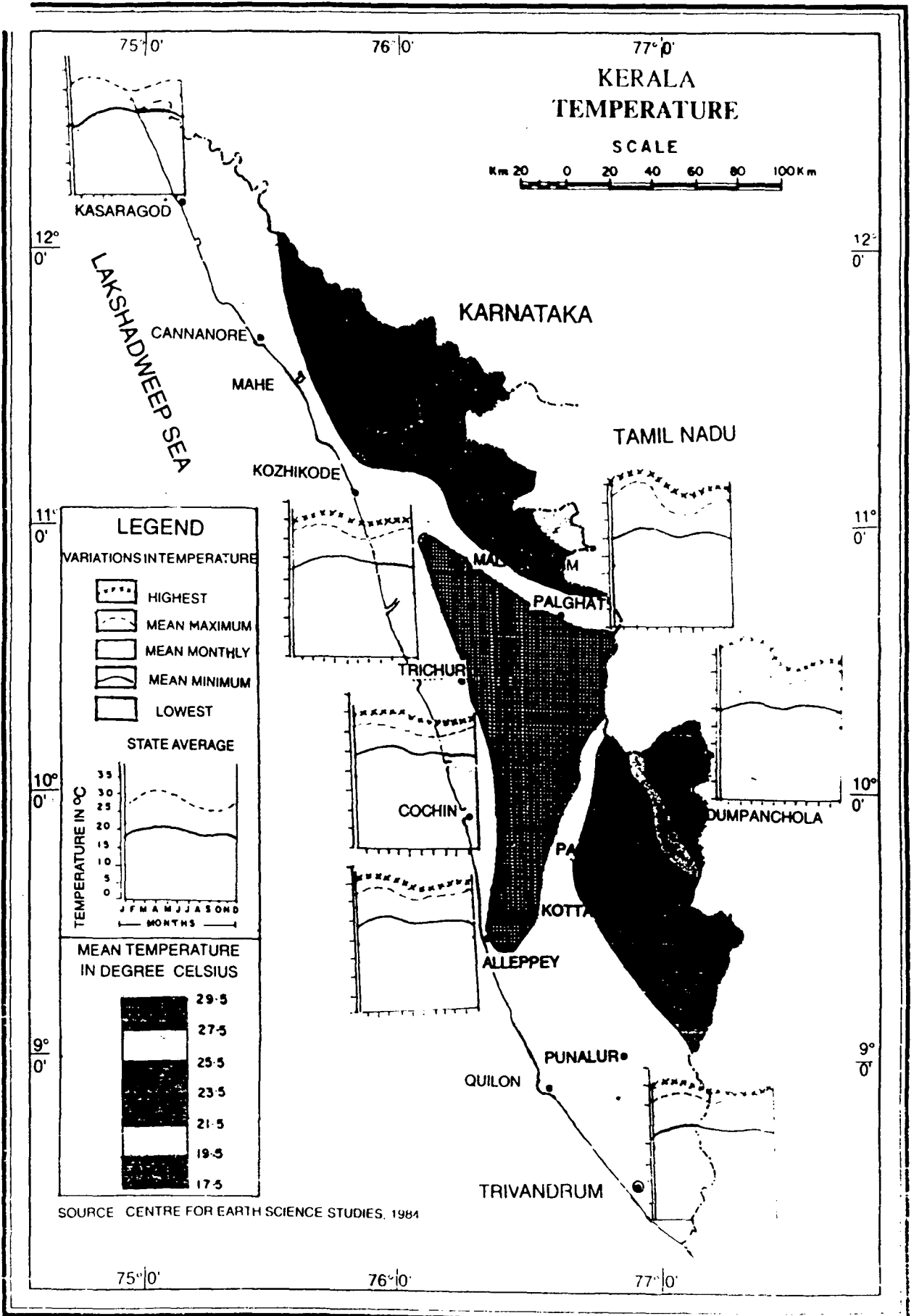
Figure 2.2 : Temperature variation over the Study Area

2.3   Geology and Geomorphological Features

The Kerala region is an important segment of the South India Precambrian terrain where major units of the Archaean continental crust, such as granulites, granites, gneisses and greenstones are preserved. Four major geological formations have been identified in the state. The chronological succession is as follows:

1. Crystalline rocks of Archaean age,
2. Sedimentary rocks of Tertiary age,
3. Laterites capping the crystallines and sedimentary rocks, and
4. Recent and Sub-recent sediments in the low lying areas and valleys.

The bulk of the rocks of Kerala, especially the granulites and associated gneisses belong to Precambrian. The charnockites are exposed in all the districts, khondalites are concentrated in the southern part and Dharwar schists and gneisses are exposed mainly northern part of the study area (Figure 2.3). These are intruded by early Paleozoic pegmatites (Soman et al., 1982) and early tertiary dolerite dykes (Furnes et al., 1983). Classification of the Kerala rocks into broad age groups, based on available data is given in Table - 2.1.

A linear coastal outcrop of late tertiary sedimentary formations, equivalent to the Rajahmundri sandstone is formed from Kottayam to beyond Trivendrum in the south. The sedimentaries are over 300 m thick in the widest part of the outcrop between Shertalai and Karungapalli.
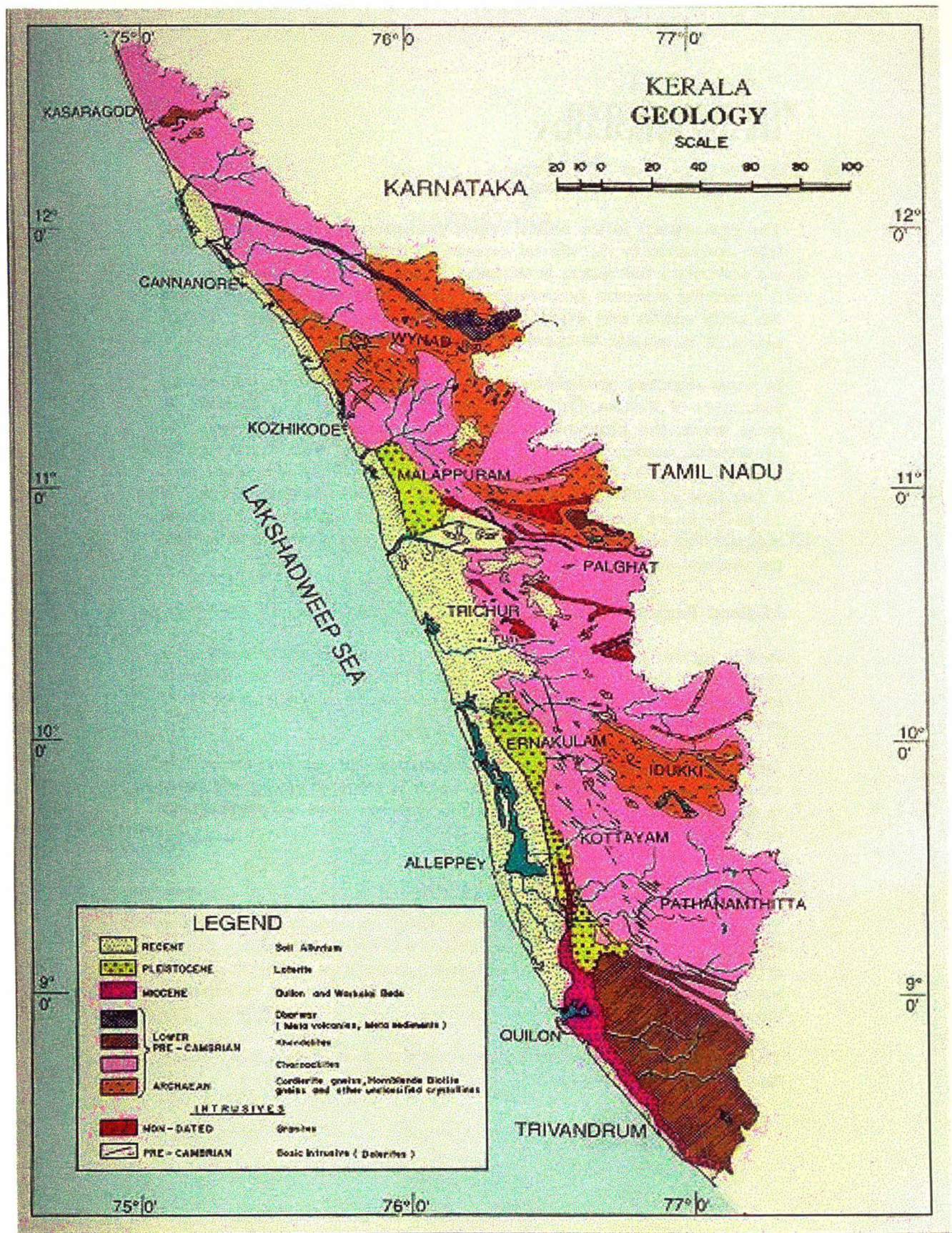
KERALA
GEOLOGY
SCALE
20 10 0   20   40   60   80   100

KARNATAKA

KASARAGOD

CANNANORE

WYNAD

KOZHIKODE

MALAPPURAM

TAMIL NADU

PALGHAT

TRICHUR

LAKSHADWEEP SEA

ERNAKULAM

IDUKKI

KOTTAYAM

ALLEPPEY

PATHANAMTHITTA

LEGEND

	RECENT	Soil Alluvium
	PLEISTOCENE	Laterite
	MIOCENE	Quilon and Warkalai Beds
		Dharwar (Meta volcanics, Meta sediments)
	LOWER PRE-CAMBRIAN	Khondalites
		Charnockites
	ARCHAEAN	Cordierite gneiss, Hornblende Biotite gneiss and other unclassified crystallines

INTRUSIVES

	NON-DATED	Granites
	PRE-CAMBRIAN	Basic Intrusive (Dolerites)

QUILON

TRIVANDRUM

Figure 2.3 : Geology Map of the Study Area

M.Y.

0	Phanerozoic		Laterites Cenozoic sediments Dolerites (61-144 Ma) No record Pegmaties (460-680Ma) Incipient Charnockite (540Ma) Acid and alkaline intrusives (505-765 Ma)
570	Proterozoic	PR3	No record
1000		PR2	Pegmatite (21420+/-20 Ma Attappadi Migmatization in South Kerala 1550 Ma Dolerite dykes (1660 Ma) Attappadi
2000		PR1	No record
3000	Archaean	AR3	Khondalite; calc-granulite and gneisses Charnockite(massive) and Charnockitic gneiss Sargur and associated schists Earliest basement
		AR2	No record of this age identified in the Kerala region
4000		AR1	
5000	Hadean		Hadean (4500-4000 Ma) Origin of Earth Pre Hadean-Early cosmic evolution

Intrusives (between Phanerozoic and Proterozoic PR3)

Intrusives (between PR2 section)

Table 2.1 : Geological Sequences of Kerala

Laterites occur extensively in the midland region of the study area; over Precambrian crystalline rocks and tertiary sedimentary formations. Laterites formation is generally linked to landform evolution (Mc Farlane, 1976) and is widely associated with terrain of low relief and condition of plantations (Thomas, 1974), often giving rise to economic mineral deposits. The high hills in the study area are devoid of laterite cover. Thick alluvial fill occurs in the interfluves and uplifted laterite caps are observed along the coastal areas that stand against erosion.

Geological formations of all ages are not represented in the study area. Therefore, it is reasonable to presume that this area was subjected to prolonged periods of erosion and non-deposition. This, on the other hand, resulted in the planation surfaces, which are essentially planar surfaces, resulting from processes of erosion. The most prominent geomorphological unit of the study area and one of the important orographic features of Peninsular India is the Western Ghats. This hill range plays a critical role in regulating the climate of south India, and most of the heavy rainfall during Southwest Monsoon occurs on the Western side of the Western Ghats.

2.4   Hydrological Features
2.4.1 Drainage

The average annual flow of the rivers in consideration to the Arabian Sea is around 32×10^9 m^3. The total basin area of the rivers in consideration constitute about 60 % of the total basin area of Kerala. All of them originate in the Western Ghats and empties themselves into Arabian Sea, either

directly or through some major lake systems of the state like Vembanad Lake, Ashtamudi Lake, etc. The streams are short and swift flowing, showing various stages of gradation. These streams are marked by cascades and waterfalls in the upper reaches, although in the plains they show evidences of maturity of development. Some of these rivers have steep gradients (1/250 or more) in their initial reaches. (Ref. Resource Atlas of Kerala, 1984). The most interesting feature of the study area is the absence of delta formation. Rejuvenation of the catchment area, closely linked with the west coast faulting and later adjustment may, in all probability, be the reason for the youthful characters of the rivers, while high energy shoreline appears to have prevented delta formation in the river mouths.

The general drainage pattern of these rivers are dendritic. Most river courses are straight which indicates nothing but the structural control. General course of the rivers coincides with the prominent lineament directions (NW-SE and NE-SW).

2.5   Soils and Vegetation
2.5.1 Soil Types

The geology and the climate have direct bearing on the soil and vegetation types of the area. The soil type most predominant in the study area, especially in the midlands, is lateritic one (Figure 2.4), which is a typical weathering product under tropical humid conditions. It shows the development of AB(c) profiles which are deep to very deep. The B horizon is well developed in most cases with abundant ferruginous and quartz
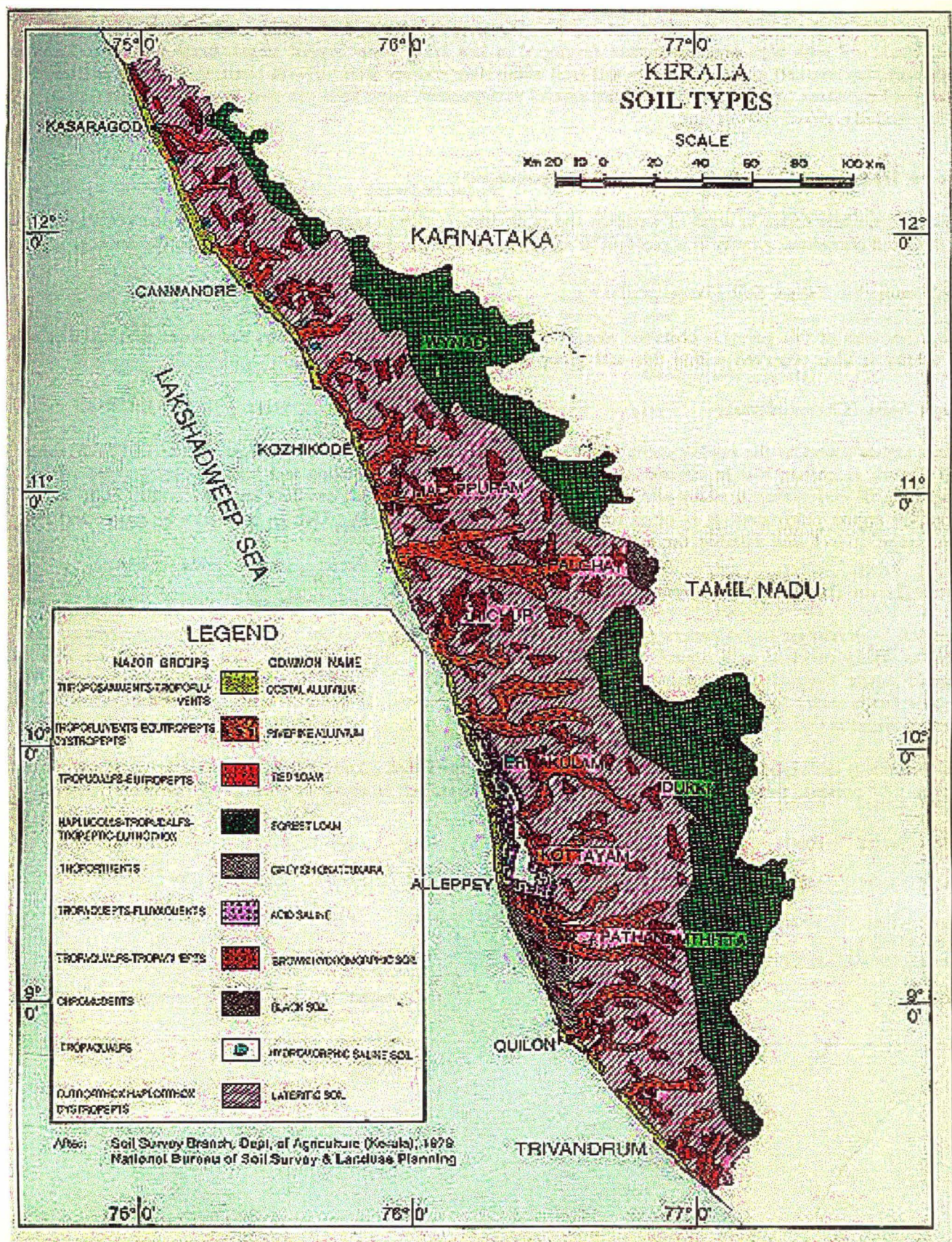
Figure 2.4 : Soil Map of the Study Area

gravels. Though this soil, in general, is acidic and poor in available N, P, potash and organic matter, it is well drained and widely cultivated.

The other dominant soil type in the study area is forest loam (Hapludolls - Tropudalfs - Tropeptic - Eutrothox) type of soil which covers the eastern part of the study area on the weathered crystalline rocks. Because of the presence of large amount of organic matter derived from decomposed leaves, the soil is dark reddish brown to black in colour. It is rich in N, but poor in bases.

Along river valleys there are well developed belt of Riverine Alluvium (Tropofluvents - Eutropepts - Dystropepts) which cut across the lateritic soil. It is very fertile having high water holding capacity and plant nutrients which are regularly replenished during monsoon.

Patches of Brown Hydromorphic soil (Tropaqualphs - Tropaquepts) are observed in areas of wetlands and is moderately rich in organic matter, N and potash and deficient in lime and phosphate.

The another soil type which is found only in the districts of Alleppey and Quilon is Greyish Onattukara (Troporthents). This grey colour soil is generally coarse grained, highly porous with limited capacity for retaining water and fertilizers. These soils are acidic and are extremely deficient in major plant nutrients.

2.5.2 Agro-Ecological Regions

The study area forms part of Agro-Ecological region 19 (Western Ghats and coastal per humid ecoregion) with red and lateritic and alluvium derived soils having a growing period of 210 to 270 days and more (Sehgal et al., 1992); however a small area around Chinnar in Idukki districts falls under Agro-Ecological region 8 (Eastern Ghats, Tamil Nadu uplands and Deccan plateau - hot semi - arid ecoregion) with red loamy soils having a growing period of 90 to 150 days.

2.5.3 Soil Moisture

The soil moisture regime over the state is ustic, with the soil moisture control section being dry in some or all parts for 90 cumulative days or more in most years, and moist in some part for more than 180 cumulative days. Based on the number of consecutive days that the soil moisture control section is moist in some or all parts , the ustic soil moisture regime is subdivided into Typic Tropustic and Udic Tropustic regimes (Wambeke, 1985). Both regimes are found in the study area.

2.5.4 Soil Temperature $TH-6764$

The soil temperature regime is isohyperthermic throughout the study area, because the mean annual soil temperature at a depth of 50 cm is $22°C$ or more, and the difference between mean summer (June to August) and mean winter (December to February) temperature is less than $5°C$.

2.5.5 Evapotranspiration

Evapotranspiration is high between March and May, monthly ET being as high as 173 mm in April and May at Palakkad. Myladumpura has the lowest annual ET of 1314 mm, and Kozhikode and Kannur have the highest, of 1730 mm. Palakkad also has a high annual ET of 1726 mm.

The soil water balance studies indicated that the soils have available water capacity 100 mm of which 87 mm is available for use by the crop. The study area in general experiences moisture deficit from middle or end of December to middle of April.

2.5.6 Natural Vegetation

The origin points of all the rivers are mainly covered by wet evergreen forest, moist deciduous forest and other unclassified plantations. The forest vegetation comprises tropical wet evergreen and semi-evergreen (50%) and tropical moist deciduous (33%) and tropical dry deciduous (2%) and forest plantations (13%).

2.5.7 Land-Utilization and Cropping Pattern

Kerala, with an area 1.18% of India , has a population of 29 million (1991 Census) or nearly 3.43% of that of the country. The resulting pressure on land has led to a cropping intensity in the study area. Net area sown is 57%. A general picture of land utilization in Kerala is given in Table - 2.2 &

Table - 2.2 : Land Utilization in Kerala 1991-92 (km^2)

Total Geographical area	3885
Forest	10815
Land put to non-agricultural uses	3014
Barren and uncultivable land	551
Permanent pasture and other grazing land	18
Land under tree crops not included in net area sown	343
Cultivable waste	928
Fallow other than current	267
Current fallow	439
Net area sown	22480
Area sown more than once	773
Total cropped area	30211

Source : Farm Guide, 1992
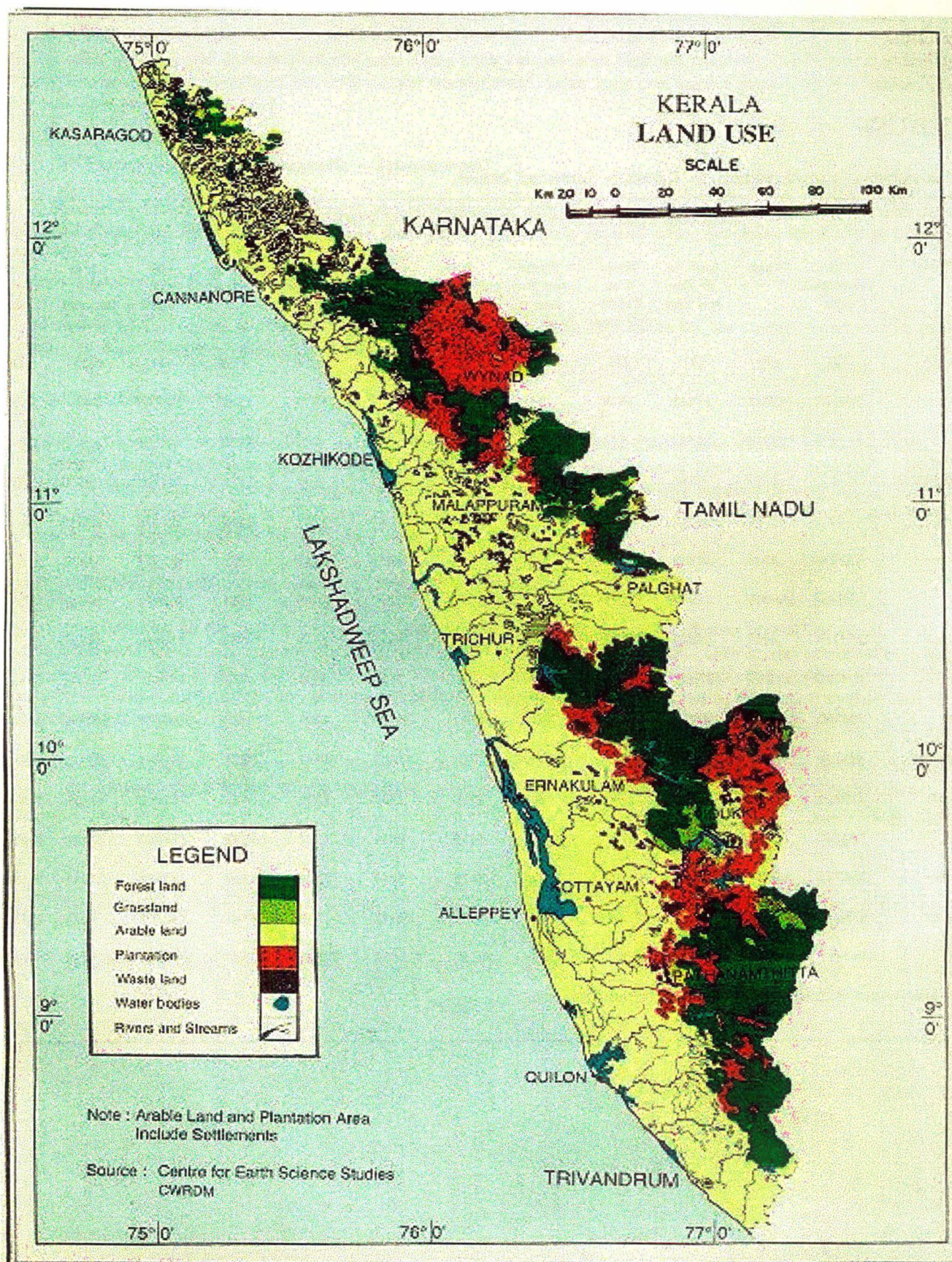
Figure 2.5 : Landuse Map of the Study Area

Figure - 2.5. The area under barren and uncultivable land includes laterite exposure and rock outcrops.

The lowlands of the coastal plains are devoted mainly to rice, coconut and banana; the midlands are chiefly cultivated to coconut, tapioca, rubber, arecanut, pepper and cashew, with rice being the main crop in the valleys.

The Palghat Gap having gently sloping lands with valleys grows rice as the primary crop, followed by coconut, groundnut, sugarcane and cotton.

Major part of the hills and uplands region is covered by forest, with small areas being used for cardamom, pepper and other spices . The lower portion of the hill ranges have rubber and coconut and the higher elevations tea, pepper and cardamom. Rice is the major crop of the valleys.

2.5.8 Socio- Economic Conditions

Density of population in the study area is 747 per sq. km. which is nearly three times that for the country. The land *per capita* is 0.14 ha and cultivated land *per capita* is only 0.11 ha. 46 percent of the holdings are marginal (<1ha), 21.55 % are small (1-2 ha), 15.28 % are semi- medium (2-4 ha), 7.41 % are medium (4-10 ha) and 9.66 % are large (>10 ha).

CHAPTER - 3
MATERIALS AND METHODS

3.1   FIELD METHODS

Rivers have various dynamic physiochemical and biological processes taking place in them. They carry fresh waters derived from rain fall and ground water. They carry suspended and dissolved materials derived from physical and chemical weathering of rocks in the catchment with anthropogenic pollutants. Systematic sampling of water and bed sediments were done in eleven rivers. The rivers and sampling location were chosen carefully in order to get maximum representation of the environment in the western ghat region. The water samples were collected in three seasons namely Premonsoon (March-April, 1997), Monsoon (August, 1997) and Post Monsoon (January, 1997). The sampling locations (Table - 3.1) are shown in Figure 3.1. The bed sediment sampling was done only once in Post Monsoon (January, 1997). The number after decimal increases downstream.

3.1.1 Water Samples

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

3.1.2. Bed Sediment Samples

Bed sediment samples were collected from the sampling locations by

Figure 3.1 : Location map of the study area

11. Chaliyar R.

Kozhikode

10. Kadalundi R.

9. Pulantod R.

8. Bharathapuzha R.

7. Chalakudi R.

5. Muvattupuzha R.

Cochin

6. Periyar R.

4. Manimala R.

Quilon

3. Pamba R.

2. Achenkovil R.

1. Kallada R.

INDIA

400   800 Km

ARABIAN SEA

BAY OF BENGAL

Lakshadweep
(India)

Andaman &
Nicobar
Islands
(India)

Trivandrum

● Water Samples

■ Bed Sediments
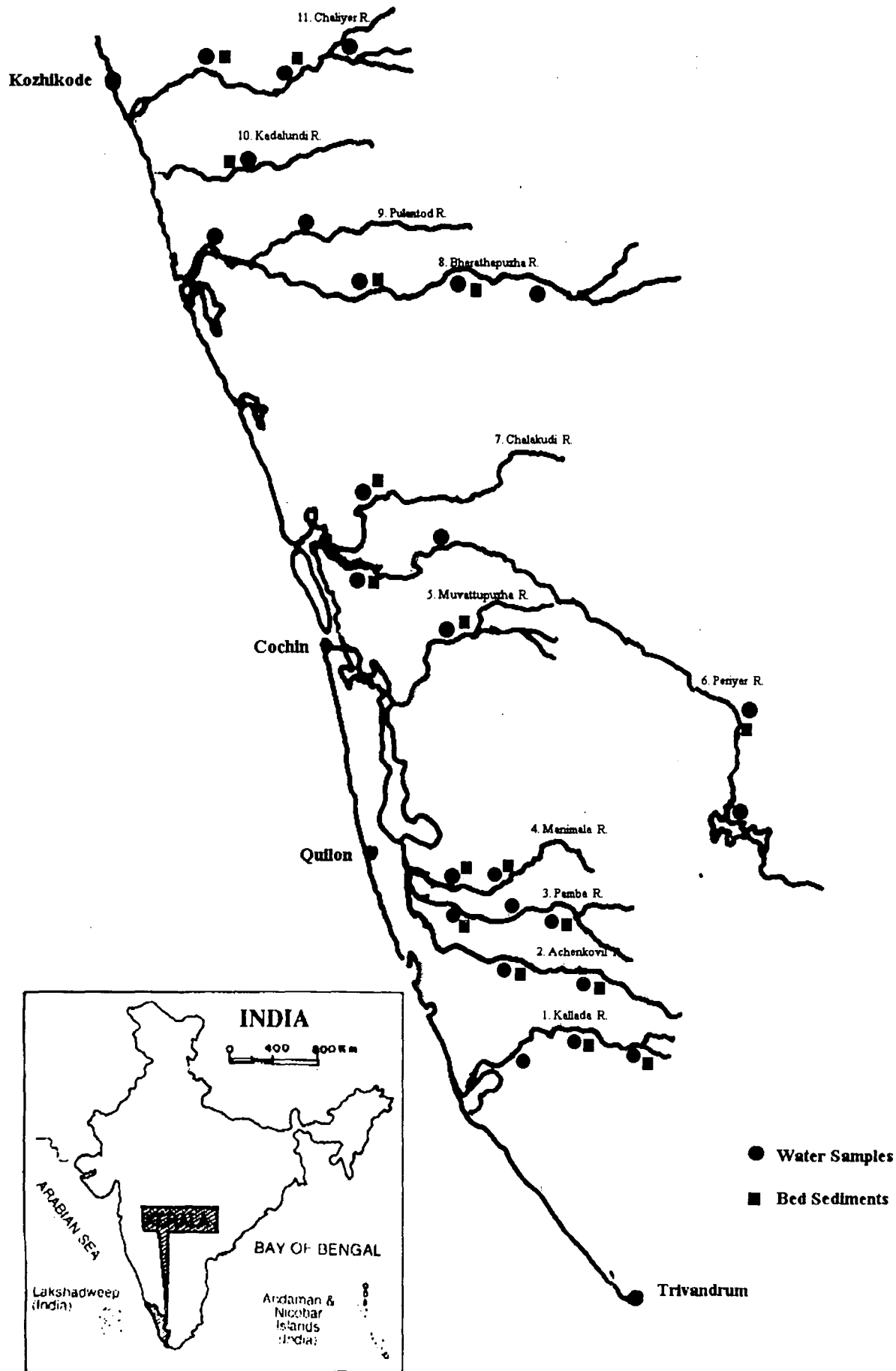
Table 3.1 : Sampling Locations for various seasons

Premonsoon			Monsoon			Post Monsoon		
2.1	Achenkovil	Konni	1.1	Kallada	Punalur	1.1	Kallada	Punalur
2.2	- do -	Pandalam	1.2	- do -	Pattanapuram	1.2	- do -	Pattanapuram
3.1	Pamba	Ranni	1.3	- do -	Shasthankotta	1.3	- do -	Shasthankotta
3.2	- do -	Chenganur	2.1	Achenkovil	Pandalam	2.1	Achenkovil	Tonallur
4.1	Manimala	Kattoor	3.1	Pamba	Ranny	3.1	Pamba	Ranny
6.1	Periyar	Kumily	3.2	- do -	Aramula	3.2	- do -	Aramula Temple
6.2	- do -	Neriyamangalam	3.3	- do -	Chenganur	3.3	- do -	Chenganur
6.3	- do -	Kaladi	4.1	Manimala	Mannar	4.1	Manimala	Tiruvalla
7.1	Chalakudi	Chalakudi	4.2	- do -	Near Sangam	5.1	Muvattupuzha	Muvattupuzha
8.1	Bharathapuzha	Ottapalam	4.3	- do -	Pulikeezhu	6.1	Periyar	Kaladi
8.2	- do -	Tritala	5.1	Muvattupuzha	Muvattupuzha	6.2	- do -	Alway
9.1	Pulantod	Pulantod	6.1	Periyar	Alwaye	8.1	Bharathapuzha	Cherutirutti
11.1	Chaliyar	Mokkam	6.2	- do -	Kaladi	8.2	- do -	Kuttipuram
11.2	- do -	Karimpuzha	7.1	Chalakudi	Chalakudi	10.1	Pamparangal	Manjeri
11.3	- do -	Mambad	8.1	Bharathapuzha	Cherutirutti	11.1	Chaliyar	Vazhikadavu
11.4	- do -	Mavur	8.2	- do -	Kuttipuram	11.2	- do -	Nilambur
			11.1	Chaliyar	Nilambur			
			11.2	- do -	Edavanna			
			11.3	- do -	Feroke			

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

3.2   LABORATORY METHODS

3.2.1 Suspended Matter Separation

Water sample bottles were shaken vigorously to make a homogeneous suspension. Known volume of this suspension was transferred immediately to the filtration unit. Sediments were collected on preweighed Millipore, 0.45 micron filter paper, which was dried to constant weight at 80°C. Then weight of total suspended matter (TSM) was calculated. The filtered water was used for analyzing cations, anions and silica content.

3.2.2 Water Analysis

pH and Conductivity

The pH and conductivity were measured in unfiltered water samples. The pH was measured by "Rachho" (Model No. 123) pH meter. The glass electrode was conditioned and calibrated with buffer solutions of pH 4, 7 and 9. The temperature of the instrument was set according to the temperature of the samples. The samples were stirred continuously to maintain homogeneity before noting the pH. Conductivity was measured in micro mhos/cm using Systronics Conductivity Meter 306. The instrument

was calibrated with 0.01 M KCl standard (1413 in mhos/cm at 25°C). The results are reported in mS/m.

Bicarbonate

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

Chloride

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

Fluoride

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

Sulphate

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

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

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

Phosphate

Phosphate was determined by the Ascorbic Acid method (APHA, 1985). Phosphate standards ranging from 0.1 to 3 mg/l were prepared from KH_2PO_4. 40 ml of each sample and standard solution was pipetted out in 50 ml volumetric flask and 5 ml of Molybdate Antimony solution (prepared by dissolving 4.8 gm of Ammonium Molybdate and 0.1 gm of Potassium. Antimony tartarate in 400 ml 4N H_2SO_4 and making the total volume to 500 ml with same acid) and 2 ml of Ascorbic Acid solution (2.0% w/v) was added and mixed well. The mixture was diluted to 50 ml and optical density was measured at 650 nm using Cecil Spectrometer (Model No. 594). A graph was plotted between concentrations of the standards and optical density and sample concentrations were obtained from this graph.

Dissolved Silica

The dissolved silica content was determined by the Molybdate Silicate Method (APHA, 1985). Silica standards were prepared, ranging from 0.1 to 10 mg/l from Sodium metasilicate nanohydrate. 20 ml of each sample and standard was pipetted out in 50 ml volumetric flask and 10 ml of Ammonium molybdate solution (prepared by dissolving 2 gm of Ammonium molybdate in 10 ml distilled water, 6 ml concentrated HCl was added and final volume was made upto 100 ml by distilled water) and 15 ml of Reducing Reagent (prepared by mixing 100 ml Metol sulphite solution, 60 ml 10% oxalic acid and 120 ml 25% Sulphuric acid and making the final volume to 300 ml by adding distilled water) was added and mixed well. Metol sulphite was prepared by dissolving 5 gm metol in 210 ml distilled

water and 3 gm Sodium sulphate was added and the volume was made upto 280 ml with distilled water. The samples were stirred properly and kept for 3 hrs. to complete the reaction. The optical density was measured at 650 nm using Cecil Spectrometer - 594. Graph between concentration of the standards and optical density was drawn and concentration of samples were recorded from it.

Calcium, Magnesium, Sodium and Potassium

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

3.2.3 Sediment analysis

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

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

Kjeldahl Nitrogen Analysis

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

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

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

Distillation process is done by transferring 10 ml of aliquot to reaction chamber and adding 5 ml Alkali mixture and starting distillation immediately. About 25 ml of distillate was collected in 5 ml Boric Acid-indicator solution. The distillate was titrated against N/140 HCl to a grey end point using microburette.

Present Kjeldahl Nitrogen was calculated using the following equation:

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

a =   ml of HCl used against sample

b =   ml of HCl used against blank

V =   ml of total digest titrated

v =   ml of digest distilled

s =   Weight of sediment taken

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

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

Carbon Analysis

Carbon was analysed using ELTRA (CS 1000) Carbon Analyser.

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

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

Analysis for the major and minor elements

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

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

(a) Solution 'A'

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

Silica Analysis

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

Ammonium molybdate solution was prepared by dissolving 1.875 gm. ammonium molybdate in 19 ml distilled water and adding 6 ml 20% (v/v) H_2SO_4 . The reducing reagent was prepared by dissolving 0.07 gm.

sodium sulphite in 1.0 ml distilled water and then 0.015 gm. 1-amino-2-naphthol-4-sulphonic acid was added and stirred well until dissolved. 9 ml of 10% (w/v) sodium bisulphite solution was added to it and mixed well.

Alumina Analysis

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

Phosphorus Analysis

Phosphorus in bed-sediments and suspended sediments were analysed from solution 'A'. Phosphate was determined by ascorbic acid method as

described in water analysis section. The standards used in this case were standard soil samples, which were digested to make solution 'A' 40 ml of each solution 'A', and sediment standard was used for analysis.

(b) Solution 'B'

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

3.2.4 Bed sediment mineralogy

The bulk bed sediments were oven dried at 80°C. Homogenised fraction of these sediment was treated with 30% (v/v) H_2O_2 (Jackson, 1973). This treatment was done repeatedly until the bubbles stopped forming, even when heated on the hot plate. This treatment removed organic matter from the sediments.

Clay was separated from these organic free sediments with the help of Attenburough cylinder. This organic free clay fraction was crushed to fine powder with help of pestle and mortar made of agate. The slides were prepared by drop on slide technique (Gibbs, 1965). The samples were run on Philips X-ray Diffractometer (XRD) (Model PW 1140) using Cu (Kα radiation) source, proportional detector and Ni filter. The chart drive was 1 cm/min, goniometer 1°/min, range 400 cps and voltage 16 mV/35 KV were maintained.

The primary peaks of various minerals were identified by comparing 2θ values for highest intensity peak, as described by Lindholm (1987). The major peaks viz. mica, quartz and feldspar were normalised to 100 percent after calculating the respective peak areas. Then, the relative abundance of the minerals from these major groups was calculated in terms of percentages.

CHAPTER - 4

RESULTS AND DISCUSSIONS

4.1 WATER CHEMISTRY

River waters carry the product of chemical erosion in the form of dissolved salts. So to understand the chemical erosion process we need to decipher the message coded in their components. The following discussion based on the results (Table - 4.1-4.3) obtained from the analysis of three season water samples reveal lot of things about the chemical and mechanical erosion processes on the Western Ghats. The analytical precision is $\pm$ 5% except for few samples where it is around $\pm$ 8 % (Table 4.5-5.7).

pH, EC, TDS:

The pH in all the rivers under consideration is between 6.40 to 8.35. The seasonal variation also is not very significant with average pH for pre-monsoon, monsoon and post monsoon seasons is in the range of 7.00 - 7.6. It shows fairly neutral character of surface water of Kerala rivers. Short term control of pH in natural water is dominated by the carbonate equilibria.

Seasonal & spatial variation in EC is quite significant. Post monsoon samples are showing high values of EC (0.04-2.65 mS) because of increased concentration of dissolved ions as a consequence of intense evaporation during non- monsoon season. The same trend is being followed by TDS (39-165 mg/L) as it is nothing but the sum total concentration of all the ions dissolved in the solution. It can be calculated by multiplying 0.7 (for fresh water) with the EC (μS/cm). Alternatively it can also be calculated by

4.1 : Pre monsoon

$y = 1.1575x - 0.0356$
$R^2 = 0.9987$

4.2 : Monsoon

$y = 1.0391x + 0.0058$
$R^2 = 0.978$

4.3 : Post monsoon

$y = 0.9339x + 0.0961$
$R^2 = 0.9995$
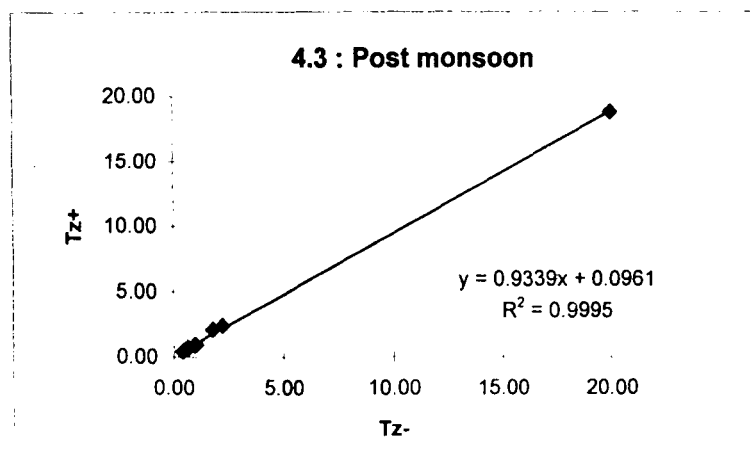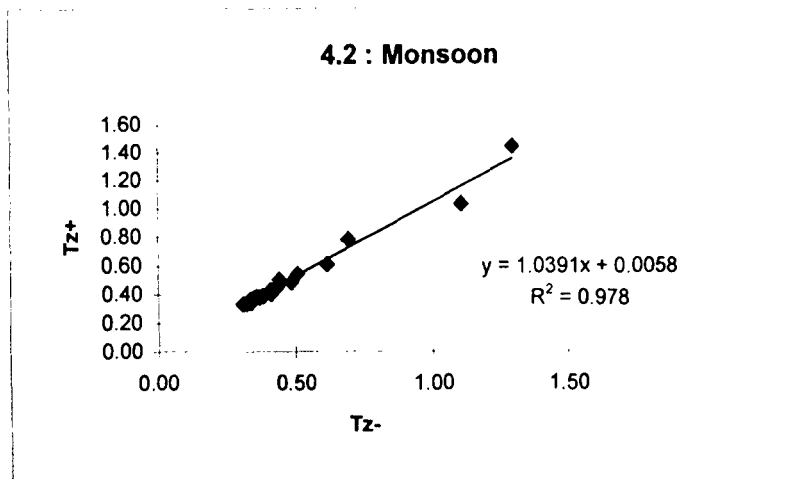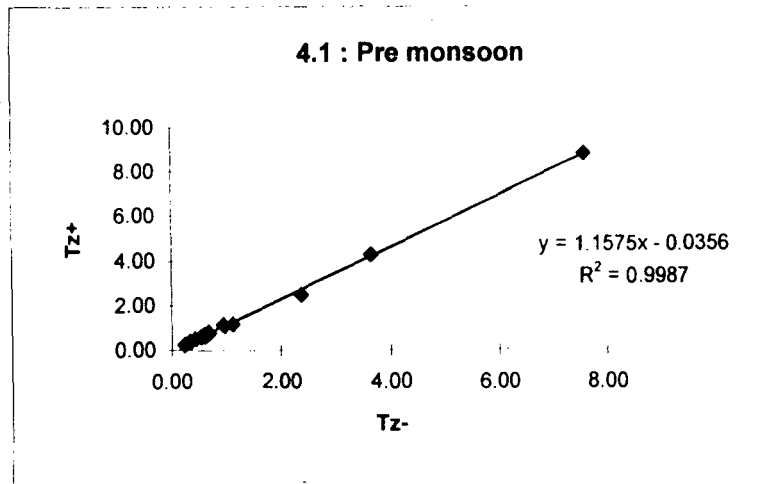
Figure 4.1, 4.2 4.3 : Graphs showing accuracy of analytical chemistry of the water samples of KeralaRivers

Table 4.1 : Water Chemistry of Kerala rivers

Pre-monsoon

Sl.No.	River Name	pH	EC(mS)	SiO_2	PO_4^{3-}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	TDS	TSM
2.1	Achenkovil	7.00	0.06	9.7	0.05	15.5	6.0	5.4	0.10	2.2	2.3	1.7	5.8	46.5	24.00
2.2	Do	7.43	0.08	11.4	0.10	19.4	7.6	6.9	0.08	3.0	3.3	1.5	7.2	57.5	16.67
3.1	Pamba	6.95	0.02	3.6	0.08	6.0	4.1	1.8	0.08	1.8	1.1	0.3	1.6	18.6	2.86
3.2	Do	6.70	0.03	4.2	0.09	8.9	5.3	2.5	0.07	2.5	1.6	0.4	2.6	25.7	20.00
4.1	Manimala	7.10	0.07	1.3	0.10	11.7	6.9	8.9	0.13	2.5	3.1	1.2	6.5	39.9	6.67
6.1	Periyar	7.35	0.10	9.7	0.09	10.2	3.7	12.2	0.19	2.7	2.3	1.1	6.2	45.7	NA
6.2	Do	7.38	0.07	8.9	0.10	23.3	6.9	5.2	0.11	4.3	3.7	1.1	5.0	54.3	17.14
6.3	Do	7.08	0.03	6.3	0.03	11.7	3.9	2.3	0.13	2.5	1.6	0.4	2.6	28.9	2.60
7.1	Chalakudi	7.15	0.05	6.0	0.04	13.7	4.7	3.7	0.14	2.2	2.5	1.0	3.6	35.4	8.57
8.1	Bharatpuzha	8.32	0.36	14.7	0.10	161.7	11.0	26.8	0.32	24.9	21.5	3.2	27.2	266.6	20.00
8.2	Do	8.00	0.23	12.9	0.06	114.8	9.2	10.2	0.25	13.0	13.3	3.4	14.8	179.0	2.50
9.1	Pulantod	7.26	0.07	13.5	0.09	23.3	6.6	5.4	0.13	3.2	4.2	2.0	5.7	60.9	16.00
11.1	Chaliyar	7.30	0.09	11.7	0.10	37.1	7.4	6.2	0.16	4.5	6.7	1.8	7.0	78.2	12.00
11.2	Do	7.52	0.10	23.5	0.11	44.4	3.7	5.3	0.13	4.1	6.3	1.5	7.5	92.4	11.43
11.3	Do	7.48	0.12	23.0	0.11	46.4	6.0	7.8	0.10	4.7	5.8	2.3	8.6	100.1	8.33
11.4	Do	7.65	1.44	13.6	0.08	36.7	52.1	208.5	0.11	13.9	46.0	8.6	94.0	459.7	5.71
Avg.		7.35	0.18	10.9	0.08	36.5	9.1	19.9	0.14	5.8	7.8	2.0	12.9	99.3	11.63

All values in mg/L, except pH & EC(mS)

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Table 4.2 : Water Chemistry of Kerala rivers

Monsoon

Sl.No.	River Name	pH	EC(mS)	SiO_2	PO_4^{3-}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	TDS	TSM
1.1	Kallada	6.54	0.08	11.5	0.05	13.4	3.9	6.4	0.06	2.9	1.7	0.6	4.3	42.0	35.56
1.2	Do	6.79	0.04	12.0	0.05	8.2	2.1	6.9	0.06	1.7	1.3	1.1	3.8	35.6	53.33
1.3	Do	6.86	0.09	10.4	0.06	8.2	6.7	29.5	0.02	2.6	3.9	2.3	12.1	73.0	22.22
2.1	Achenkovil	6.86	0.03	10.8	0.14	10.2	4.2	6.3	0.05	2.4	2.0	0.8	4.5	39.1	84.44
3.1	Pamba	7.05	0.02	8.5	0.05	6.4	2.8	4.8	0.07	1.5	1.2	0.3	3.5	27.7	48.89
3.2	Do	6.85	0.03	8.2	0.04	8.4	3.8	4.2	0.14	1.7	1.3	0.4	3.8	30.4	48.89
3.3	Do	7.35	0.02	8.1	0.17	7.6	4.1	4.6	0.16	1.6	1.5	0.6	3.8	30.6	71.11
4.1	Manimala	6.85	0.03	7.6	0.06	6.4	3.8	5.3	0.14	1.5	1.3	0.6	4.1	29.3	124.44
4.2	Do	6.58	0.03	8.6	0.06	6.4	1.9	6.0	0.03	1.2	1.1	0.5	3.9	28.6	0.00
4.3	Do	6.90	0.03	8.9	0.05	6.4	3.2	5.4	0.08	1.4	1.2	0.5	4.1	29.9	84.44
5.1	Muvatupuzha	7.05	0.03	8.5	0.06	8.2	11.8	4.4	0.06	2.9	2.2	0.6	4.7	40.5	35.56
6.1	Periyar	8.33	0.02	5.7	0.05	6.4	4.7	6.8	0.19	2.1	1.5	0.5	4.3	30.2	75.56
6.2	Do	6.74	0.03	8.2	0.04	12.2	3.4	5.7	0.05	2.4	1.9	0.3	4.1	35.9	35.56
7.1	Chalakudi	6.85	0.03	8.6	0.04	6.4	3.6	5.3	0.10	1.5	1.9	0.4	2.2	28.6	26.67
8.1	Bharatpuzha	7.25	0.10	12.2	0.05	51.6	4.5	12.4	0.08	8.4	8.2	1.3	7.4	97.8	62.22
8.2	Do	7.36	0.06	10.8	0.04	24.0	3.9	7.6	0.10	7.1	0.9	1.0	7.7	56.1	66.67
11.1	Chaliyar	6.95	0.04	12.7	0.06	15.2	2.1	3.7	0.16	1.6	1.4	0.3	4.5	40.1	106.67
11.2	Do	7.70	0.04	12.4	0.08	13.4	0.9	4.0	0.19	1.3	1.2	0.3	4.7	37.2	106.67
11.3	Do	6.80	0.04	3.0	0.02	19.9	4.8	6.6	0.06	4.0	1.7	0.8	5.7	42.7	53.33
Avg.		7.03	0.04	9.3	0.06	12.6	4.0	7.2	0.10	2.6	2.0	0.7	4.9	40.8	60.12

All values in mg/L, except pH & EC (mS)

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Table 4.3 : Water Chemistry of Kerala rivers

Post Monsoon

Sl.No.	River Name	pH	EC(mS)	SiO_2	PO_4^{3-}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	TDS	TSM
1.1	Kallada	7.29	0.04	11.5	0.01	10.7	5.1	5.4	0.17	2.1	1.3	0.8	5.0	39.9	4.00
1.2	Do	7.26	0.04	12.5	0.03	8.2	5.5	5.4	0.08	2.2	1.4	1.0	4.1	38.2	3.46
1.3	Do	6.40	2.65	11.0	0.02	18.2	47.4	663.5	0.04	20.9	21.8	126.6	291.3	1179.8	2.60
2.1	Achenkovil	7.43	0.06	13.7	0.03	18.2	4.5	7.6	0.07	3.4	2.4	1.4	5.2	53.1	5.29
3.1	Pamba	7.57	0.04	8.8	0.01	10.7	4.7	4.9	0.02	1.6	2.4	0.7	3.5	35.9	0.00
3.2	Do	7.40	0.04	9.3	0.02	10.7	5.5	5.6	0.14	2.5	2.2	0.9	3.7	37.9	8.74
3.3	Do	7.27	0.05	9.1	0.01	10.7	6.2	7.0	0.03	3.0	2.3	1.1	4.4	40.9	7.93
4.1	Manimala	7.55	0.05	11.0	0.01	10.7	9.6	8.3	0.04	2.9	2.9	1.3	5.4	49.2	9.52
5.1	Muvattupuzh	7.80	0.05	13.0	0.03	10.7	16.6	14.5	0.04	3.2	2.4	1.2	12.0	70.4	2.62
6.1	Periyar	8.05	0.05	12.0	0.10	15.7	5.6	5.1	0.07	3.3	2.4	1.0	4.6	46.8	2.62
6.2	Do	8.35	0.67	10.0	0.01	13.2	9.4	8.3	0.03	2.6	2.9	0.9	7.8	52.5	8.74
8.1	Bharatpuzha	7.80	0.42	16.0	0.21	98.2	6.2	16.6	0.31	14.8	13.0	1.7	12.4	164.6	4.33
8.2	Do	7.40	0.48	16.1	0.04	78.2	5.3	14.0	0.19	10.1	13.0	1.7	10.6	139.0	5.00
10.1	Kadalundi	7.69	0.07	16.5	0.03	20.7	7.8	6.1	0.07	3.2	3.3	1.3	5.8	61.5	1.82
11.1	Chaliyar	7.82	0.24	30.2	0.04	38.2	10.4	4.7	0.07	6.0	4.0	1.1	6.5	95.2	24.91
11.2	Chaliyar	8.02	0.23	29.4	0.08	35.7	14.7	4.5	0.05	5.3	4.9	0.6	6.0	95.9	4.35
Avg.		7.57	0.32	14.4	0.04	25.6	10.3	48.8	0.09	5.4	5.2	9.0	24.3	137.6	5.99

All values in mg/L; except pH & EC (mS)

Table 4.4 : Correlation coefficient matrix of variables determining water chemistry of Kerala Rivers

Premonsoon

	pH	EC	SiO_2	PO_4^{3-}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	Ca^{2+}	Mg^{2+}	K^+	Na^+
pH	1.00											
EC	0.42	1.00										
SiO_2	0.58	0.22	1.00									
PO_4^{3-}	0.27	-0.01	0.46	1.00								
HCO_3^-	0.90	0.24	0.45	0.19	1.00							
SO_4^{2-}	0.31	0.99	0.14	-0.02	0.14	1.00						
Cl^-	0.29	0.99	0.15	-0.03	0.10	0.99	1.00					
F^-	0.79	0.10	0.19	0.02	0.86	-0.01	-0.02	1.00				
Ca^{2+}	0.87	0.56	0.33	0.14	0.91	0.47	0.44	0.78	1.00			
Mg^{2+}	0.59	0.97	0.30	0.05	0.46	0.94	0.93	0.30	0.73	1.00		
K^+	0.56	0.96	0.37	0.06	0.39	0.94	0.92	0.22	0.63	0.97	1.00	
Na^+	0.43	1.00	0.22	0.01	0.26	0.99	0.99	0.12	0.58	0.98	0.96	1.00

Monsoon

	pH	EC	SiO_2	PO_4^{3-}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	Ca^{2+}	Mg^{2+}	K^+	Na^+
pH	1.00											
EC	-0.09	1.00										
SiO_2	-0.08	0.46	1.00									
PO_4^{3-}	0.15	-0.18	0.20	1.00								
HCO_3^-	0.12	0.70	0.30	-0.19	1.00							
SO_4^{2-}	0.03	0.18	-0.26	0.01	0.01	1.00						
Cl^-	-0.06	0.67	0.15	-0.06	0.17	0.28	1.00					
F^-	0.70	-0.33	-0.01	0.21	-0.04	-0.28	-0.42	1.00				
Ca^{2+}	0.15	0.72	0.16	-0.24	0.90	0.24	0.27	-0.18	1.00			
Mg^{2+}	0.04	0.73	0.27	-0.04	0.78	0.27	0.52	-0.22	0.66	1.00		
K^+	-0.08	0.73	0.21	0.01	0.32	0.33	0.92	-0.46	0.45	0.57	1.00	
Na^+	0.06	0.76	0.20	-0.09	0.39	0.32	0.89	-0.31	0.52	0.50	0.88	1.00

Post Monsoon

	pH	EC	SiO_2	PO_4^{3-}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	Ca^{2+}	Mg^{2+}	K^+	Na^+
pH	1.00											
EC	-0.56	1.00										
SiO_2	0.33	-0.07	1.00									
PO_4^{3-}	0.32	-0.02	0.31	1.00								
HCO_3^-	0.14	0.11	0.41	0.75	1.00							
SO_4^{2-}	-0.54	0.91	0.03	-0.11	-0.09	1.00						
Cl^-	-0.70	0.96	-0.14	-0.11	-0.06	0.94	1.00					
F^-	-0.03	-0.06	0.05	0.67	0.77	-0.27	-0.15	1.00				
Ca^{2+}	-0.48	0.84	0.13	0.42	0.57	0.72	0.78	0.37	1.00			
Mg^{2+}	-0.51	0.86	0.07	0.32	0.55	0.71	0.79	0.33	0.98	1.00		
K^+	-0.71	0.96	-0.14	-0.11	-0.07	0.94	1.00	-0.15	0.77	0.78	1.00	
Na^+	-0.69	0.96	-0.13	-0.10	-0.05	0.95	1.00	-0.14	0.79	0.79	1.00	1.00

summing up all the dissolved ions concentration. From correlation matrix (table 4.4) it is quite obvious that in pre-monsoon and post monsoon samples EC shows very good correlation with all the major ions except HCO_3^- & SiO_2 where it is showing very bad correlation, but in the monsoon samples it is showing fairly good correlation with HCO_3^- (r = 0.70) and satisfactory correlation with SiO_2 (r = 0.46). It may be explained by the extensive weathering of carbonate and silicate rocks in monsoon which results in increase in their concentration and so the increase in EC. There is seasonal variation observed in correlation between EC and TDS (Figure 4.4).

Bicarbonate

HCO_3^- is one of the major ions in the surface water. It is basically a measure of chemical weathering (Subramanian, 1979). Raymahashay, 1987 concluded that river water is the imprint of complex atmosphere-hydrosphere-lithosphere interaction. The possible sources of HCO_3^- in surface water are atmospheric CO_2, dissolution of limestone and dolomite, weathering of primary and secondary minerals and organic activities (Garrel & Mackenzie, 1971).

There is wide spatial variation observed in the concentration of HCO_3^- in Kerala rivers although the seasonal variation is not that significant. The HCO_3^- concentration is varying in the range of 6.00 mg/L to 47 mg/L, except for samples from Bharathapuzha rivers where the values

Pre-monsoon

TDS (mg/L)

EC (mS)

Monsoon

TDS (mg/L)

EC (mS)

Post monsoon

TDS (mg/L)

EC (mS)
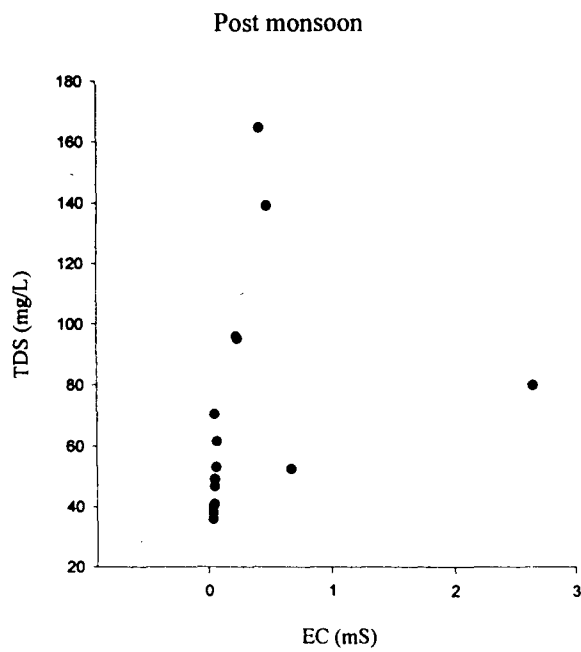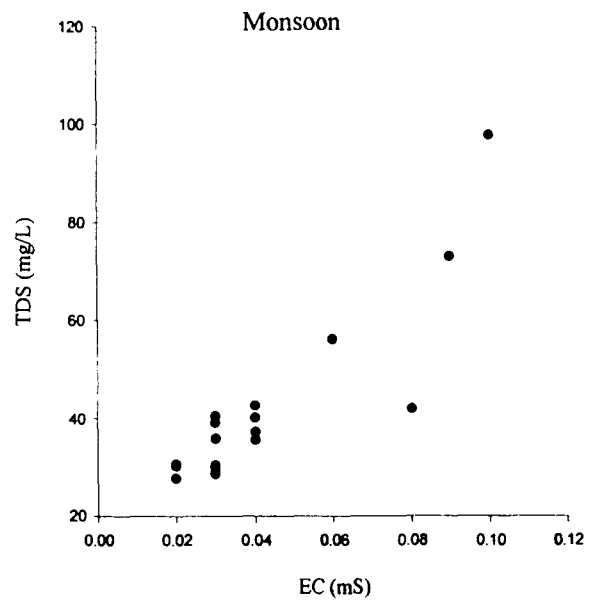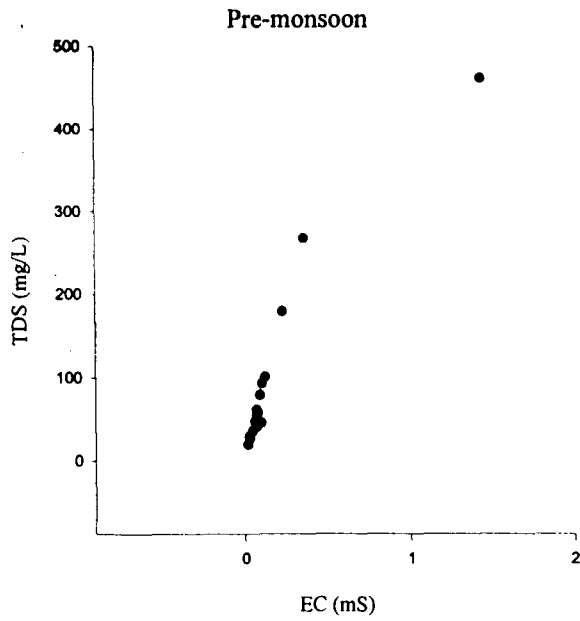
Figure 4.4 : Seasonal trend in correlation between EC and TDS

Table 4.5 : Water Chemistry of Kerala Rivers

Premonsoon

Sl.No.	River	HCO_3^-	SO_4^{2+}	Cl⁻	F⁻	Ca^{2+}	Mg^{2+}	K^+	Na^+	Tz-	Tz+	d%	$(Ca^{2+}+Mg^{2+})/(Na++K+)$
2.1	Achenkovil	0.25	0.13	0.15	0.01	0.11	0.19	0.04	0.25	0.54	0.59	4.86	1.01
2.2	Do	0.32	0.16	0.19	0.00	0.15	0.27	0.04	0.31	0.68	0.78	6.70	1.22
3.1	Pamba	0.10	0.08	0.05	0.00	0.09	0.09	0.01	0.07	0.24	0.26	3.44	2.35
3.2	Do	0.15	0.11	0.07	0.00	0.12	0.13	0.01	0.11	0.33	0.38	6.57	2.05
4.1	Manimala	0.19	0.14	0.25	0.01	0.12	0.25	0.03	0.28	0.60	0.69	7.28	1.19
6.1	Periyar	0.17	0.08	0.34	0.01	0.13	0.19	0.03	0.27	0.60	0.62	1.41	1.08
6.2	Do	0.38	0.14	0.15	0.01	0.22	0.30	0.03	0.22	0.68	0.77	5.97	2.09
6.3	Do	0.19	0.08	0.06	0.01	0.12	0.13	0.01	0.11	0.35	0.38	4.51	2.07
7.1	Chalakudi	0.22	0.10	0.10	0.01	0.11	0.20	0.03	0.16	0.43	0.50	6.75	1.71
8.1	Bharatpuzha	2.65	0.23	0.76	0.02	1.24	1.76	0.08	1.18	3.66	4.27	7.75	2.38
8.2	Do	1.88	0.19	0.29	0.01	0.65	1.09	0.09	0.65	2.38	2.47	1.91	2.38
9.1	Pulantod	0.38	0.14	0.15	0.01	0.16	0.34	0.05	0.25	0.68	0.81	8.36	1.68
11.1	Chaliyar	0.61	0.15	0.17	0.01	0.22	0.55	0.05	0.30	0.95	1.12	8.37	2.21
11.2	Do	0.73	0.08	0.15	0.01	0.20	0.51	0.04	0.33	0.96	1.08	5.67	1.96
11.3	Do	0.76	0.13	0.22	0.01	0.24	0.48	0.06	0.37	1.11	1.15	1.47	1.65
11.4	Do	0.60	1.08	5.88	0.01	0.69	3.77	0.22	4.09	7.57	8.77	7.31	1.04

All values in meq/L

Table 4.6 : Water Chemistry of Kerala Rivers

Monsoon

Sl.No.	River	HCO$_3^-$	SO$_4^{2+}$	Cl$^-$	F$^-$	Ca^{2+}	Mg^{2+}	K$^+$	Na$^+$	Tz-	Tz+	d%	(Ca^{2+}+Mg^{2+})/ (Na++K+)
1.1	Kallada	0.22	0.08	0.18	0.00	0.14	0.14	0.02	0.19	0.49	0.48	-0.16	1.38
1.2	Do	0.13	0.04	0.20	0.00	0.09	0.11	0.03	0.17	0.38	0.39	1.27	0.99
1.3	Do	0.13	0.14	0.83	0.00	0.13	0.32	0.06	0.53	1.11	1.03	-3.49	0.77
2.1	Achenkovil	0.17	0.09	0.18	0.00	0.12	0.17	0.02	0.20	0.44	0.50	6.79	1.31
3.1	Pamba	0.10	0.06	0.14	0.00	0.08	0.10	0.01	0.15	0.31	0.33	4.20	1.11
3.2	Do	0.14	0.08	0.12	0.01	0.09	0.11	0.01	0.17	0.34	0.37	3.90	1.11
3.3	Do	0.13	0.09	0.13	0.01	0.08	0.12	0.01	0.16	0.35	0.38	3.54	1.13
4.1	Manimala	0.10	0.08	0.15	0.01	0.08	0.11	0.01	0.18	0.34	0.37	4.27	0.94
4.2	Do	0.10	0.04	0.17	0.00	0.06	0.09	0.01	0.17	0.32	0.33	2.35	0.85
4.3	Do	0.10	0.07	0.15	0.00	0.07	0.10	0.01	0.18	0.33	0.36	4.49	0.88
5.1	Muvatupuzha	0.13	0.25	0.12	0.00	0.14	0.18	0.02	0.20	0.51	0.54	3.29	1.50
6.1	Periyar	0.10	0.10	0.19	0.01	0.11	0.12	0.01	0.19	0.41	0.43	2.43	1.14
6.2	Do	0.20	0.07	0.16	0.00	0.12	0.15	0.01	0.18	0.43	0.46	3.02	1.47
7.1	Chalakudi	0.10	0.08	0.15	0.01	0.08	0.16	0.01	0.10	0.34	0.34	0.92	2.15
8.1	Bharatpuzha	0.85	0.09	0.35	0.00	0.42	0.67	0.03	0.32	1.30	1.44	5.32	3.07
8.2	Do	0.39	0.08	0.21	0.01	0.35	0.07	0.03	0.34	0.70	0.79	6.02	1.17
11.1	Chaliyar	0.25	0.04	0.10	0.01	0.08	0.12	0.01	0.20	0.41	0.40	-0.57	0.98 *
11.2	Do	0.22	0.02	0.11	0.01	0.07	0.10	0.01	0.20	0.37	0.38	1.80	0.80
11.3	Do	0.33	0.10	0.19	0.00	0.20	0.14	0.02	0.25	0.62	0.61	-0.51	1.27

All values in meq/L

Table 4.7 : Water Chemistry of Kerala Rivers

Post Monsoon

Sl.No.	River	HCO_3^-	SO_4^{2+}	Cl^-	F^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	Tz-	Tz+	d%	$(Ca^{2+}+Mg^{2+})/$ $(Na++K+)$
1.1	Kallada	0.18	0.11	0.15	0.01	0.10	0.11	0.02	0.22	0.44	0.45	0.84	0.88
1.2	Do	0.13	0.11	0.15	0.00	0.11	0.12	0.03	0.18	0.40	0.43	3.21	1.12
1.3	Do	0.30	0.99	18.71	0.00	1.04	1.79	3.24	12.67	20.00	18.74	-3.25	0.18
2.1	Achenkovil	0.30	0.09	0.21	0.00	0.17	0.20	0.04	0.22	0.61	0.63	1.70	1.42
3.1	Pamba	0.18	0.10	0.14	0.00	0.08	0.20	0.02	0.15	0.41	0.45	4.70	1.65
3.2	Do	0.18	0.11	0.16	0.01	0.12	0.18	0.02	0.16	0.46	0.48	2.85	1.65
3.3	Do	0.18	0.13	0.20	0.00	0.15	0.19	0.03	0.19	0.50	0.56	5.19	1.56
4.1	Manimala	0.18	0.20	0.23	0.00	0.14	0.24	0.03	0.23	0.61	0.65	2.99	1.44
5.1	Muvattupuzh	0.18	0.35	0.41	0.00	0.16	0.19	0.03	0.52	0.93	0.90	-1.60	0.65
6.1	Periyar	0.26	0.12	0.15	0.00	0.16	0.19	0.03	0.20	0.53	0.59	5.30	1.57
6.2	Do	0.22	0.19	0.23	0.00	0.13	0.24	0.02	0.34	0.65	0.73	5.73	1.01
8.1	Bharatpuzha	1.61	0.13	0.47	0.02	0.74	1.06	0.04	0.54	2.23	2.39	3.33	3.10
8.2	Do	1.28	0.11	0.39	0.01	0.50	1.06	0.04	0.46	1.80	2.07	7.05	3.10
10.1	Kadalundi	0.34	0.16	0.17	0.00	0.16	0.27	0.03	0.25	0.68	0.71	2.34	1.51
11.1	Chaliyar	0.63	0.22	0.13	0.00	0.30	0.33	0.03	0.28	0.98	0.94	-2.22	2.00
11.2	Chaliyar	0.59	0.31	0.13	0.00	0.27	0.40	0.01	0.26	1.02	0.94	-3.97	2.42

All values in meq/L

are quite high (114mg/L-162mg/L) for pre-monsoon samples. For the monsoon seasons also the samples from Bharathapuzha rivers are showing comparatively higher values (24mg/L-52mg/L) than other river samples (6.40 mg/L-20 mg/L). For post monsoon season also the samples from Bharathapuzha rivers are showing values in the range 78mg/L-99mg/L, whereas the samples from other rivers are showing HCO_3^- values in the range 8 mg/L-40mg/L. The high values of HCO_3^- in Bharathapuzha river can be due to abundance of HCO_3^- rocks (dolomite and limestone) in the Palghat gap through which the river drains. But if we closely look at the data for bicarbonate a very interesting trend is observed in HCO_3^- concentration for all the seasons. Around and above Palghat gap there is significant increase in the values of HCO_3^- in the water. On the basis of this preliminary study it is difficult to explain the exact reason of this anomaly because geology and soil structures are almost same throughout the study area. But a careful study of land-use pattern in the study area (Table - 4.8) can help explaining this anomaly. The area around and north Palghat gap is much more irrigated than the other portion. So because of surface runoff from irrigated land may result in high concentration of HCO_3^- in the study area.

Raymahashay (1986) formulated a methodology to estimate the percentage of bicarbonate coming from different kind of rock weathering and he showed that the variation in the bicarbonate in the Indian rivers is primarily controlled by varying silicate fractions resulting from kaolinization reactions. Based on that methodology (Appendix-I), it was estimated that 60-75% of bicarbonates in Kerala rivers are coming from

LANDUSE

The districtwise landuse pattern in Kerala is furnished below:

LANDUSE CLASSIFICATION IN DISTRICTS OF KERALA (1985-86)

District	Total Geographical Area	Forest	Land Put To Non-agrl. Uses	Barren & un-Cultivable Land	Perma-nent Pas-tures & Grazing Land	Land Under Miscellaneous Tree Crops	Culti-vable Waste	Fallow Other than Current Fallow	Current Fallow	Net Area Shown	Area Sown More than Once	Total Cropped Area *(in hectars)*
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
Trivandrum	218600	49861	17815	2438	31	222	2378	1474	1364	143017	74994	218011
Quilon	251838	81438	23554	882	26	284	801	905	1153	142795	80676	223471
Pathanamthitta	268750	155214	9168	948	6	158	512	531	1112	101101	10260	111361
Alleppey	136058	..	26540	467	10	134	2091	1287	2510	103019	53015	156034
Kottayam	219550	8141	20169	2124	47	280	1259	2255	2702	182573	55933	238506
Idukki	514962	260907	13969	19215	2082	14320	35270	1245	1983	165971	30616	196587
Ernakulam	235319	8163	34628	2433	156	1114	5315	2312	2808	178430	68745	247175
Trichur	299390	103619	22653	2261	136	1361	5503	3087	4891	155879	63102	218981
Palghat	438980	136257	30223	13295	237	8581	24698	4204	5436	216049	102392	318441
Malappuram	363230	103417	19638	7845	320	3054	14463	4343	8876	201274	33921	235195
Kozhikode	233330	41386	17795	1944	111	2849	2949	1376	2451	162469	41876	204345
Waynad	212560	78787	5724	2078	144	3419	4841	1512	1852	114203	31174	145377
Cannanore	296797	48734	22365	14113	530	8575	6464	2348	4167	189501	21941	211442
Kasaragod	196133	5625	14360	13064	387	5877	19015	1159	1942	134704	6922	141626
STATE	3885497	1081509	278601	83107	4223	50228	125559	28038	-43247	2190985	675567	2866552

Source: Directorate of Economics & Statistics, Trivandrum.

Table 4.8 : Landuse pattern of the Study Area

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Carbonate weathering and 25-40% coming from silicate weathering (Table - 4.9-4.11). But this is true only for the rivers flowing below Palghat gap. Other rivers above Palghat gap, viz. Bharathapuzha, Kadalundi and Chaliyar get substantial amount of HCO_3- from silicate weathering. At some locations the contribution of silicate weathering is more than the carbonate weathering. The average value of pCO_2 in Kerala rivers is less than the atmospheric value of $10^{-3.5}$ atm which is in conformity with global trend. The $(HCO_3^-)_{Si}/SiO_2$ ratio is within the limit of kaolinisation (Rayamahashay, 1986).

The high values of HCO_3^- in all the rivers in pre- monsoon samples may be due to extensive evaporation and very low discharge during this period. It is quite clear from the data that 30-40% contribution to the TDS is from HCO_3^-.

Fairly good correlation between HCO_3^- and Ca^{2+} & Mg^{2+} in all the seasons shows their origin from the same source that is rock weathering (Figures 4.5 & 4.6).

Dissolved SiO_2

The contribution of dissolved silica to the surface water is entirely from silicate rocks. The dissolved silica in the surface water is present largely as H_4SiO_4. The data shows clearly the relatively high abundance of silicate rocks in Chaliyar and Bharathapuzha basin. Stallard (1980) found

Pre-monsoon

r = 0.91

Ca =0.13(HCO3) + 0.85

HCO$_3^-$

Monsoon

r = 0.90

Ca =0.16(HCO3) +0.58

HCO$_3^-$

Post Monsoon

r = 0.57

Ca=0.12(HCO3)+ 2.44

HCO3 (mg/L)
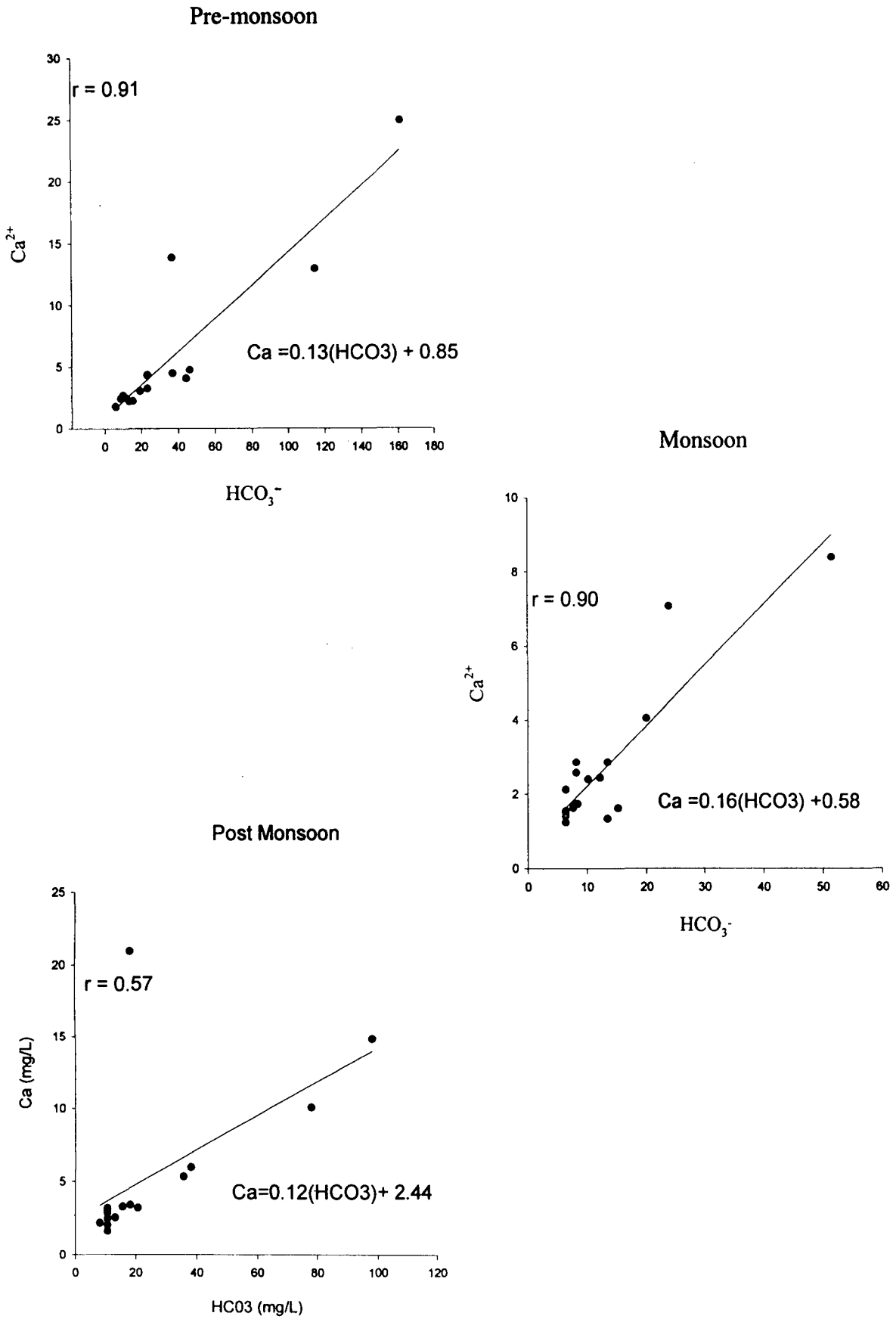
Figure 4.5 : Graph showing seasonal trend in correlation between HCO$_3^-$ & Ca^{2+}

55

Premonsoon

r = 0.55

Mg = 0.12(HCO$_3^-$)+3.35

HCO$_3^-$ (mg/L)

Mg (mg/L)

Monsoon

r = 0.78

Mg = 0.12 (HCO$_3^-$)+0.47

Mg^{2+} (mg/L)

HCO$_3^-$ (mg/L)

Post Monsoon

r = 0.55

Mg = 0.12(HCO$_3^-$) + 2.07

Mg (mg/L)

HCO3 (mg/L)
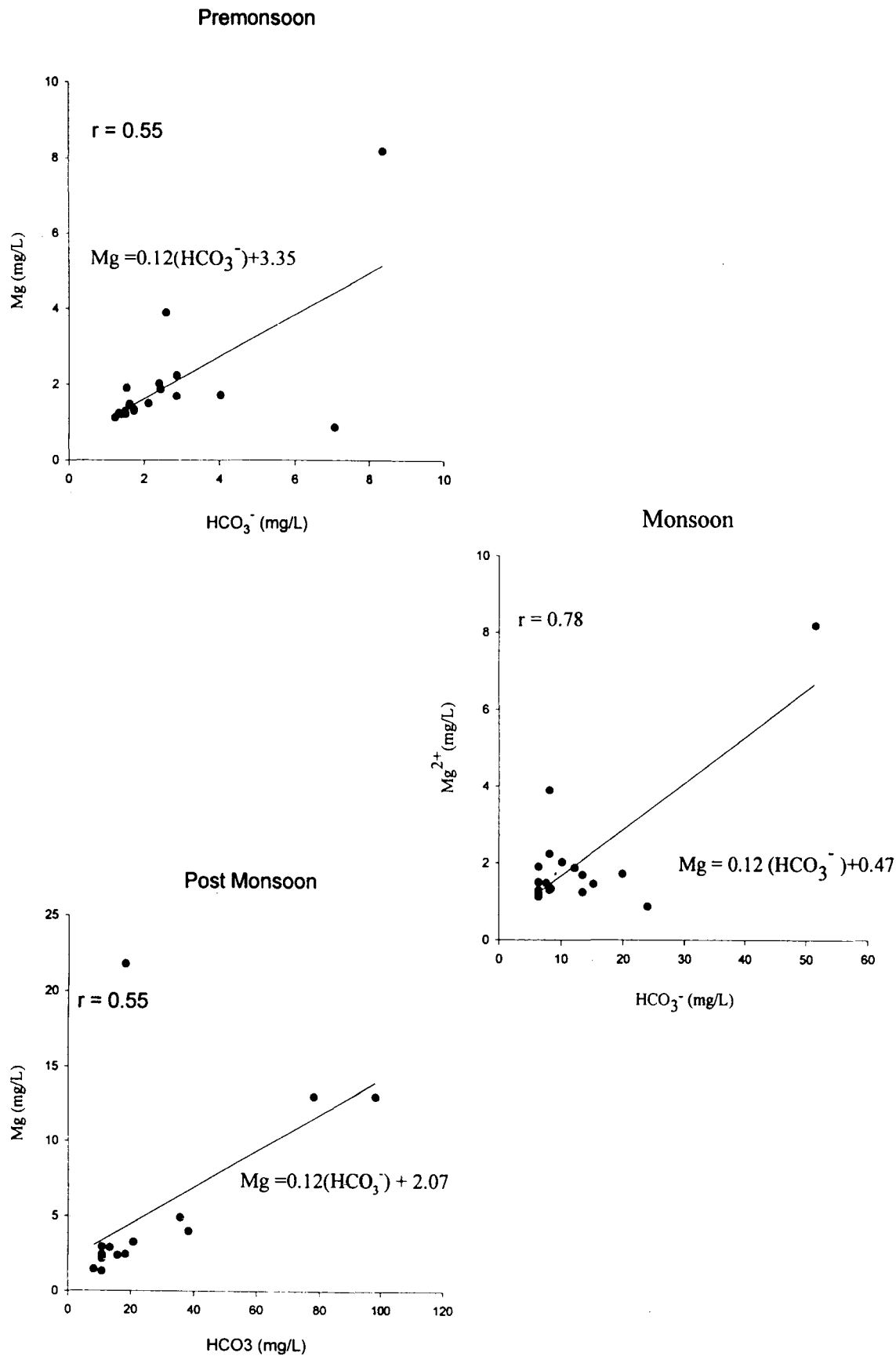
Figure 4.6 : Graph showing seasonal trend in the correlation between HCO$_3^-$ and M{

Table 4.9 : Bicarbonate derived from weathering in Kerala rivers.

Premonsoon

Sl.No.	River Name	(HCO₃)tot	(Ca)tot	(Mg)tot	(SiO₂)tot	log(pCO₂)	(HCO₃)c	(HCO₃)si	(HCO₃)si/SiO₂
2.1	Achenkovil	0.25	0.11	0.19	0.16	-2.69	0.16	0.10	0.60
2.2	Do	0.32	0.15	0.27	0.19	-3.03	0.22	0.10	0.51
3.1	Pamba	0.10	0.09	0.09	0.06	-3.06	0.10	0.00	-0.08
3.2	Do	0.15	0.12	0.13	0.07	-2.64	0.14	0.00	0.03
4.1	Manimala	0.19	0.12	0.25	0.02	-2.92	0.19	0.00	0.01
6.1	Periyar	0.17	0.13	0.19	0.16	-3.23	0.17	-0.01	-0.04
6.2	Do	0.38	0.22	0.30	0.15	-2.90	0.28	0.10	0.68
6.3	Do	0.19	0.12	0.13	0.10	-2.90	0.14	0.05	0.46
7.1	Chalakudi	0.22	0.11	0.20	0.10	-2.90	0.16	0.06	0.60
8.1	Bharatpuzha	2.65	1.24	1.76	0.25	-3.00	1.63	1.03	4.19
8.2	Do	1.88	0.65	1.09	0.22	-2.83	0.91	0.97	4.49
9.1	Pulantod	0.38	0.16	0.34	0.22	-2.78	0.26	0.12	0.55
11.1	Chaliyar	0.61	0.22	0.55	0.20	-2.62	0.39	0.22	1.14
11.2	Do	0.73	0.20	0.51	0.39	-2.76	0.36	0.37	0.95
11.3	Do	0.76	0.24	0.48	0.38	-2.70	0.37	0.39	1.03
11.4	Do	0.60	0.69	3.77	0.23	-2.97	2.02	-1.42	-6.26

All values in meq/l except SiO2 in mMoles/L

Table 4.10 : Bicarbonate derived from weathering in Kerala rivers.

Monsoon

Sl.No.	River Name	$(HCO_3)tot$	$(Ca)tot$	$(Mg)tot$	$(SiO_2)tot$	$log(pCO_2)$	$(HCO_3)c$	$(HCO_3)si$	$(HCO_3)si/SiO_2$
1.1	Kallada	0.22	0.14	0.14	0.19	-2.30	0.16	0.06	0.31
1.2	Do	0.13	0.09	0.11	0.20	-2.76	0.11	0.03	0.14
1.3	Do	0.13	0.13	0.32	0.17	-2.83	0.22	-0.09	-0.52
2.1	Achenkovil	0.17	0.12	0.17	0.18	-2.74	0.16	0.01	0.06
3.1	Pamba	0.10	0.08	0.10	0.14	-3.13	0.10	0.01	0.06
3.2	Do	0.14	0.09	0.11	0.14	-2.81	0.11	0.03	0.22
3.3	Do	0.13	0.08	0.12	0.13	-3.35	0.11	0.02	0.13
4.1	Manimala	0.10	0.08	0.11	0.13	-2.93	0.10	0.01	0.06
4.2	Do	0.10	0.06	0.09	0.14	-2.66	0.08	0.02	0.16
4.3	Do	0.10	0.07	0.10	0.15	-2.98	0.09	0.01	0.09
5.1	Muvatupuzha	0.13	0.14	0.18	0.14	-3.02	0.18	-0.05	-0.32
6.1	Periyar	0.10	0.11	0.12	0.10	-3.41	0.13	-0.02	-0.23
6.2	Do	0.20	0.12	0.15	0.14	-2.54	0.15	0.05	0.35
7.1	Chalakudi	0.10	0.08	0.16	0.14	-2.93	0.12	-0.01	-0.10
8.1	Bharatpuzha	0.85	0.42	0.67	0.20	-2.42	0.58	0.27	1.32
8.2	Do	0.39	0.35	0.07	0.18	-2.86	0.29	0.10	0.58
11.1	Chaliyar	0.25	0.08	0.12	0.21	-2.65	0.11	0.14	0.68
11.2	Do	0.22	0.07	0.10	0.21	-3.46	0.09	0.13	0.64
11.3	Do	0.33	0.20	0.14	0.05	-2.39	0.21	0.12	2.43

All values in meq/l except SiO2 in mMoles/L

Table 4.11 : Bicarbonate derived from weathering in Kerala rivers.

Post Monsoon

Sl.No.	River Name	(HCO₃)tot	(Ca)tot	(Mg)tot	(SiO₂)tot	log(pCO₂)	(HCO₃)c	(HCO₃)si	(HCO₃)si/SiO₂
1.1	Kallada	0.18	0.10	0.11	0.19	-3.15	0.12	0.06	0.29
1.2	Do	0.13	0.11	0.12	0.21	-3.23	0.13	0.01	0.03
1.3	Do	0.30	1.04	1.79	0.18	-2.03	1.49	-1.19	-6.49
2.1	Achenkovil	0.30	0.17	0.20	0.23	-3.06	0.21	0.09	0.41
3.1	Pamba	0.18	0.08	0.20	0.15	-3.43	0.14	0.03	0.24
3.2	Do	0.18	0.12	0.18	0.15	-3.26	0.16	0.01	0.09
3.3	Do	0.18	0.15	0.19	0.15	-3.13	0.19	-0.01	-0.08
4.1	Manimala	0.18	0.14	0.24	0.18	-3.41	0.20	-0.03	-0.14
5.1	Muvattupuzha	0.18	0.16	0.19	0.22	-3.40	0.20	-0.02	-0.10
6.1	Periyar	0.26	0.16	0.19	0.20	-3.43	0.20	0.06	0.29
6.2	Do	0.22	0.13	0.24	0.17	-3.11	0.19	0.03	0.16
8.1	Bharatpuzha	1.61	0.74	1.06	0.27	-2.69	0.97	0.64	2.39
8.2	Do	1.28	0.50	1.06	0.27	-2.39	0.80	0.49	1.81
10.1	Kadalundi	0.34	0.16	0.27	0.27	-3.26	0.23	0.11	0.42
11.1	Chaliyar	0.63	0.30	0.33	0.50	-3.12	0.35	0.28	0.55
11.2	Chaliyar	0.59	0.27	0.40	0.49	-3.35	0.36	0.23	0.47

All values in meq/l except SiO2 in mMoles/L

greater silica concentration in river basin underlain by sedimentary silicates (sandstones and shales), which releases less silica, because they consist largely of detrital materials (Qtz+Fs+Ca-silicates) that are basically resistant to weathering. So in the case of Chaliyar and Bharathapuzha rivers the weathering of the crystalline silicate rocks (granite, gneiss, charnockites) in the basin might have contributed to higher concentration (12-30 mg/L) of the dissolved silica. In all the seasons the SiO_2 concentration in these two rivers is more than the Indian average of 7 mg/L (Subramanian, 1987) and world average of 10.4 mg/L (Meybeck, 1979). For that matter, the average SiO_2 concentration in Kerala rivers is generally more than Indian average and somewhat comparable to world average. It may be because of the presence of the granitic and charnockite terrain in the study area.

Dissolved SiO_2 is not showing good correlation with any other parameters because of its altogether different origin and so the independence.

Sulphate

The presence of the SO_4^{2-} in the surface water is mainly due to drainage of mines and dissolution of gypsum. For the locations very near to the sea the concentration of SO_4^{2-} may be added through sea spray.

In the rivers of Kerala normally the values of SO_4^{2-} are fairly higher than major peninsular rivers of India due to proximity of Kerala rivers to the sea (Subramanian et al., 1987). The concentration in non monsoon season

varies between 5 and 50mg/L but during monsoon the range is 1-12mg/L. The good correlation of SO_4^{2-} with Cl^- & Na^+ in pre- and post monsoon samples substantiate the idea that it is because of proximity to the sea. It can also be observed that as we proceed away from the sea the concentration of SO_4^{2-} shows decreasing trend. But SO_4^{2-} is showing good correlation with Ca^{2+} and Mg^{2+} also which may be due to the weathering of gypsum rocks.

Chloride

The source of Cl^- in the surface water is mainly atmospheric input. The world average of Cl^- is 3.7 mg/L (Sarin and Krishnaswami, 1984) and the Indian average is 15 mg/L (Subramanian, 1983). The values of Cl- from Kerala rivers shows annual average of about 5.53 mg/L which is more than the world average and less than Indian average. The reason of higher values than the world average lies definitely in proximity of these rivers to the sea. The monsoon samples are showing very low values (3.5 mg/L - 29.5mg/L) obviously because of very high discharge during this period. In pre-monsoon and post monsoon period the locations near the river mouth are showing very high values because of increased influence of sea waves during lean season. As expected, Cl^- is showing extremely fantastic correlation with Na^+ and K^+.

Dissoloved P:

Generally the presence of phosphatic nodules (Vaidyanathan et al., 1990), extensive agricultural activity and urban effluents along the course of river, enhance the phosphate level.

Subramanian (1984) calculated Indian average and world average for the dissolved P as 0.12 mg/L and 0.06 mg/L respectively. The average PO_4^{3-} concentration in Kerala rivers is 0.03 mg/L. The lower value than Indian average is may be due to settling of insoluble phosphorus as a component of fertilizers used extensively due to intensive agricultural practices. The PO_4^{3-} does not show consistently good correlation with any of the parameters.

Fluoride

Like phosphate, fluoride also is not the major ion in surface water. The sources of F^- in surface water may be from weathering of fluorapatite minerals and effluent discharge from aluminium & cement factories. Deshmukh (1974) reported higher value (0.5 mg/L) for the river flowing through crystalline rocks like granite but the values for F^- in all the rivers of Kerala are very low (<0.15 ppm).

Calcium & Magnesium

The major source of Ca^{2+} and Mg^{2+} in the surface water is from weathering of rocks. For Ca^{2+} the sources are calcite, dolomite, calcium plagioclase and

gypsum. The sources for Mg are amphiboles, pyroxene, olivine, biotite as well as dolomite. Ca^{2+} and Mg^{2+} have similar behaviour as observed in the hydrosphere. The Ca^{2+} and Mg^{2+} ions in the surface water of the Kerala show seasonal variation but the spatial variation is not very significant. The concentration of Ca^{2+} non monsoon period varies between 2 and 21 mg/L while for monsoon it dips down to 1-9 mg/L. For Mg^{2+} the values vary between 1-45 mg/L during non-monsoon and 1-9 mg/L during monsoon period. The average values for both Ca^{2+} and Mg^{2+} are much lower than the average for Indian rivers (30mg/L for Ca^{2+} and 7.0 mg/L for Mg^{2+}). The concentration during monsoon reduces for obvious reason i.e. high discharge during the period. Ca^{2+} and Mg^{2+} show good correlation among themselves and also with bicarbonate in all the seasons (Figure 4.7).

Sodium and Potassium

Na^+ contributes to 13% of the TDS in monsoon with the seasonal variation in average concentration between 4.3 - 5.5 mg/L. While contribution of K^+ during monsoon is only around 2%. The seasonal variation in average concentration of K^+ is between 0.5 - 1.5 mg/L. Considering the monsoon samples as real representative sample, as we are getting very homogeneous results for the period, the spatial variation of Na^+ and K^+ concentration is in the very narrow range. The higher values of Na^+ and K^+ in the rivers north of Palghat gap coincides with higher values for dissolved SiO_2 in the same rivers. This coincidence substantiate the idea of dominant silicate weathering in the area.

Na^+ and K^+ show very good correlation among the two and with the Cl⁻ also in all the seasons indicating the influence of atmospheric input to the river and

r = 0.73

Mg =1.33(Ca) + 0.18

Mg^{2+}

Ca^{2+}

Monsoon

r = 0.66

Mg = 0.55(Ca)+ 0.52

Mg^{2+}

Ca^{2+}

Postmonsoon

r = 0.98

Mg=1.04(Ca)-0.51

Mg (mg/L)

Ca(mg/L)
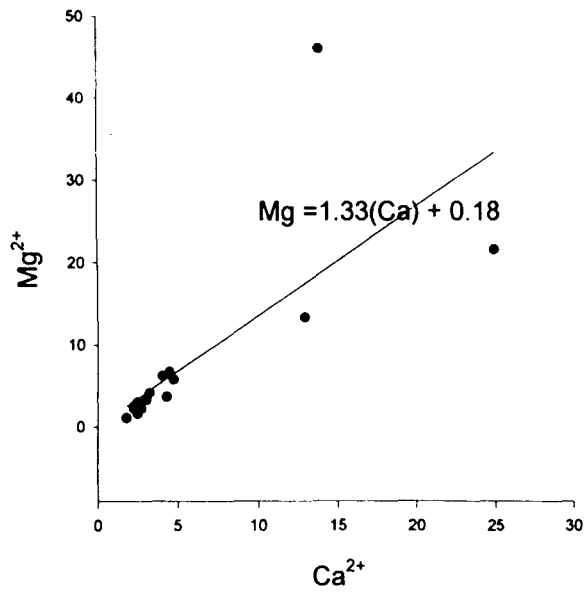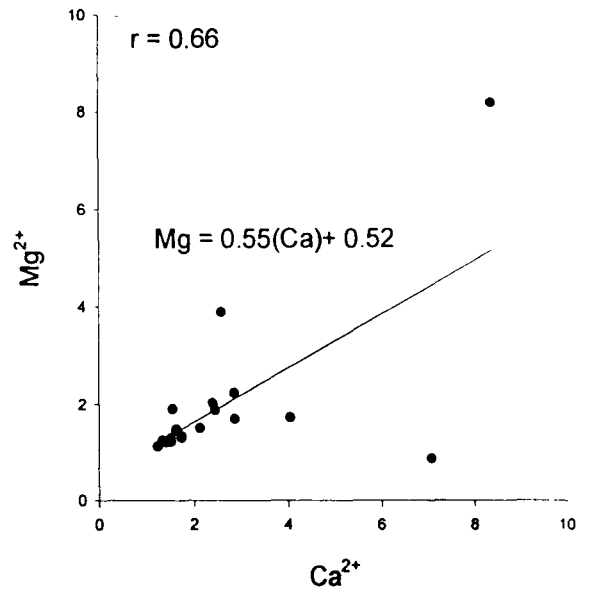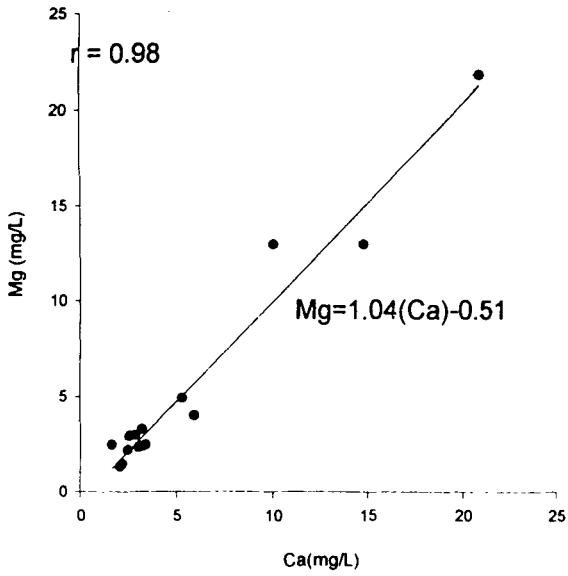
Figure 4.7 : Graph showing seasonal trend in correlation between Ca^{2+} and Mg^{2+}

marine recycling as the study area is very close to the sea. Depending on the environmental setting of the river basin and the ionic constituents involved, the significance of atmospheric inputs to the river solute content varies. Meybeck (1983) concluded that natural wet and dry fall-out contribute 53% Na^+ and 72% Cl^-. Garrels and Meckenzie (1971) estimated that 55% Cl^- in the river water is derived from rocks and the rest 45 % from recycling through the atmosphere.

The study area receives very high amount of rainfall (3-4 cm). So the rain water will definitely have a considerable influence on the river chemistry (Subramanian,1983). The other possible sources of Na^+, K^+ and Cl^- ions are ground water and surface runoff.

The ratio $(Ca^{2+} + Mg^{2+})$: $(Na^+ + K^+)$ is an index which is used to understand the relative dominance of carbonate and silicate weathering in a river basin (Sarin & Krishnaswamy, 1984). The ratio for Kerala rivers (Table - 4.5-4.7) suggest that silicate and carbonate weathering contributes almost equally during monsoon to these ions.

Classification of Kerala rivers on the basis of Gibbs classification (1970):

Gibbs (1970) classified rivers into three groups. These are (1) Low TDS, high Na/(Na+Ca) waters controlled by rainfall, (2) Intermediate TDS, low Na/(Na+Ca) waters controlled by rock weathering and high TDS, high Na/(Na+Ca) waters controlled by evaporation. Later work by Stallard and Edmond (1983), as discussed by Berner and Berner (1987) indicated that the three groups of Gibbs (1970) are, in fact, representative of three types of rock weathering. For

example, the first group occurs in unreactive drainage basins containing cation-poor siliceous sediments and soils which have undergone intensive weathering (e.g. Negro river). The second group includes most of the major rivers of the world and is controlled by weathering of sedimentary rocks dominated by a $CaCO_3$ component. As a result Ca^{2+} and HCO_3^- are the main dissolved ions. The Ganga river belongs to this group. The third group, on the other hand, represents weathering of evaporite beds. The TDS of these rivers (e.g. Colorado, Table:4.12) is typically more than 250 mg/l with relatively high concentration of Na^+, Cl^+ and SO_4^{2-}. So based on this classification Kerala rivers can be put under first type of rivers that is the rivers undergoing weathering of cation -poor rocks.

The seasonal variation in average concentration of major ions in water can be shown through the Figure 4.8.

4.2 Sediment Chemistry

Time and again it has been proved that study of bed sediments is essential for calculation of individual elemental fluxes and their mass balance studies. Sediment load represents the mechanical erosion in the basin. The finer sediments are exported while staying in suspension and called as suspended load and bigger ones move rolling and called as bed load. Although export of bed sediments is very less in comparison to the suspended load but still their study is important as they are the source and sink for many heavy metals. Due to practical problems study of one season bed sediments only could be undertaken for the present work. The results (Table - 4.13) and discussion follows:

Table 4.12 : Comparison of dissolved load of Kerala rivers with other rivers of the world

	Negro	Ganga	Colarado	Oubangui	Kerala R.
Ca	0.2	24.5	83	2.6	2.59
Mg	0.1	5	24	1.64	1.97
Na	0.4	4.9	95	1.45	4.49
K	0.3	3.1	5	-	0.65
Cl	0.3	3.4	82	0.78	6.51
SO_4	0.2	8.5	270	-	4.25
HCO_3	0.7	105	135	-	11.9
SiO_2	4.1	12.8	9.3	-	8.83
TDS	6	167	703	-	38.76
Na/Na+Ca	0.67	0.17	0.53	0.36	0.65
Na/Cl	1.33	1.44	1.16	1.86	0.74

Figure 4.8 : Seasonal Variation of Water Chemistry, TDS and TSM
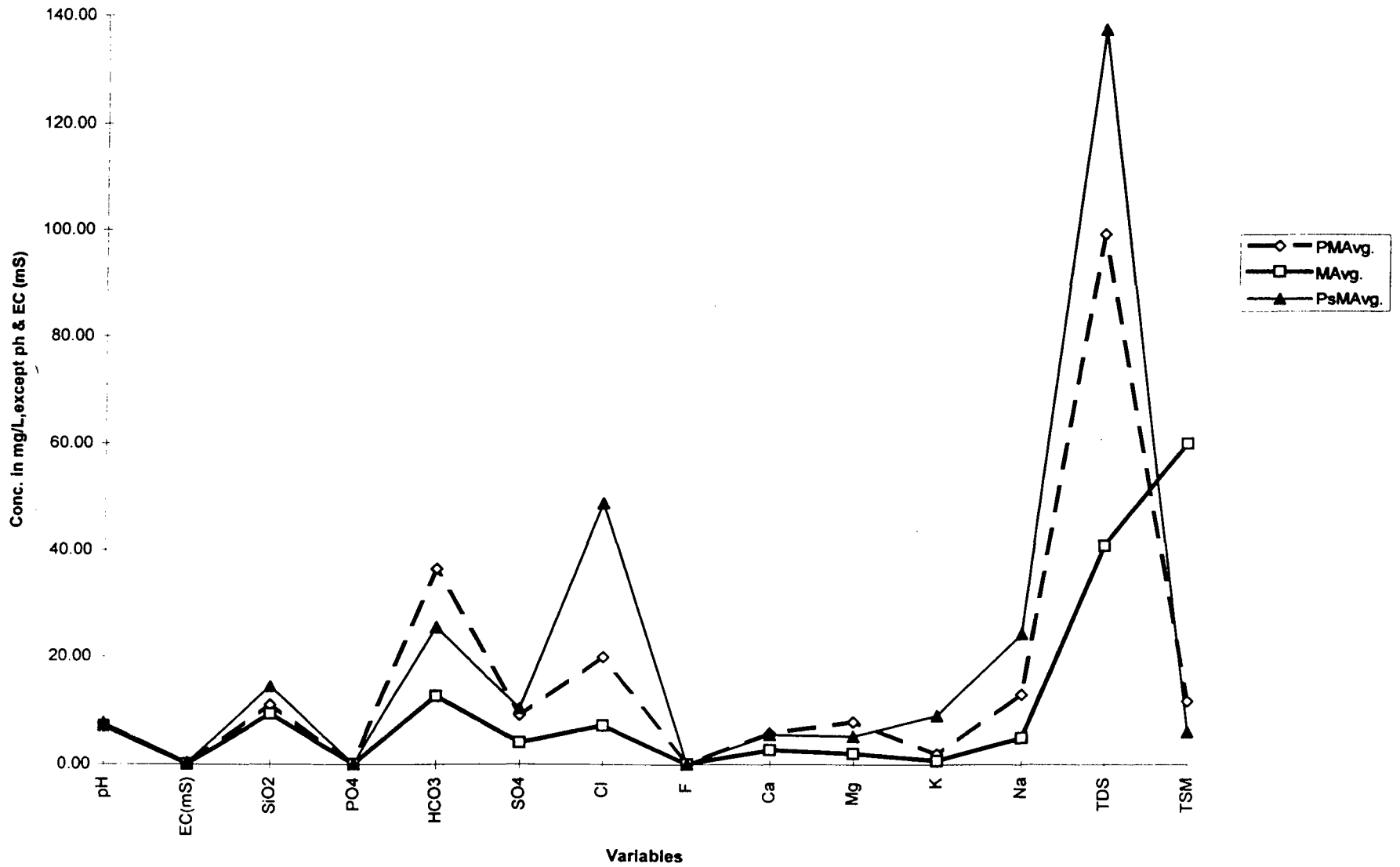
Table 4.13 : Chemistry of bed sediments of Kerala rivers

Sampling station	Sl.No.	Na	K	Ca	Mg	Al	Si	Fe	Mn	Zn	Cu	P	N
Punallur	1.1	8825	12819	6167	8075	34999	299084	27477	433	115	7	200	500
Shasthankota	1.2	9975	15707	6167	5035	31218	140154	23516	260	75	14	100	800
Pandalam	2.1	16450	12608	18500	8815	31294	234421	88867	693	65	21	1000	450
Tonallur	2.2	8800	15425	14800	7525	31369	315444	21784	340	95	21	300	500
Ranni	3.1	10525	10037	27133	8335	30538	325572	28715	520	45	14	1900	350
Chenganaur	3.2	4925	9896	18500	6295	24792	336479	14357	87	80	14	100	300
Tiruvalla	4.1	7850	14016	19733	6575	41576	340374	20051	87	75	14	1400	1800
Kattoor	4.2	8975	10107	11100	5765	28118	274932	42825	693	90	14	100	1600
Main Town	5.1	12225	26941	12333	7585	37267	253898	29952	260	155	28	6300	2200
Neriyamangalam	6.1	10650	23137	20967	9345	32504	234421	53716	607	125	84	600	600
Kaladi	6.2	8675	9685	22200	6115	31218	214944	190854	1560	125	14	4200	800
Chalakudi	7.1	8775	13347	40700	8645	28118	192352	54707	607	125	14	200	600
Cherutirutti	8.1	8975	951	27133	7745	32579	345828	20546	347	60	14	300	500
Tritala	8.2	170625	26659	8633	7015	39762	281165	14357	693	100	14	800	550
Near Manjeri	10.1	24900	20320	23433	8545	31369	225072	36389	347	75	14	7300	800
Nilambur	11.1	9425	1127	35767	7925	38779	368421	18566	260	50	21	700	300
Mavur	11.2	20650	3557	22200	9115	30916	276491	43567	780	75	14	1700	450
	Avg.	20660	13314	19733	7556	32730	274062	42956	504	90	20	1600	771
	S.D.	38963	7759	9623	1248	4431	61972	42555	347	30	17	2213	556

All values in μg/g

1: Kallada; 2: Achenkovil; 3: Pamba; 4: Manimala; 5: Muvattupuzha; 6: Periyar

7: Chalakudi; 8: Bharatpuzha; 9: Pulantod; 10:Kadalundi; 11: Chaliyar

Silicon

The contribution from Si to the elemental chemistry of bed sediments of eleven rivers of Kerala was found to be around 66% on average. This indicates the dominance of quartz in the underlain bed. The concentration varies between 14 and 36%, but the variation is not symmetric. The Si concentration is very high in Manimala, Bharathapuzha and Chaliyar river (34-36%) and in the same season high values of SiO_2 was recorded in the same rivers which indicates dominance of quartz weathering in the catchment of these rivers bed. The average concentration of Si in Kerala rivers is 27% which is comparable to other Indian rivers.

Aluminium

Al constitute 8% of total elemental concentration of in the bed sediments of the study area. There is no significant fluctuation observed throughout the study area. Close study of the data indicates the downstream decrease in concentration except for Bharathapuzha river . The decrease is due to virtually immobile nature of Al in the bed sediments.

The average concentration of Al in the Kerala rivers, which is 3.3%, is slightly lower than other Indian rivers due to absence of bauxite in the area.

Iron & Manganese

Fe makes 10% of the total elemental concentration of Kerala rivers. The high percentage of Fe can easily be explained in terms of presence of laterite

patches which cut across almost all the river beds throughout the state. The other possibility may be the presence of some iron bearing mineral like pyrite or hydroxide. But nothing concrete can be explained on the basis of this preliminary study. Abnormally high concentration at some places also is perhaps due to abundance of laterite or addition of organic matter which complexes with the Fe.

Fe concentration is decreasing downstream except for river Manimala and Periyar. But on the basis of this preliminary study it is difficult to explain the exact reason for such trend.

Mn makes only 0.10 % of the total concentration of the elemental concentration but the role played by it is very significant. The average concentration of Mn is 504 ppm which is comparable to other India rivers. The normal downstream trend observed here is decrease in Mn concentration, except for Periyar and Bharathapuzha.

Fe & Mn shows good correlation (r = 0.87) indicating that Fe and Mn phases are not geochemically separated.

Sodium & Potassium

Na and K account for 5% and 3% respectively of elemental chemistry of bed sediments of the Kerala rivers. The variation in concentration is asymmetric throughout the study area. The average concentration of Na, 2.0%, is more than world average. The reason may be the occurrence of alkaline and saline soil patches in the basin and sodium rich feldspar (albite) in the bed sediment.

Lower values of K indicates the less abundance of K- rich clay mineral which is substantiated by bed sediment mineralogy.

Calcium & Magnesium

Mg contributes around 2% of total elemental concentration of the bed sediment in the study area, while the contribution of Ca is just 5%. The average concentration of Ca is 1.9% which is comparable to other Indian rivers and world rivers average but concentration of Mg is lower than the Indian average of 1.47%. But it is comparable to the concentration of Mg in Cauvery river. The low value is definitely due to the lack of carbonate rocks in the study area. This argument is substantiated by clay mineralogy being discussed in later section.

The poor correlation of Ca and Mg with Fe and Mn may be because of their less absorption/ adsorption on Fe-Mn hydroxide because of high speed of river flow resulting from steep gradient.

Copper

Cu is extracted from silicates, sulphides and oxides during their decomposition due to rock weathering. The contribution of Cu to the total element concentration in the bed sediment is very little i.e. 0.005%. The average concentration in the bed sediments is 20 ppm which is comparable to Indian average (28 ppm) but it is much less than world average (100 ppm). The Cu concentration is almost same all throughout the study area except at the upstream location of Periyar (Figure 4.9). This exceptional high concentration may be
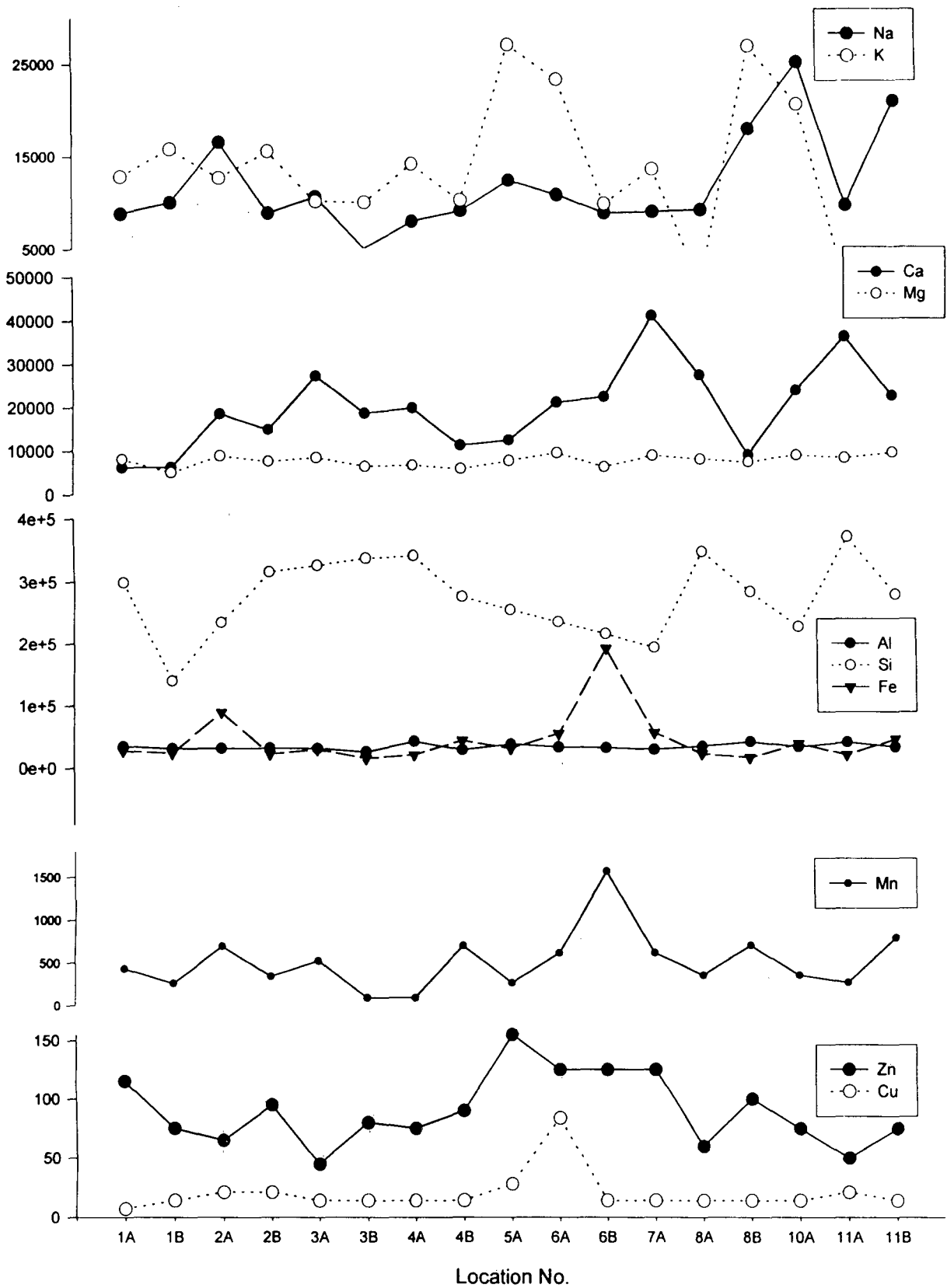
Figure 4.9 : Spatial variation in the chemistry of bed sediments of Kerala rivers

Table 4.14 : Correlation Coefficient matrix for bed sediment chemistry of Kerala Rivers

	Na	K	Ca	Mg	Al	Si	Fe	Mn	Zn	Cu	P	N
Na	1.00											
K	0.46	1.00										
Ca	-0.29	-0.47	1.00									
Mg	-0.05	0.00	0.47	1.00								
Al	0.41	0.26	-0.14	0.03	1.00							
Si	-0.01	-0.43	0.17	0.10	0.29	1.00						
Fe	-0.16	-0.09	0.14	-0.04	-0.22	-0.43	1.00					
Mn	0.16	-0.07	0.06	0.04	-0.19	-0.38	0.87	1.00				
Zn	0.06	0.61	-0.24	0.00	0.05	-0.43	0.31	0.29	1.00			
Cu	-0.09	0.38	0.06	0.39	0.04	-0.15	0.06	0.03	0.33	1.00		
P	-0.02	0.38	0.03	0.14	0.15	-0.23	0.28	0.14	0.27	-0.02	1.00	
N	-0.11	0.41	-0.31	-0.35	0.34	-0.12	-0.01	-0.14	0.44	0.02	0.42	1.00

because of disproportionate high concentration of chalcopyrite in the sediment sample as this area has abundance of Fe ore.

Zinc

Zn also is a trace contributor to the elemental concentration in the bed sediment in this area. Its % contribution is 0.02 and the average concentration is 90 ppm which is comparable to other India rivers. The major source of Zn in the bed sediment is from the sulphides.

Phosphorus and Kjeldahl Nitrogen

The natural source of P in sediments is P bearing minerals like apatite and fluorapatite. The P concentration in the sediments of the study area is very high and the correlation of P with Ca is very poor which shows that due to extensive use of fertilizer in the area the insoluble phosphate does not leach and just settles down in the bed sediments. It is because of this reason we are not getting high values of dissolved phosphorus in the river waters of Kerala as we discussed earlier in water chemistry section.

Although the % contribution of N to the total elemental concentration of the bed sediment is very very low (0.2%) but its significance is very high as it is indicator of anthropogenic activities. The concentration of Kjeldahl N (NH_3 + Organic Nitrogen), which reflects the addition of organic matter from the basin and as well as from biological activities within the system, varying from one basin to another. Very high concentration in location no. 5.1 i.e. Muvattupuzha is

Table 4.15 : Comparison of observed concentration of various elements in USGS rock and Canadian soil standards with thepublished data. All concentrations are in μg/g.

Rock/ Soil	Result	P	Al	Si	Ca	Mg	Fe	Cu	Na	K	Mn	Zn
SO1	Published		93800		18000		60000	61	17000			146
	Observed		69414		18500		53964	63	15250			139
SO2	Published			249900	19600	5400	55600			24500	720	124
	Observed			253602	22200	5200	53716			24054	693	129
SO3	Published		30500	158600				17	7000	11600		52
	Observed		28700	145333				14	8375	12502		49
SO4	Published	900	54600	319700			23700	22	10000	17300		
	Observed	800	58557	298648			23516	21	10225	17960		

Table 4.16 : Comparative values of chemical composition of river borne sediments.
(Elements Si through K in %, all others μg/g)

Element N =	Kerala* Avg. 18	Cauvery 16	Krishna 19	Godavari 23	Mahanadi 19	Ganges 35	Brahmputra 21	Indian Avg. 128	Bay of Bengal 12	World Average 10	World Surficial rocks
Si	66	27.2 (16.7)	26.3	27.0	11.94	31.2	28.4	24.5	-------	28.5	27.5
Al	8	6.5 (3.2)	3.38	4.78	6.22	4.66	5.6	5.0	7.60	9.4	6.93
Fe	10	1.6 (6.8)	2.5 (13.2)	6.00 (7.63)	5.61	2.2(10.9)	2.9 (10.9)	2.9	3.9	4.8	3.59
Mg	2	0.5	1.30	1.15	1.10	1.32	1.66	1.47	1.43	1.18	1.64
Ca	5	1.5 (3.5)	5.34	3.81	1.36	2.34	1.93	2.46	1.98	2.15	4.50
Na	5	2.4 (5.3)	5.56	-----	-----	-----	------	-----	-----	0.71	1.42
K	3	0.8 (1.8)	3.82	1.02	-----	1.33	1.24	1.21	-----	1.42	2.44
Mn	504	655 (2935)	906 (2540)	1060 (1780)	2020	400(3450)	644 (4450)	605	529	1050	720
P	1600	1255 (1072)	774	-----	-----	-----	------	-----	-----	170	97
Cu	20	39 (161)	35 (220)	73 (150)	57	21 (252)	17 (108)	28	26	100	32

* Present study

All values includes 10% of bed and 90% suspended sediments composition. Whether values are represented in the parentheses indicate separate values for bed and suspension (parentheses).

Ref.: Cauvery (Ramanathan, 1990); Krishna (Ramesh et al., 1989); Godavari (Biksham and Subramanian, 1988); Ganges and Brahmaputra (Subramanian et al., 1987); World average and World Surficial rocks (Martin and Meybeck, 1979); Bay of Bengal (Sarin et al., 1979); Other Indian rivers (Subramanian et al., 1985).

because this area gets all the domestic wastes from densely populated city, Muvattupuzha. Apart from that because of the post monsoon season the flow is very sluggish which favours the biological activity and so the more and more of N is released which finally settles down in the sediments. Another area of high KjN concentration is Manimala river. Both the location are sort of dumping place of domestic sewage from the urban area of Tiruvalla and Kattoor. Another reason here may be the addition of N from surface runoff from agricultural fields. Here also the flow is very sluggish during post monsoon season providing the opportunity for high biological productivity.

Except for the above three locations the KjN concentration does not vary drastically in other location and there is no definite trend observed. But the values are quite higher than normal KjN concentration in the river bed sediments which implies that throughout the study area land use and anthropogenic activities have its impact on the river biogeochemistry in this area.

Metal/Aluminium ratio

This ratio is very important tool to find out the mobility of different elements. By using this ratio the effects of grain size on the distribution of heavy metals and is nullified since Al is a major and chemically unreactive constituent of clay minerals. Variation in this ratio may be due to influence of tributaries, water-sediment exchange of elements and increase in authigenic deposition rates.

Si/Al ratio has the highest value for all the locations throughout the study area. It implies that excess amount of Si is added from the detrital quartz which is

Table 4.17 : Relative mobility of elements with respect to Al in the bed sediments of Kerala Rivers

Sampling ocation	N	Na/Al	K/Al	Ca/Al	Mg/Al	Si/Al	Fe/Al	Mn/Al	Zn/Al	Cu/Al	P/Al	N/Al
Punallur	1.1	0.25	0.37	0.18	0.23	9	0.8	0.012	0.003	0.0002	0.005715	0.014
Shasthank	1.2	0.32	0.50	0.20	0.16	4	0.8	0.008	0.002	0.0004	0.003203	0.026
Pandalam	2.1	0.53	0.40	0.59	0.28	7	2.8	0.022	0.002	0.0007	0.031955	0.014
Tonallur	2.2	0.28	0.49	0.47	0.24	10	0.7	0.011	0.003	0.0007	0.009563	0.016
Ranni	3.1	0.34	0.33	0.89	0.27	11	0.9	0.017	0.001	0.0005	0.062218	0.011
Chengana	3.2	0.20	0.40	0.75	0.25	14	0.6	0.003	0.003	0.0006	0.004034	0.012
Tiruvalla	4.1	0.19	0.34	0.47	0.16	8	0.5	0.002	0.002	0.0003	0.033673	0.043
Kattoor	4.2	0.32	0.36	0.39	0.21	10	1.5	0.025	0.003	0.0005	0.003556	0.057
Main Tow	5.1	0.33	0.72	0.33	0.20	7	0.8	0.007	0.004	0.0008	0.169051	0.059
Neriyaman	6.1	0.33	0.71	0.65	0.29	7	1.7	0.019	0.004	0.0026	0.01846	0.018
Kaladi	6.2	0.28	0.31	0.71	0.20	7	6.1	0.050	0.004	0.0004	0.134537	0.026
Chalakudi	7.1	0.31	0.47	1.45	0.31	7	1.9	0.022	0.004	0.0005	0.007113	0.021
Cherutirutt	8.1	0.28	0.03	0.83	0.24	11	0.6	0.011	0.002	0.0004	0.009208	0.015
Tritala	8.2	4.29	0.67	0.22	0.18	7	0.4	0.017	0.003	0.0004	0.02012	0.014
Near Manj	10.1	0.79	0.65	0.75	0.27	7	1.2	0.011	0.002	0.0004	0.232711	0.026
Nilambur	11.1	0.24	0.03	0.92	0.20	10	0.5	0.007	0.001	0.0005	0.018051	0.008
Mavur	11.2	0.67	0.12	0.72	0.29	9	1.4	0.025	0.002	0.0005	0.054988	0.014556

All values in µg/g

1: Kallada; 2: Achenkovil; 3: Pamba; 4: Manimala; 5: Muvattupuzha; 6: Periyar

7: Chalakudi; 8: Bharatpuzha; 9: Pulantod; 10:Kadalundi; 11: Chaliyar

in abundance in the river sediments. There is sudden increase in Fe/Al value in the downstream of Periyar river . This might be due to the abundance of laterite in this region. The values for other M/Al ratio does not show significant variation.

4.3 Carbon, Nitrogen and Phosphorus in the sediments

The input of carbon from the river to ocean is an important link in biogeochemical cycling of C between its two major pools viz. land and ocean. C in these pools exists largely in the form of carbonates, bicarbonates and organic matter. Weathering of rocks in the catchment area gives carbonates and bicarbonates.

Source of organic matter in rivers are:

1) Organic matter washed away from the river catchment (allochthonous pool)

2) Organic matter from *in situ* biological production (autochthonous pool)

3) Organic wastes from the industries, agricultural and household activities (anthropogenic source).

The allochthonous pool supplies stable and biologically inert metal complexed humic materials, polyphenols and carbohydrates. But the autocthonous pool supplies rather unstable compounds such as polypeptides, fatty acids and carbohydrates which get easily decomposed in the riverine environment (Degens, 1982).

The organic matter in sediments can give valuable information about the organisms and environment at the time of deposition. To make the most efficient use of this information, the nature of distribution, source and fate of the organic matter in contemporary aquatic environment must be studied (Goldberg, 1978). Besides the erosion of bed rocks effected by river water, part of weathered material is flushed out into the rivers from their catchment area. Many authors have printed out the strong influence of continental weathering in the geological carbon cycle (Walker et al, 1981; Berner et al, 1983; Berner 1991 and Berner, 1992).

Total Organic Carbon (TOC)

Total transport by the rivers to the oceans 0.03×10^{15} g C/anumn (Williams, 1971) to 1.0×10^{15} g C/anumn (Rockey et al. 1980). Systematic study to measure riverine TOC fluxes on global scale was initiated in 1981 by the SCOPE/UNEP project 'Transport of C and minerals in major world rivers.

On a world average 0.5 gigatons organic carbon is being transported by the rivers annually to the ocean. Though river input is only 7.5% of primary production because of its stable nature its contribution to total carbon burial in the coastal areas may be sufficient (Degens and Ittekkot, 1985).

The amount of organic matter transported by rivers at any given point of time is extremely low in comparison to the two C-pools linked by rivers.

Table 4.18 : Spatial variation of C, N and P in the bed sediments of Kerala rivers

Sampling Station	Sl.No.	TC	TIC	TOC	P	N	C/N	N/P
Punallur	1.1	2959	1540	1419	200	500	6	15
Shasthankota	1.2	2388	1712	676	100	800	3	24
Pandalam	2.1	2765	2007	758	1000	450	6	3
Tonallur	2.2	3528	1700	1828	300	500	7	12
Ranni	3.1	3020	1592	1428	1900	350	9	2
Chenganaur	3.2	1712	748	964	100	300	6	17
Tiruvalla	4.1	2069	1683	386	1400	1800	1	1
Kattoor	4.2	5788	3377	2411	100	1600	4	58
Main Town	5.1	21472	2010	19462	6300	2200	10	3
Neriyamangalam	6.1	24635	3360	21275	600	600	41	41
Kaladi	6.2	2660	2229	431	4200	800	3	1
Chalakudi	7.1	4373	3255	1118	200	600	7	22
Cherutirutti	8.1	2184	1465	719	300	500	4	7
Tritala	8.2	2139	1876	263	800	550	4	3
Near Manjeri	10.1	10868	1903	8965	7300	800	14	1
Nilambur	11.1	6301	1357	4944	700	300	21	9
Mavur	11.2	3293	2620	673	1700	450	7	2

All values in µg/g

1: Kallada; 2: Achenkovil; 3: Pamba; 4: Manimala; 5: Muvattupuzha; 6: Periyar
7: Chalakudi; 8: Bharatpuzha; 9: Pulantod; 10: Paraparangadi; 11: Chaliyar

Nevertheless, episodic events like flood or tropical storms may introduce considerable quantity of the organic matter from the catchment area into the rivers water and ultimately into the ocean. Such events may have a greater influence on the riverine transport of organic matter by medium sized rivers.

A global particulate N - transport by rivers amounts to 33×10^{12} g N/anumn, more than 80% of which occurs in rivers having high suspended matter concentration such as the Ganges, Bra.., Mekong and Huangho (Ittekkot and Zhang, 1989). Deforestation in the drainage basin has been found to increase loss of elements from the soils and their transport via rivers (Vitousek, 1983). In addition to this wide application of fertilizers in catchment area and waste disposal directly into the river channel have led together to a five fold increase in riverine input of N (Van Bennekomand Salomons, 1981).

Total Carbon

The combined effects of the physical condition of water flow, sediment load and geological characteristics lead to irregular distribution pattern of Corg in the bed sediments. The total Carbon in Kerala rivers does not show any symmetric variation spatially. Total carbon at different stations varies between 1.7 mg/g to 24 mg/g (Table - 4.18 & Figure 4.10). The lower value than reported by Bhosle et.al. for the shelf and slope regions of Cochin is due to the season of sampling i.e. non - monsoon season. During monsoon season the input of organic matter to the river is very high. That is why high values of total carbon have been reported during southwest monsoon season (June-September).

At all the locations the inorganic carbon constitutes a major portion of total carbon. But for the inorganic carbon also there is no regular trend observed along the stream. Muvattupuzha and Periyar rivers are shoeing very high amount of organic carbon (19.2 and 21.2 mg/g respectively) at one location. This is due to the high population density around the sampling location. All other rivers are showing almost similar values.

Total Phosphorus ✓

The values for total phosphorus is quite high at few locations otherwise it is comparable to the value for other Indian rivers. But the spatial variation in values of total P along the stream is almost symmetric. For the rivers south of Palghat gap, total P decreases as we go downstream while for the rivers north of Palghat gap the trend is opposite. This again can be linked to land-use pattern and water chemistry in both the region. Looking at the table for land-use pattern for different district of Kerala one can notice that the area irrigated north of Palghat is much more than the area irrigated in the south. So because of surface runoff from the irrigated land will add up insoluble P along the stream and so it will simply settle down in the sediments.
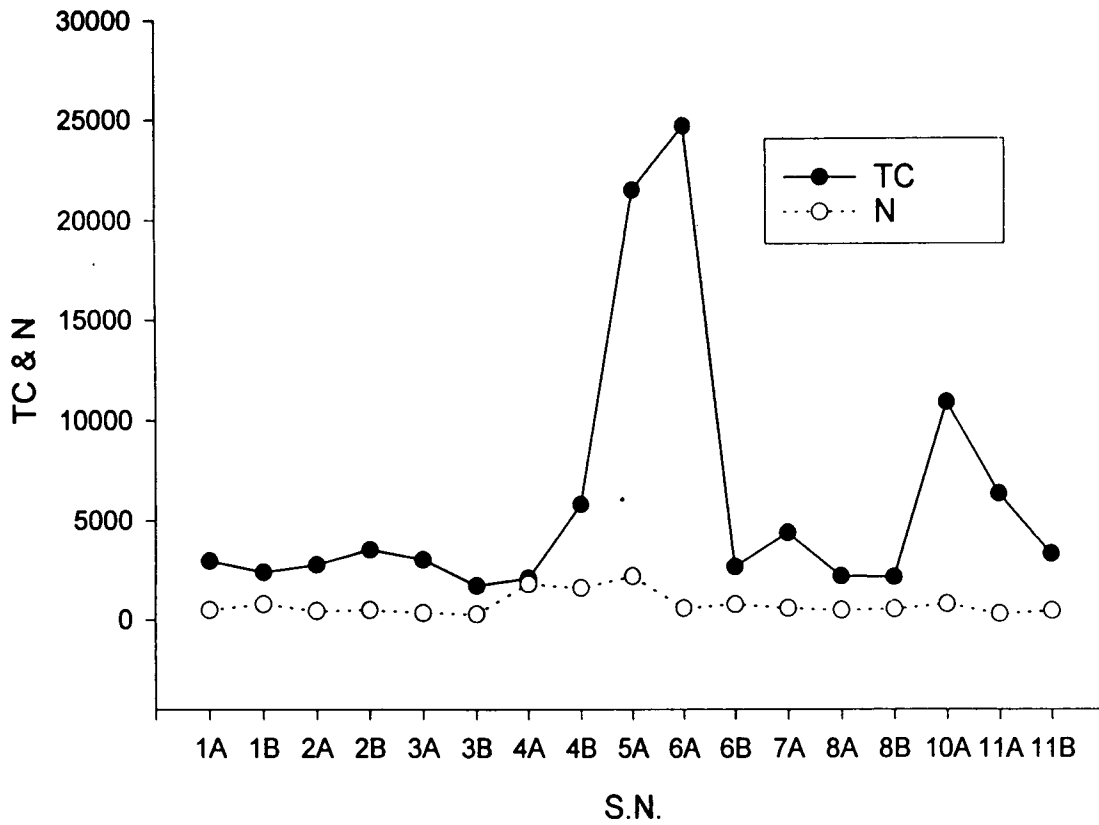
Figure 4.10 : Spatial Variation of TC & N in Kerala rivers
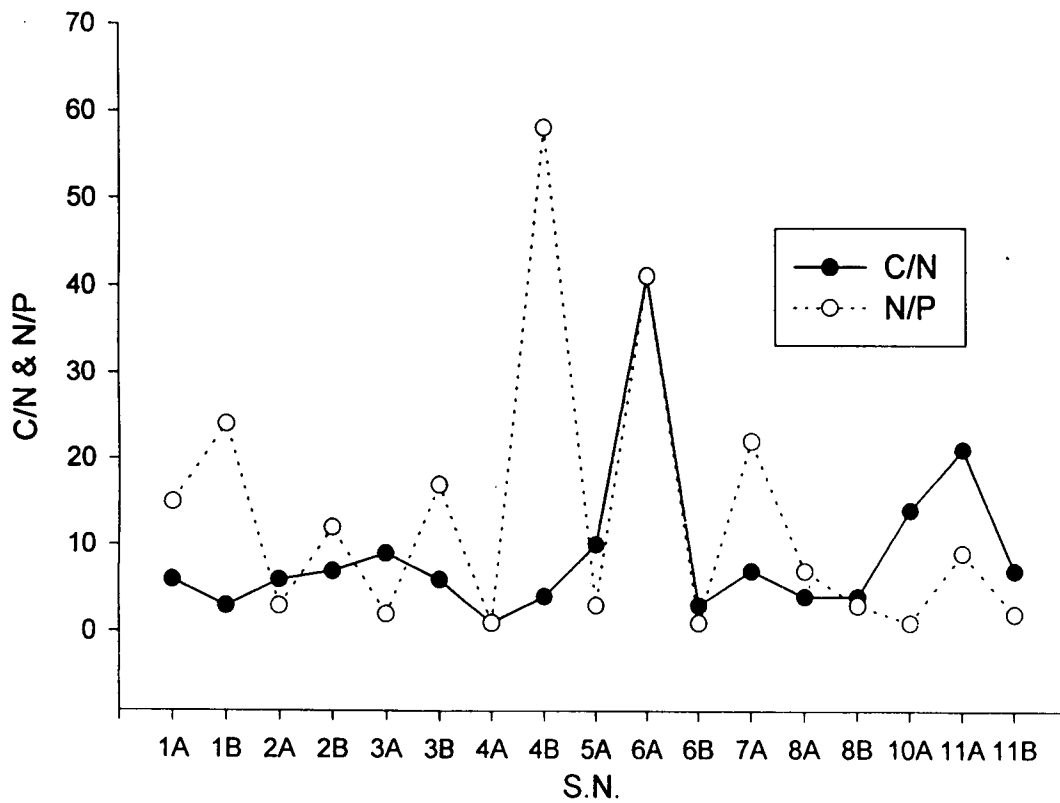(suffix A and B indicates the upstream and downstream samples respetively)

Figure 4.11 : Spatial variation in C/N and N/P ratio in Kerala Rivers
(suffix A & B indicates the upstream and downstream samples respectively)

Total Nitrogen

The values for total nitrogen in the bed sediments of Kerala rivers vary between 0.3 to 2.2 mg/g. The spatial variation of nitrogen does not follow any definite pattern. In some rivers it is decreasing along the stream and in some it is increasing down the stream. So nothing concrete can be said about this sort of variation on the basis of one season data.

Carbon/nitrogen ratio (C/N)

C/N ratio (by weight) in the river bed sediments of Kerala varies between 1.0 and 9.0, except at one location (Figure 4.11) each for Periyar, Kadalundi and Chaliyar where it ranges between 10-41. This might be due to large addition of domestic waste to the river. Because there is very high population density around above locations.

Nitrogen/Phosphorus ratio (N/P)

The N/P ratios in Kerala rivers vary between 1 and 58 (Figure 4.11). The very high values observed in Kallada, Manimala, Muvattupuzha and Periyar may be due to insignificant contribution of P by surface runoff from agricultural land other sources in the environment and very high rate of degradation of organic matter in these rivers.

4.4 Clay Mineralogy

The relative abundance of minerals and clay minerals in the bed sediments of Kerala rivers have been shown in Table-4.19. As the samples are from middle or towards the end of the course of the river it represents the soil genesis processes as well as the nature of catchment rocks. From the limited XRD results available we can see the dominance of quartz, kaolinite and mica.

Looking closely at these results here also we find substantial difference in the mineralogy between the north and south of Palghat. Although both the sides have high percentage of quartz but as we proceed northwards from Palghat Gap there is significant increase in kaolinite and mica. In the clay fraction of the bed sediemnts of Kadalundi and Chaliyar river the contribution from kaolinite is between 57 and 75%.

Kaolinite indicates the intensity of weathering, hence it can be stressed here that clay mineralogy of the bed sdiments substantiates what we discussed in earlier sections.

One more thing can be noticed here is spatial variation in Quartz/Feldspar ratio. We can notice sudden change in Q/F ratio in the north of Palghat Gap. The ratio decreases sharply in Chaliyar river. It may be due to intense kaolinisation in the rivers to the north of Palghat Gap.

Table 4.19 : Clay mineralogy of the bed sediments from Kerala Rivers

| Sl. No. | River Name | Location Name | <----------Peak area normalised to 100%----------> | | | | |
			Quartz	Feldspar	Carbonate	Kaolinite	Mica
2	Achenkovil	Pandalam	37.2	<1	1.2	53.9	5.4
3	Pamba	Ranni	58.3	<1	10	25	5
6	Periyar	Kaladi	19.6	<1	<1	43.3	37
7	Chalakudi	Chalakudi	35.2	3.5	<1	55.4	5.9
8	Bharatpuzha	Tritala	42.6	3.5	<1	<1	51.2
10	Kadalundi	Manjeri	4.01	<1	<1	74.46	21.42
11	Chaliyar	Mavur	29.5	12.7	<1	57.8	<1

4.5   General Discussion

Kerala, the most densely populated state in India situated on the southwest coast of India is drained by 44 small rivers. Because of its very interesting geographical and geological setting it provides every reason to study the chemistry of rivers originating in the Western Ghats. The eleven rivers studied here for water chemistry, sediment chemistry and clay mineralogy reveals many interesting facts about the area.

On the basis of results and discussion in the last section it was observed that as we proceed from south of Kerala to north there is wide variation in water and sediment chemistry of the rivers. Although the pH does not vary seasonally very significantly but there is marked increase in pH towards north of Palghat Gap. The same trend was observed for almost all the major ions and SiO_2. The higher pH values can be because of very high rainfall which is completely of marine origin, over the area. As geology and lithology of entire study area is nearly similar it is surprising to get the marked increase in the concentration of other components after Palghat Gap. This necessitates the need to understand the budgeting of various dissolved components of river water.

If we closely study the concentration of dissolved load in the river we can easily figure out few important points. If we take the concentration of Cl⁻ in the river water we can write the following equation depending on the possible sources :

$$Cl_{river} = Cl_{rainwater} + Cl_{anthropogenic} + Cl_{evaporite}$$

Table 4.20: Seasonal Variation of Discharge Weighted Concentration of major elements in Kerala Rivers

Monsoon Season (Discharge Weighted in mg/L)

River Name	Sl.No.	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	SiO_2	TDS	Na/Na+Ca	Na/Cl
Kallada	1	2.3	2.2	6.6	1.3	13.8	4.1	9.6	11.0	48.7	0.7	0.5
Achenkovil	2	2.3	2.0	4.4	0.8	6.1	4.1	9.9	10.5	38.0	0.7	0.7
Pamba	3	1.5	1.3	3.5	0.4	4.3	3.4	7.1	7.8	28.0	0.7	0.8
Manimala	4	1.3	1.2	3.9	0.5	5.4	2.9	6.2	8.2	28.4	0.7	0.7
Muvatupuzha	5	2.4	1.9	3.9	0.5	3.7	9.8	6.8	7.1	33.7	0.6	1.1
Periyar ·	6	2.1	1.5	3.9	0.4	5.8	3.8	8.5	6.4	30.4	0.6	0.7
Chalakudi	7	1.5	1.8	2.1	0.4	5.0	3.4	6.0	8.1	27.0	0.6	0.4
Bharatpuzha	8	7.6	4.4	7.4	1.1	9.8	4.2	37.1	11.3	75.5	0.5	0.8
Chaliyar	11	2.3	1.4	4.9	0.4	4.7	2.6	15.8	9.1	39.2	0.7	1.0
Avg.	--	2.6	2.0	4.5	0.7	6.5	4.2	11.9	8.8	38.8	0.7	0.7

Non Monsoon (Discharge Weighted in mg/L)

River Name	Sl.No.	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	SiO_2	TDS	Na/Na+Ca	Na/Cl
Kallada	1	0.1	0.0	0.1	0.0	0.2	0.2	0.3	0.4	1.2	0.7	0.8
Achenkovil	2	0.0	0.0	0.1	0.0	0.1	0.1	0.3	0.2	0.7	0.7	0.8
Pamba	3	0.3	0.3	0.4	0.1	0.6	0.8	1.4	1.0	4.5	0.6	0.7
Manimala	4	0.1	0.1	0.2	0.0	0.2	0.2	0.3	0.2	1.3	0.7	0.7
Muvattupuzha	5	0.5	0.4	2.0	0.2	2.5	2.8	1.8	2.2	11.9	0.8	0.8
Periyar	6	0.2	0.2	0.4	0.1	0.5	0.5	1.2	0.8	3.7	0.6	0.8
Chalakudi	7	0.1	0.1	0.2	0.1	0.2	0.3	0.8	0.3	1.9	0.6	1.0
Bharatpuzha	8	0.3	0.3	0.3	0.0	0.3	0.1	2.1	0.3	3.4	0.5	1.0
Pulantod	9	0.1	0.1	0.2	0.1	0.1	0.2	0.6	0.4	1.6	0.6	1.1
Kadalundi	10	0.0	0.0	0.1	0.0	0.1	0.1	0.2	0.2	0.6	0.6	0.9
Chaliyar	11	0.1	0.1	0.1	0.0	0.1	0.2	0.8	0.5	2.0	0.6	1.3
Avg.		0.2	0.2	0.4	0.1	0.4	0.5	0.9	0.6	3.0	0.6	0.9

Table 4.21 : Discharge weighted average chemical composition (mg/L) of Indian, Chinese and World Rivers

River	Discharge 10^6m^3	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	Ca^{++}	Mg^{++}	Na^+	K^+	TDS	References
Kerala Avg$	4710	12	6.5	4.25	9.0	2.6	2.0	4.5	0.65	38.76	Present Study
Cauvery	21000	135	20.0	13.0	23.0	21.0	9.0	43.0	4.0	272	Ramanathan (1990)
Gomti	7400	274	8.6	14.5	15.2	29.8	19.0	26.9	4.9	393.6	Lallan (1993)
Krishna	29000	178	38.0	49.0	24.0	29.0	8.0	30.0	2.4	360	Ramesh & Subramanian (1988)
Godavari	92000	105	17.0	8.0	10.0	22.0	5.0	12.0	3.0	181	Biksham & Subramanian (1990)
Mahanadi	66000	122	23.0	3.0	17.0	24.0	13.0	14.0	8.3	224	Chakrapani & Subramanian, (1990)
Narmada	40750	225	20.0	5.0	9.0	14.0	20.0	27.0	2.0	322	Subramanian (1983)
Tapti	17000	150	65.0	0.6	16.0	19.0	22.0	48.0	3.0	322	Subramanian (1983)
Indus	210000	64	9.2	15.0	5.3	27.0	0.7	1.3	2.1	122	Subramanian (1983)
Brahmaputra	510000[*1]	56	11.0	4.0	7.0	14.0	5.0	7.0	3.0		Mahanta & Subramanian (1993)
Ganges	468700	128	10.0	11.0	18.0	25.0	8.0	11.0	3.0	214	Singh (1987)
Indian rivers	1700000	74	15.0	13.0	7.0	30.0	7.0	12.0	3.0	159	Subramanian (1983)
Chinese rivers[#]	177000	113	7.0	14.0	3.0	33.0	5.5	5.0	1.5	181	Hu-Ming Hui et. al. (1982)
Zaire	1230000	11.2	3.0	3.0	10.0	2.4	1.3	1.7	1.1	33	Meybeck (1979)
Amazon	5500000[*2]	Upper	6.5	10.5	23.8	19.1	2.3	6.4	1.1		Stallard & Edmond (1983)
		Lower	1.1	2.6	15.4	5.2	1.0	1.4	0.8		
World Avg.	35000000[*3]	51.9	5.7	8.3	10.2	13.4	3.3	5.2	1.3		Meybeck & Helmer (1989)

$ based on monsoon discharge weighted average of nine rivers of Kerala
*1 Subramanian (1983)
*2 Gibbs (1972)
*3 Milliman (1991)
including Mekong

In this case the major source of the Cl in the river water must be from rain as the study area is very close to the sea and the influence of southwest monsoon is very high over the area. So Cl/Na in the rainwater in the region which has essentially equal value to the seawater i.e. 1.81 was found greater than the Cl/Na in river water on almost all the locations throughout the study area. This shows that generally there is no input of Cl from anthropogenic sources and chances of occurrence of evaporite in the region is minimal.

Similarly we can write the budget equation for each standard element Z (Z = Na, Ca, Mg, & K) as:

$$Zriver = Zrw + Z\ evap + Z\ sil + Z\ car$$

where   rw = rainwater

evap= saltrocks

sil = silicate rocks

car = carbonate rocks

To calculate the contribution to concentration of standard elements from rocks the following equation can be used (Negrel et al; 1993):

$$Z_{rock} = Z_{river} - Cl_{river}\ X\ (Z/Cl)_{sea};\ \text{where}\ Z = Na^+, K^+, Ca^{2+}, Mg^{2+}\ \&\ SO_4^{2-}$$

Using the above equation we can see that the values for SO_4^{2-} and Na^+ (Table - 4.22) the values are positive which indicates the contribution of these elements to the river water from rocks. It may be implied here that there is chance

Table 4.22: Seasonal variation in contribution of major elements to the rivers of Kerala

Monsoon Season

River Name	Sl.No.	(Na)rock	(Ca)rock	Mg(rock)	K(rock)	SO_4(rock)
Kallada	1	-1.08	-5.31	0.94	0.00	2.83
Achenkovil	2	0.99	-1.06	0.68	-0.46	2.80
Pamba	3	1.10	-0.85	0.43	-0.44	2.55
Manimala	4	0.93	-1.66	0.43	-0.25	2.15
Muvatupuzha	5	1.84	0.36	0.54	-0.82	8.51
Periyar	6	0.68	-1.08	0.39	-0.77	2.59
Chalakudi	7	-0.64	-1.29	0.99	-0.40	2.60
Bharatpuzha	8	1.99	2.16	0.25	-3.05	-0.02
Chaliyar	11	2.29	-0.30	0.18	-0.81	1.31
Avg.		0.90	-1.00	0.54	-0.78	2.81

Non Monsoon Season

River Name	Sl.No.	(Na)rock	(Ca)rock	(Mg)rock	(K)rock	(SO_4)rock
Kallada	1	0.05	-0.03	0.01	-0.01	0.12
Achenkovil	2	0.03	-0.01	0.01	0.00	0.06
Pamba	3	0.12	0.01	0.09	-0.09	0.57
Manimala	4	0.03	-0.06	0.04	-0.01	0.20
Muvattupuzha	5	0.66	-0.81	0.10	-0.10	2.51
Periyar	6	0.14	-0.05	0.07	-0.06	0.36
Chalakudi	7	0.09	0.01	0.07	-0.01	0.19
Bharatpuzha	8	0.13	0.12	0.12	-0.11	-0.01
Pulantod	9	0.07	0.01	0.06	0.00	0.13
Kadalundi	10	0.02	0.00	0.01	0.00	0.05
Chaliyar	11	0.08	0.04	0.06	-0.03	0.14
Avg.		0.13	-0.07	0.06	-0.04	0.39

of occurrence of pyrite or it can be contributed directly through sea spray. The negative values for other elements can not really be explained but at this point this much can be said that carbonate rocks are not responsible for the concentration of Ca & Mg in the study area and clay mineralogy shows the lack of carbonate rocks throughout the study area. The lower bicarbonate values than other Indian rivers in the river water of Kerala substantiates the same view.

If we compare the above results with other rivers in the world we find that Kerala rivers behave almost similar to Oubangui river in Cameroon (Negre et al., 1993) although the contribution of Ca & Mg from rocks is not similar.

If we see the Ca/Na rivers for Kerala the average value comes out to be 0.51 which is in conformity with the values for charnockitic terrain without carbonate. For this type of terrain the values have been found to be between 0.5-1.5 (Negre et al., 1993). For few locations the Ca/Na value is around 0.35 which is typical for the contribution from silicate rocks.

Calculation of runoff and evaporation from the rivers of the study area:

The values for runoff and evaporation (Table - 4.23) do not show symmetric variation but the values for the runoff are quite high in comparison to other rivers of the world. This may be due to the favourable longitudinal profile of the rivers (Figure 4.12).

Here one thing can be said that rate of mechanical and chemical erosion (Table - 4.24) in the rivers of Kerala is very less although the area receives very

Table 4.23 : Calculation for Runoff and Evaporation

River No.	River Name	Basin area	Average Annual discharge (Mm3)	Runoff (m)	Rainfall (m)	Evaporation (m)
1	Kallada	1699	3374.86	1.99	2.8	0.81
2	Achenkovil	1484	1484	1.00	2.6	1.60
3	Pamba	2235	3427.3	1.53	3.6	2.07
4	Manimala	847	1560.74	1.84	3.3	1.46
5	Muvattupuzha	1554	3560	2.29	3.1	0.81
6	Periyar	5398	4867.9	0.90	3.2	2.30
7	Chalakudi	1704	1629.3	0.96	3.6	2.64
8	Bharatpuzha	6186	5082.9	0.82	2.3	1.48
10	Kadalundi	1122	1137.3	1.01	3.4	2.39
11	Chaliyar	2923	5902	2.02	3.8	1.78

DISTANCE Km
MANIMALA RIVER

DISTANCE Km
PAMBA RIVER

DISTANCE Km
ACHENCOIL RIVER

DISTANCE Km
BHARATHAPUZHA RIVER

DISTANCE Km
CHALAKUDY RIVER

DISTANCE Km
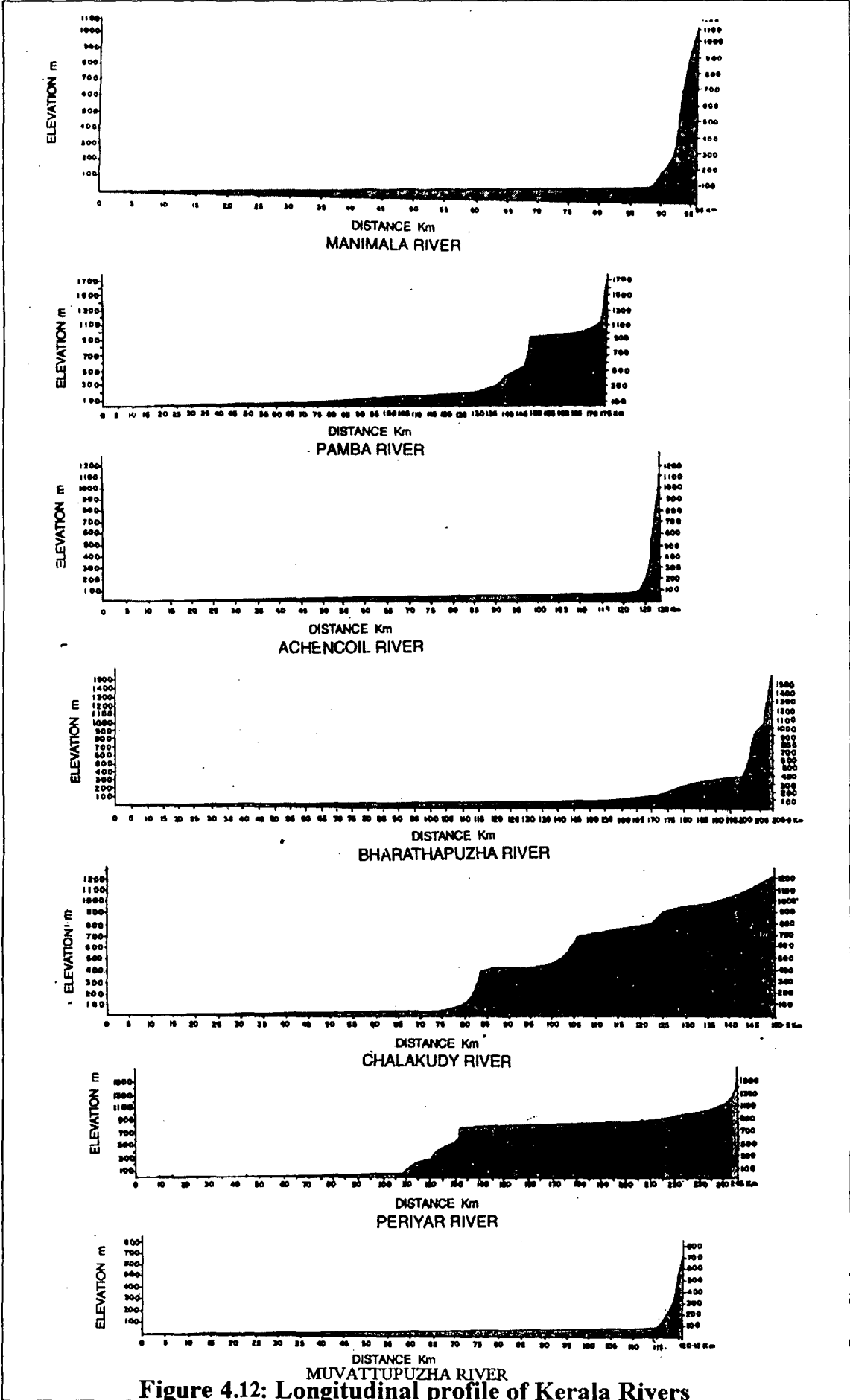PERIYAR RIVER

DISTANCE Km
MUVATTUPUZHA RIVER

Figure 4.12: Longitudinal profile of Kerala Rivers

high amount of rainfall (3-4 cm) during monsoon. The low TDS and TSM values proves this point. So it can be said that conditions are not favourable for the chemical erosion in the area, which might be due to steep gradients of the rivers which provides little time for the rainwater to be in contact with the rocks.

In those parts of a drainage basin where the anthropogenic component is small, the total of mechanical and chemical erosion rates gives the net material transport (E). Assuming the basins in the study area is close to pristine and average density of river - borne materials is 2.64 g/cm^3, a convenient relationship can be derived (Raymahashay; 1988):

$$\text{Lowering of land (cm/}10^3\text{yr)} = 0.038 \times E \text{ (tonnes/ km}^2\text{-yr)}$$
$$= 0.038 \times 89.02$$
$$= 3.38$$

With the help of the above rate of lowering it can be estimated that how many million years it will take to wash away the entire western ghat.

From the Figures 4.13 & 4.14 we see that there is fairly good correlation (r=0.65) exists between the two but there is no good correlation between rate of mechanical erosion and runoff. So it again raises the finger on the validity of very good correlation between log (Sediment exportation) and runoff published for various rivers.

The bed sediment chemistry is dominated by Si which contributes to 66% of the total elemental chemistry followed by Fe, Al, Na, Ca, etc. High concentration of Si is reflection of detrital quartz which makes about 40-50 % of the clay

Table 4.24: Calculation for Rate of Mechanical and Chemical Erosion

River No.	River Name	Basin area (km²)	Monsoon discharge (X10⁶m³)	Basin Elevation (m)	TDS (mg/L)	TSM (mg/L)	Rate of Mechanical Erosion tonnes/km²-yr	Rate of Chemical Erosion tonnes/km2-yr
1	Kallada	1699	3190.54	100-1000	48.65	3.35	6.29	91.36
2	Achenkovil	1484	2146.86	100-1100	38.02	5.29	7.65	55.00
3	Pamba	2235	5914.08	300-1700	27.99	8.33	22.04	74.06
4	Manimala	847	2695.64	150-1100	28.41	9.52	30.30	90.42
5	Muvattupuzha	1554	5869.37	100-800	33.65	2.62	9.90	127.09
6	Periyar	5398	9530.34	100-1500	30.41	5.68	10.03	53.69
7	Chalakudi	1704	2488.53	100-1200	26.99	-	-	39.42
8	Bharatpuzha	6186	6946.12	100-1500	75.53	4.67	5.24	84.81
10	Kadalundi	1122	2080.1	100-200	26.99	1.82	3.37	50.04
11	Chaliyar	2923	6242.34	150-1500	39.16	14.63	31.24	83.63
Avg.		2515.20	4710.39		37.58	6.21	14.01	74.95

Figure 4.13 : Dependence of chemical and mechanical erosion on the runoff in rivers of Kerla
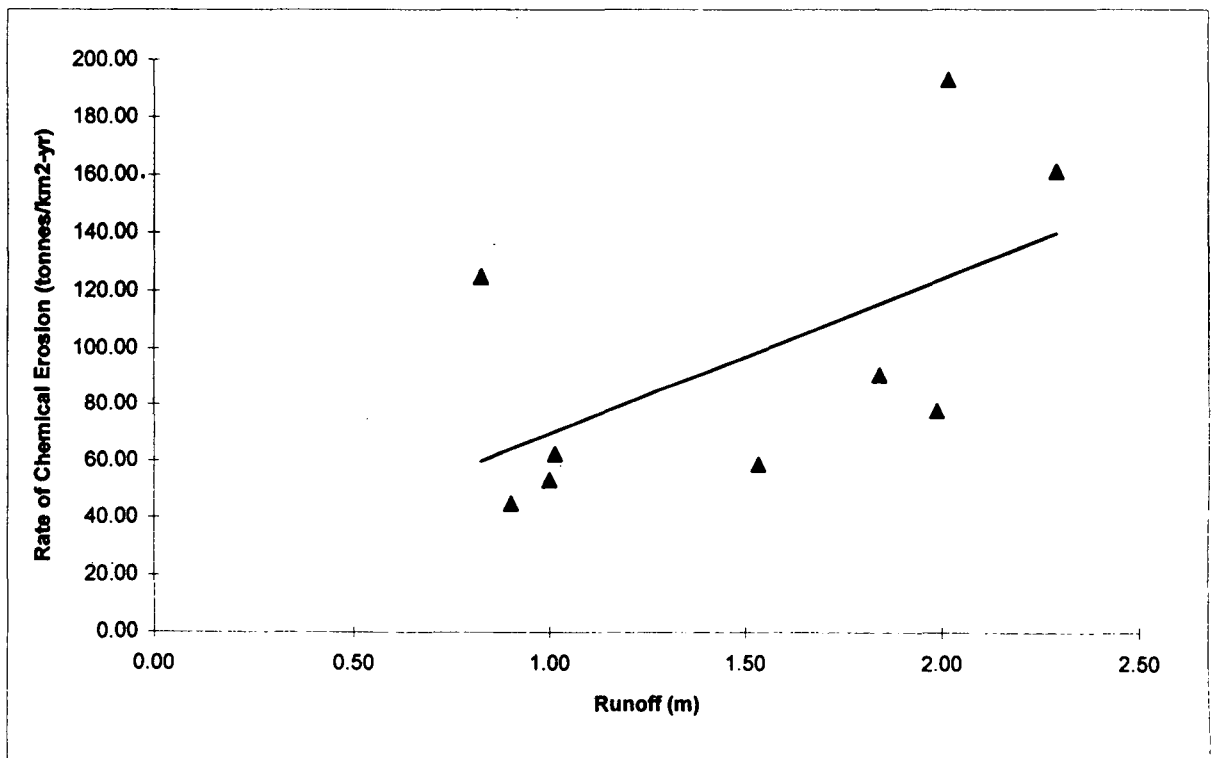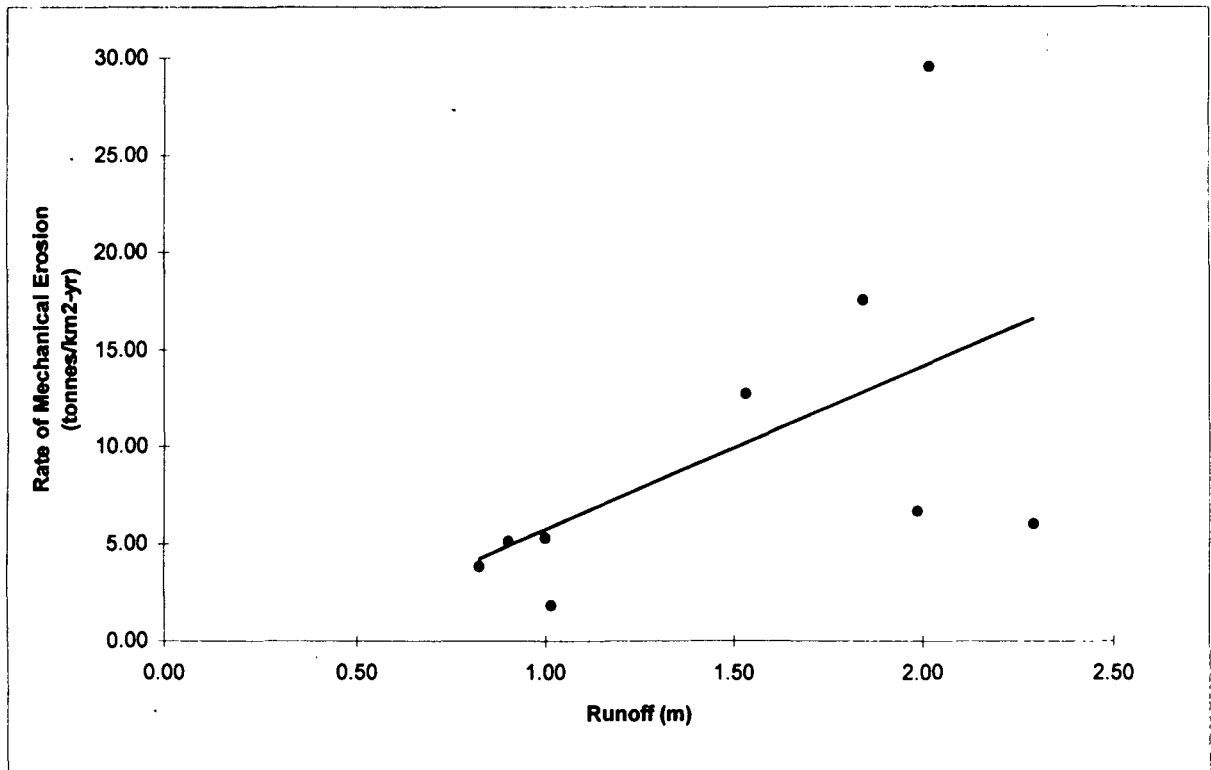
mineralogy of the bed sediments in the Kerala rivers. The average kjeldahl nitrogen concentration is around 500 µg/g which indicates, indirectly the amount of organic matter present in the sediments. The relative abundance of elements in the bed sediments of the Kerala rivers is:

Si > Fe > Al > Na = Ca > K > Mg > P > KjN > Cu

Looking at the clay mineralogy done for limited samples we can see that major contribution is from quartz, kaolinites and mica. Presence of these minerals in abundance explains the dominance of Si in the bed sediments and water.

Table 4.25: Comparison of Sediment yield from Kerala rivers with other river basins of India (Subramanian, 1988)

River Basin	Sediment Yield (tonnes/km^2-yr)	Basin Elevation (m)
Kerala Rivers[#]	14.07	100-1500
Brahmaputra	865.5	150-5000
Ganga	591.5	100-3000
Mahanadi	156.0	500
Narmada	58.7	760
Godavari	56.0	400
Krishna	42.2	420
Tapti	41.7	740
Cauvery	8.1	630

Present study

Table 4.26: Comparison of Sediment yield from Kerala rivers with other river basins of India (Subramanian, 1988)

River Basin	Rate of Chemical Erosion (tonnes/km^2-yr)
Kerala Rivers[#]	74.95
Brahmputra	112.5
Ganga	133.3
Mahanadi	78.2
Narmada	134.6
Godavari	81.3
Krishna	76.1
Tapti	85.5
Cauvery	78.3

Present Study

CHAPTER - 5
CONCLUSION

5.0   Conclusion

Having done the three season water chemistry, one season bed sediment chemistry and some clay mineralogy we are in position to highlight few points which we discussed in previous sections. The points are:

- There is significant seasonal variation in major ion chemistry throughout the study area. The monsoon values are higher as expected.

- There is a significant change in water chemistry as one crosses the Palghat Gap. The values of pH and all major ions increase after this line. Otherwise to the south of it the spatial variation in water chemistry is quite nominal.

- The values of dissolved silica in the water are very high to the north of the Palghat Gap which is explained by the dominance of abundance of Si in the bed sediments which further again is explained by the clay mineralogy.

- The most interesting is the value of dissolved P in the water which is very low but the values of P in bed sediments is quite high to the north of Palghat Gap. Having the same geology and lithology throughout the study area the only explanation could be given for this is the difference in landuse pattern between the two sides of the Gap. Hence, the northern part may be using lots of fertilizers, for which the data is not

really available, which in turn might cause the settling of insoluble P in the sediments.

- The clay mineralogy also changes as we cross the Palghat Gap. There is sudden increase in kaolinites and feldspars.

At the end it can be said that there is an apparent dividing line at Palghat Gap which separates the nature of erosion processes north and south of it. But in the absence of seasonal variation of detail sediment chemistry and its mineralogy the conclusion in the preceding section has inherent limitations and hence nothing concrete can be said at this point. So in order to understand it fully, more detail systematic sampling on the both sides of the Palghat Gap for the study of seasonal and spatial variation of water chemistry, sediment chemistry and sediment mineralogy is needed to be done.

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APPENDIX

APPENDIX - I

Calculation of log PCO_2
(Adopted after B. C. Raymaheshay, 1986)

Example:

pH = 8

HCO_3 = 98 ppm

Therefore, $mHCO_3 = 98/(1000 \times 61) = 1.60656 \times 10^{-3}$

and $\log mHCO_3 = -2.7941$

Using the formula $\log PCO_2 = 7.9 + \log mHCO_3 - pH$

$\log PCO_2 = 7.9 - 2.7941 - 8 = -2.89$

Calculation of Bicarbonate derived from rock weathering:

$(Ca)_{tot} = X$ meq

$(Mg)_{tot} = Y$ meq

$(HCO3)_C = 0.74 X + 0.4 Y$

$(HCO_3)_{tot} = Z$ meq

Using the formula:

$(HCO_3)_{Si} = (HCO_3)_{tot} - (HCO_3)_C$

$(HCO_3)_{Si} = Z - (0.74 X + 0.4 Y)$ meq

Appendix - II

The table shows 2θ value and 'd' spacing of the minerals identified from XRD charts (as Lindholm, 1987).

Minerals	2θ value	'd' spacing (A)
Quartz	26.66	3.343
Feldspars:		
Microcline	27.49	3.244
Oligoclase	27.88	3.200
Orthoclase	28.06	3.180
Carbonate:		
Calcite	29.48	3.030
Dolomite	30.99	2.886
Amphibole :		
Hornblende	10.53	8.400
Tremolite	10.56	8.380
Kaolinite	12.36- 12.40	7.13- 7.16
Mica	8.85- 8.80	9.99- 10.4
Illite	8.70	10.16
Chlorite	6.27- 6.22	14.1- 14.2
Montmorillonite	5.70	15.4