

WATER QUALITY PARAMETER ANALYSIS

3.1 BACKGROUND

Of all water on earth, 97.5% is salt water and of the remaining 2.5% fresh water, some 70% is frozen in the polar icecaps. The other 30% is mostly present as soil moisture or lies in underground aquifers. In the end, less than 1% of the world's fresh water or (about 0.007% of all water on earth) is readily accessible for direct human uses. It is found in lakes, rivers, and reservoirs and in underground sources shallow enough to be tapped at affordable cost. Evaporation and precipitation make this water available on a sustainable basis. Much of the approximately 110000 km³ of precipitation that falls on the continents each year evaporates back into the atmosphere, or is absorbed by plants. About, 42700 km³ of water that falls back on earth flows through the world's rivers. Dividing the world's total river flow by its 2000 population gives an average of 7300 km³ of water per person per year, a drop of 37% per person since 1970 because of the growing world population.

Fresh water resources are unevenly distributed: in terms of precipitation, there is a range from almost no rainfall in deserts to several meters per year in the most humid regions. Most of the flow is in a limited number of rivers: the Amazon carries 16% of global runoff, while the Congo-Zaire river basin carries one third of the river flow in all of Africa. Arid and semi-arid zones of the world, constituting 40% of the landmass have only 2% of global runoff. River flow, however, varies greatly over time and evaporation plays an important role whether a country can be classified as humid or semi-arid. The average annual runoff is determined by the population size. Per capita availability of water is lowest in Asia, even though it has the world's greatest river flow.

In Australia/Oceania on the other hand, the per capita runoff is high, in spite of the fact that most of the continent is dry. Experts have estimated the amount of the world's river flow that is readily accessible for human use at about 9000 km³ a year. They add another 3500 km³ of river flow that is captured and stored by dams and reservoirs. Currently, humans are using about half of the 12500 km³ available. This may seem to leave a lot of room, but in reality, water needs to be left to sustain health ecosystems (in particular wetlands and their biodiversity) to permit fisheries and to keep an adequate amount of water available for recreation, navigation and hydropower generation. High quality freshwater is limited in quantity and there is a need for comprehensive water management involving representatives of all those who use water. Effective management must ensure that the best use is made of available supplies, including protection from pollution and should seek to limit conflicts over access to freshwater.

The presence of nutrients excesses in river basins leads to modifications in the aquatic ecosystems. Are these modifications within the limits of what the ecosystems can handle, or are they leading to their destruction. Such a question can only be answered if more insight is gained into the pathways of nutrients through river catchments, from their emission to their behavior in the river. Knowing these pathways enables an estimate of the impact of nutrient abatement on the environmental quality. In combination with economic impact assessment, the most sustainable approaches can be determined. This enables a more successful river basin management. Biodiversity of inland water is a source of food, income and livelihood. Other values of these ecosystems include: water supply, energy production, transport, recreation and tourism, maintenance of the hydrological balance, retention of sediments and nutrients and provision of habitats for various fauna and flora. River ecosystems are often extensively modified by man, more so than marine or terrestrial systems and appear to be the most threatened ecosystem type of all. Physical alteration, habitat loss and

degradation, water withdrawal, overexploitation and pollution are main threats to these ecosystems and their associated biological resources. 41% of the world's population lives in river basins under water stress. More than 20% of the world's 10,000 freshwater fish species have become extinct, threatened or endangered in recent decades. Industrial revolution, rapid economic development and population growth, have brought about transformations of these ecosystems and biodiversity loss on an unprecedented scale. There is an increasing concern for maintenance of the richness of river biodiversity and reducing the risks many species face so that the goods and services they deliver will be maintained as well.

In India, rivers, ponds and groundwater are used for domestic and agricultural purposes. The quality of water may be described according to their physicochemical and microbial characteristics. For effective maintenance of water quality through appropriate control measures, continuous monitoring of large number of quality parameters is essential. The quality and quantity of surface water in a river basin is influenced by natural factors such as rainfall, temperature and weathering of rocks and anthropogenic changes that curtail natural flow of the river or alter its hydrochemistry. Rivers and streams are highly heterogeneous at spatial as well as temporal scales and several investigators have documented this heterogeneity focusing on the physicochemical dynamics of rivers. Variation in the quality and quantity of river water is widely studied in the case of several world rivers (Riedel et al 2000). Continental weathering and erosion are major components of the exogenic cycles of elements on the earth. Weathering breaks down rocks and the resulting dissolved and particulate materials are transported by rivers to the sea. Chemical weathering of rocks and minerals determines the flux of dissolved materials carried by rivers whereas physical weathering regulates the particulate transport. This makes the study of dissolved and particulate components of rivers important to characterize and quantify weathering and erosion (Krishnaswami and Singh 2005). Rivers play a major role in integrating and

organizing the landscape and moulding the ecological setting of a basin. They are the prime factors controlling the global water cycle and in the hydrologic cycle, they are the most dynamic agents of transport (Garrels et al 1975). Rivers carry elements, in suspended or in dissolved form, from their source and deposit them sequentially based on their physicochemical nature at different locations. The suspended load in the river can act as a sink for nutrients and other elements in certain cases and as a source in certain other cases (Horowitz 1995 & 1997; Gaur et al 2005). In spite of their wide ranging role, presently rivers are under severe threat due to various anthropogenic pressures (Singh and Singh 2007). Monitoring the surface run-off of a river on a regular basis provides valuable information on the eco-hydrologic conditions of a river basin. Such data provide valuable insights into spatial and temporal variation in water quantity and quality, considered as a measure of the health of a river and also a measure of the reliability of water quality models and their predictability (Rode and Suhr 2007).

Among Indian rivers, those flowing through the Indo-Gangetic plains are the most studied. Subramanian (1983) documented inconsistent down-stream variations in river water chemistry. Singh and Singh (2007), Mukherjee et al (1993) documented the physical, chemical and biological aspects of the Ganga river. There are several studies on the tributaries of the Ganges, including the rivers Yamuna (Saxena et al 2001; Dalai et al 2004; Singh et al 2007); Gomti (Gaur et al 2005; Singh et al 2005) and Hindon river basin Jain and Sharma (2002) documenting different physico-chemical aspects. Panigrahy and Raymahashay (2005) studied the Mahanadi basin and Hasnain and Singh (1998) reported for the Damodar basin. Shrihari and Avvannavar (2008) documented the water quality of river Netravathi in Karnataka. Ramanathan et al (1994) studied the details of Cauvery river basin and Ravichandran et al (1995); James (2000) documented the biogeochemical studied the river basin of Tamiraparani.

Water quality and suitability of the river water for irrigation use depends upon the minerals constituent present in the water. The major physicochemical parameters, which decide the suitability of river water for irrigation, are pH, EC, TDS, hardness, chloride, sulfate, carbonate, bicarbonate, nitrate, sodium, potassium, calcium, magnesium, etc. silica, iron, and boron are usually present in very small amounts and are determined in special circumstances, for example when industrial waste alone is to be used for irrigation (Deo and Ali 1993). Stallard and Edmond (1983) established the dominant role of chemical weathering of calcareous rocks in the Amazon river basin through mass balance and solution equilibria. Meybeck (1987) in an extensive study covering a number of large watersheds in France emphasized silicate and carbonate weathering effects on water quality. Ohri and Mitchell (1998) have demonstrated control of weathering products on water chemistry of small Japanese rivers. A comprehensive review of coupling between weathering and water quality has been reported by (Berner and Berner 1987; Drever 1988) for the world's major river basins. A large volume of work is on record pertaining to the sediment mineralogy and river erosion in the major river basins of the Indian subcontinent. Subramanian (1987) provided a comprehensive overview of such studies. Naidu et al (1985) have described clay mineral characteristics of river bed sediments. (Raymahashay 1986) suggested a chemical weathering model based on bicarbonate content in river water. An evaluation of the Mahanadi river water chemistry has been carried out by (Chakrapani and Subramanian 1990). Ray et al (1984); Naidu et al (1985) have pointed out certain limitations about the nature and source of sediment mineralogy reported in earlier studies by Subramanian and his co-workers. There have been very few attempts to evaluate water quality through analysis of lithology and soil formation in the drainage basins of India. Anthropogenic activities and improper management of natural resources also led to unequal distribution of major and minor elements in nature (Ramesh et al 1995).

Multivariate analyses are especially useful because the relative importance of the combinations of chemical variables can be evaluated. They are used as analytical tools to reduce and organize large hydro-geochemical datasets into groups with similar characteristics. Correlation analysis is widely used in geochemistry; it is useful for interpreting commonly collected river water quality data and relating them to specific hydro-geological processes. The basic purpose of such an analysis to the study of the hydro-geochemistry of an aquifer is to find a set of factors, few in number, which can explain a large amount of the variance of the analytical data (Ruiz et al 1990). In this present study, two multivariate techniques such as principle component analysis/factor analysis (PCA/FA) and cluster analysis (CA) were used for the water quality assessment and interpretation of the results and this chapter deals with the spatial and temporal variation of water chemistry of the river and factors controlled by supply of various elements and nutrients from both natural and anthropogenic sources.

3.2 GEOCHEMISTRY OF SURFACE WATER

3.2.1 pH, Electrical conductivity and calculated total dissolved solids

The average annual chemical compositions of the water in different parts of the world river basin including the major tributaries are listed in Table 3.1 and Tables 3.2 to 3.5 shows the chemical composition of river and its tributaries for four different seasons. The pH of the sample were slightly alkaline in nature with average values of 7.5; 7.3; 7.5 and 7.2 during 2007–08 in different seasons such as premonsoon, monsoon, postmonsoon and summer seasons, respectively. The pH value of all water samples lies in the ranges from 6.3 to 8.5. The upstream region of the river water derives excessive amount of humic and fulvic acids and others such as oxalic acid substances in the catchment area of the Western Ghats region due to water has acidic in nature, mid and down stream area is slightly alkaline in nature are due to urbanization and industrial activities. (James 2000) made similar observations for Tamiraparani river

Table 3.1 Average chemical composition (ppm) of Tamiraparani in comparison with South Asian and World rivers

River	HCO₃⁻	Cl⁻	SO₄²⁻	Ca²⁺	Mg²⁺	Na⁺	K⁺	H₄SiO₄	TDS	References
Tamiraparani	67	43	67	11	4	20	8	4	248	Present work
Kerala rivers	12	7	4	3	2	5	1	9	39	Subramanian (2004)
Cauvery	135	20	13	21	9	43	4	23	272	Ramanathan et al (1994)
Gomti	274	9	15	30	19	27	5	15	394	Gupta and Subramanian (1994)
Krishna	178	38	49	29	8	30	2	24	360	Ramesh and Subramanian (1988)
Godavari	105	17	8	22	5	12	3	10	181	Biksham and Subramanian (1988)
Mahanadi	122	23	3	24	13	14	8	17	224	Chakrapani and Subramanian (1990)
Narmada	225	20	5	14	20	27	2	9	322	Subramanian (1983)
Tapti	150	65	1	19	22	48	3	16	322	Subramanian (1983)
Indus	64	5	23	54	12	10	0.3	5	173	Subramanian (1983)
Brahmaputra	56	11	4	14	5	7	3	7	107	Datta and Subramanian (1998)
Ganges	128	10	11	25	8	11	3	18	241	Sarin et al (1984)
Indian average	74	15	13	30	7	12	3	7	159	Subramanian (2004)
Chinese rivers	113	7	14	33	5.5	5	1.5	3	181	Huming-Hui et al (1982)
World average	62.2	3.7	9.2	16	4	4.4	1.5	12.4	115	Sarin et al (1989)
Zaire	11.2	3	3	2.4	1.3	1.7	1.1	10	33	Meybeck (1979)
Amazon	23	4	3	6.5	1	3.1	1	11.2	53	Gibbs (1972)

basin (pH-5.8 to 6.8). In this study, pH was marked ranges to the minimum of 6.3 at Karayar (S1) and the maximum of 8.5 at Eral (S7) during postmonsoon season.

Electrical conductivity (EC) in water is due to ionization of dissolved inorganic solids and becomes a measure of calculated total dissolved solids (TDS). It is used as a basic index to select the suitability of water for all purposes. TDS refer to any minerals, salts, metals, cations or anions dissolved in water, which includes anything present in water other than pure water (H₂O) molecules and suspended solids. According to Langenegger (1990), the importance of EC is its measure of salinity. The EC for water is expressed as micro siemens per centimeter ($\mu\text{S}/\text{cm}$) and salt concentration is also reported as TDS in mg/l. On the basis of EC values of the water samples stations from S1–S9 (upstream) and S10–S16, S17-S20 were mid and down stream considered respectively. In the fresh water zone the EC ranged from 177 to 828.8 $\mu\text{S}/\text{cm}$, 139 to 493 $\mu\text{S}/\text{cm}$, 163.3 to 1174.6 $\mu\text{S}/\text{cm}$ and 95.3 to 1294.4 $\mu\text{S}/\text{cm}$ and similarly the TDS concentrations ranged from 111.6 to 522.0 mg l⁻¹; 87.6 to 310.6 mg l⁻¹; 102.9 to 740.0 mg l⁻¹ and 60.0 to 818.0 mg l⁻¹ during premonsoon, monsoon, postmonsoon and summer seasons respectively, during the study.

3.2.2 Major anions

The alkalinity of the fresh water is determined by the direct measure of bicarbonate (HCO₃⁻) concentration. It is generally accepted that the river water is an imprint of a complex atmosphere-hydrosphere-lithosphere interaction (Raymahasay 1987). The bicarbonate concentration varies between 15.1 and 109.8 mg l⁻¹ and 15.6 to 256.2 mg l⁻¹ during monsoon and summer season, indicating that intense chemical weathering is taking place in the river basin particularly during summer season. Sulphate contributes >36.3% of the average chemical composition followed by bicarbonate (27%); chloride (17.5%) and H₄SiO₄ (1.7%) in the river basin.

Table 3.2 Concentration of major ions and nutrients during premonsoon season

	S.No*	Ca ²⁺ (mg l ⁻¹)	Mg ²⁺ (mg l ⁻¹)	Na ⁺ (mg l ⁻¹)	K ⁺ (mg l ⁻¹)	HCO ₃ ⁻ (mg l ⁻¹)	Cl ⁻ (mg l ⁻¹)	H ₄ SiO ₄ (mg l ⁻¹)	SO ₄ ²⁻ (mg l ⁻¹)	N-NO ₃ ²⁻ (µg l ⁻¹)	PO ₄ ³⁻ (µg l ⁻¹)	TDS (mg l ⁻¹)	EC (µS/cm)	pH
Upstream	1	4.4	2.1	3.0	2.0	19.8	8.9	9.8	65.3	2.3	2.0	115.3	183.0	6.3
	2	5.0	2.5	6.0	2.3	18.9	9.6	9.7	69.2	2.4	2.1	123.2	195.5	6.6
	3	22.0	6.0	3.0	2.0	24.4	17.7	5.0	126.0	2.1	3.1	206.1	327.2	7.1
	4	4.8	2.8	1.5	1.3	21.7	20.1	4.2	55.2	1.9	2.7	111.6	177.1	7.0
	5	5.0	2.3	1.9	1.9	19.3	23.7	9.2	64.2	2.0	2.9	127.5	202.3	6.8
	6	12.0	5.1	11.0	34.0	24.4	17.7	10.6	101.5	1.8	0.6	216.3	343.3	7.1
	7	38.0	10.8	62.0	12.0	176.9	106.4	14.7	73.8	1.6	5.0	494.6	785.0	7.6
	8	22.0	5.0	3.0	2.5	23.5	16.7	15.6	67.2	2.1	2.8	155.5	246.9	7.1
	9	19.1	3.8	3.2	2.5	25.2	14.7	16.8	70.7	1.9	3.0	156.0	247.6	7.1
Midstream	10	4.8	1.9	3.4	2.1	32.9	15.6	7.2	75.8	0.9	3.2	143.7	228.1	7.2
	11	8.0	1.2	14.0	3.0	36.6	26.6	12.4	120.0	0.8	11.5	221.8	352.0	7.3
	12	11.0	9.4	19.0	5.1	50.2	30.1	18.8	100.2	0.7	15.2	243.8	387.0	7.4
	13	16.0	2.4	28.0	5.0	67.1	35.5	18.3	110.8	0.8	16.7	283.1	449.4	7.5
	14	19.1	2.3	35.3	6.0	73.1	45.2	18.8	96.2	0.9	15.2	296.0	469.8	7.4
	15	20.0	2.4	40.0	7.0	115.9	62.0	15.0	83.0	0.8	13.9	345.3	548.1	8.2
	16	18.0	4.3	53.4	11.2	119.2	65.3	16.7	93.4	0.7	14.9	381.5	605.5	8.2
Downstream	17	16.0	7.2	63.0	15.0	134.2	88.6	16.9	110.0	0.8	16.4	450.9	715.8	8.1
	18	16.0	9.6	71.0	15.0	164.7	88.2	14.1	89.2	0.8	15.8	467.8	742.5	8.5
	19	20.0	15.2	88.0	21.0	178.3	96.3	2.7	92.3	0.7	17.3	513.8	815.5	8.4
	20	21.0	16.2	89.2	22.1	179.3	97.4	3.6	93.2	0.7	16.8	522.0	828.6	8.3

*Refer Fig 2.1 for sampling locations

Table 3.3 Concentration of major ions and nutrients during monsoon season

	S.No*	Ca ²⁺ (mg l ⁻¹)	Mg ²⁺ (mg l ⁻¹)	Na ⁺ (mg l ⁻¹)	K ⁺ (mg l ⁻¹)	HCO ₃ ⁻ (mg l ⁻¹)	Cl ⁻ (mg l ⁻¹)	H ₄ SiO ₄ (mg l ⁻¹)	SO ₄ ²⁻ (mg l ⁻¹)	N-NO ₂ ⁻ (µg l ⁻¹)	PO ₄ ³⁻ (µg l ⁻¹)	TDS (mg l ⁻¹)	EC (µS/cm)	pH
Upstream	1	2.0	1.2	2.9	0.8	15.1	7.7	7.0	51.3	0.4	1.8	88.0	139.6	6.4
	2	4.0	1.2	3.4	1.0	18.3	8.9	1.6	49.2	0.5	2.1	87.6	139.0	6.6
	3	8.0	1.2	6.0	1.3	30.5	35.5	2.0	126.2	0.3	3.1	210.7	334.3	7.4
	4	4.0	1.2	5.1	0.8	21.0	22.3	1.7	62.0	0.4	2.5	118.1	187.4	7.4
	5	2.0	1.2	3.0	1.1	18.3	8.9	1.5	64.2	0.4	2.9	100.2	159.0	6.7
	6	2.0	1.2	3.0	0.8	30.5	26.6	1.8	101.5	0.3	0.6	167.3	265.6	7.5
	7	26.0	6.0	12.4	3.1	109.8	53.2	1.6	73.8	3.5	5.0	285.9	453.8	7.5
	8	2.0	1.2	1.4	1.5	22.1	25.6	1.5	71.3	0.4	3.2	126.6	201.0	6.9
	9	2.0	1.2	1.6	1.6	25.3	10.3	1.5	73.0	0.4	2.9	116.5	185.0	6.6
Midstream	10	2.0	3.6	1.7	1.4	42.7	48.9	1.2	95.8	1.5	3.2	197.3	313.2	6.9
	11	14.0	1.2	11.3	4.0	79.3	53.2	1.5	120.0	1.5	11.5	284.5	451.6	7.7
	12	16.0	2.4	13.2	2.8	71.5	60.1	1.6	105.1	2.8	15.3	272.7	432.8	7.5
	13	14.0	2.4	15.0	4.9	85.4	62.0	1.6	110.8	3.5	16.7	296.1	470.0	7.3
	14	12.0	3.6	15.5	3.8	84.5	58.2	1.6	96.0	2.3	15.3	275.2	436.8	7.5
	15	18.0	3.6	16.9	4.6	85.4	53.2	1.8	83.0	1.4	13.9	266.5	423.0	7.6
	16	16.0	3.6	17.2	7.8	88.1	57.1	1.6	98.3	1.3	14.2	289.7	459.8	7.4
Downstream	17	18.0	3.6	18.4	5.1	91.5	62.0	2.0	110.0	1.8	16.4	310.6	493.1	7.7
	18	20.0	4.8	16.1	4.8	79.3	44.3	0.1	89.2	1.7	15.8	258.6	410.5	7.9
	19	18.0	5.3	14.5	12.1	86.2	63.2	0.2	76.1	1.3	14.3	275.6	437.5	7.8
	20	19.3	5.2	19.3	15.2	87.2	65.2	0.2	75.6	1.2	15.2	287.2	455.8	7.6

*Refer Fig 2.1 for sampling locations

Table 3.4 Concentration of major ions and nutrients during postmonsoon season

	S.No*	Ca ²⁺ (mg l ⁻¹)	Mg ²⁺ (mg l ⁻¹)	Na ⁺ (mg l ⁻¹)	K ⁺ (mg l ⁻¹)	HCO ₃ ⁻ (mg l ⁻¹)	Cl ⁻ (mg l ⁻¹)	H ₄ SiO ₄ (mg l ⁻¹)	SO ₄ ²⁻ (mg l ⁻¹)	N-NO ²⁻ (µg l ⁻¹)	PO ₄ ³⁻ (µg l ⁻¹)	TDS (mg l ⁻¹)	EC (µS/cm)	pH
Upstream	1	3.9	1.2	1.7	1.4	17.8	8.9	5.5	62.5	0.5	2.2	102.9	163.3	7.3
	2	4.0	1.2	3.4	1.3	18.3	8.9	1.6	69.2	0.5	2.1	107.8	171.2	7.6
	3	2.0	1.2	3.8	1.2	24.4	8.9	1.6	105.9	1.3	3.1	148.9	236.3	7.3
	4	2.0	1.2	4.3	1.4	21.2	8.9	1.7	65.6	0.7	2.5	106.2	168.6	7.0
	5	2.0	1.2	10.7	1.3	18.3	8.9	1.6	64.2	0.5	2.9	108.2	171.7	7.1
	6	8.0	3.6	13.7	2.1	54.9	8.9	1.6	73.5	0.1	0.6	166.3	263.9	7.9
	7	34.0	15.6	16.7	3.8	250.1	97.5	1.5	115.6	9.8	5.0	534.8	848.9	7.4
	8	4.0	2.4	2.9	0.9	25.4	8.9	1.6	67.3	0.7	2.8	113.4	180.1	7.3
	9	6.0	3.6	3.4	1.0	35.6	17.7	1.6	70.2	0.6	3.1	139.1	220.8	7.3
	Midstream	10	2.0	3.6	2.6	0.9	42.7	8.9	1.7	75.8	1.4	3.2	138.1	219.2
	11	2.0	1.2	2.9	0.8	36.6	35.5	1.6	110.0	2.0	11.5	190.6	302.5	7.3
	12	3.8	1.2	3.0	1.1	31.8	17.7	1.5	100.4	2.9	12.3	160.5	254.8	7.4
	13	4.0	2.4	9.4	3.9	30.5	8.9	1.9	90.8	3.4	13.7	151.8	240.9	7.7
	14	6.0	3.6	24.6	3.9	64.1	12.5	1.7	85.3	2.8	10.3	201.5	319.9	7.5
	15	10.0	7.2	2.3	0.9	97.6	26.6	2.1	83.0	3.0	9.9	229.7	364.6	7.7
	16	13.0	5.2	2.9	0.9	96.5	35.5	0.1	84.0	2.7	11.2	238.1	377.9	7.5
Downstream	17	16.0	6.0	22.7	4.2	97.6	44.3	0.3	85.0	2.8	14.4	276.0	438.1	7.9
	18	16.0	8.4	27.4	32.9	158.6	79.5	0.7	76.2	2.34	13.8	399.7	634.4	7.8
	19	12.0	8.2	150.2	19.3	163.2	210.3	0.2	89.3	2.29	10.5	652.7	1036.0	7.7
	20	14.9	7.2	168.3	18.9	174.5	260.5	0.2	95.5	3.25	11.2	740.0	1174.6	7.9

*Refer Fig 2.1 for sampling locations

Table 3.5 Concentration of major ions and nutrients during summer season

	S.No*	Ca ²⁺ (mg l ⁻¹)	Mg ²⁺ (mg l ⁻¹)	Na ⁺ (mg l ⁻¹)	K ⁺ (mg l ⁻¹)	HCO ₃ ⁻ (mg l ⁻¹)	Cl ⁻ (mg l ⁻¹)	H ₄ SiO ₄ (mg l ⁻¹)	SO ₄ ²⁻ (mg l ⁻¹)	N-NO ²⁻ (µg l ⁻¹)	PO ₄ ³⁻ (µg l ⁻¹)	TDS (mg l ⁻¹)	EC (µS/cm)	pH
Upstream	1	3.9	1.3	2.9	0.9	15.6	7.6	7.2	23.2	8.5	2.3	62.6	99.4	6.5
	2	3.8	1.5	2.5	0.9	17.0	7.7	2.0	24.7	7.3	2.5	60.0	95.3	6.6
	3	4.0	3.6	2.6	0.8	18.3	8.9	1.5	27.2	10.2	5.3	66.9	106.2	6.8
	4	7.2	4.3	3.1	2.9	19.5	20.5	1.8	40.0	5.1	6.2	99.3	157.5	6.8
	5	2.0	1.2	2.5	1.1	16.5	10.6	1.6	27.1	7.9	2.1	62.6	99.4	6.8
	6	10.0	4.8	3.2	3.5	67.1	35.5	1.5	102.6	5.2	12.4	228.2	362.3	7.0
	7	38.0	18.0	26.0	5.7	256.2	106.4	1.5	362.6	47.1	7.1	814.4	1292.7	7.4
	8	3.5	2.1	2.7	1.5	16.8	10.4	1.2	27.2	8.9	2.5	65.4	103.9	7.0
	9	3.9	2.3	2.9	1.3	20.6	13.4	1.5	34.0	7.8	3.1	79.9	126.8	7.0
Midstream	10	2.0	1.2	4.3	1.2	24.4	17.7	1.6	42.1	21.4	5.5	94.5	149.9	7.0
	11	4.0	2.4	5.1	1.3	18.3	17.7	1.6	36.0	2.1	6.1	86.4	137.1	6.6
	12	5.0	2.3	6.4	1.5	24.4	26.6	1.6	51.0	2.5	5.6	118.8	188.5	6.7
	13	6.0	2.4	7.7	1.6	30.5	35.5	1.8	66.0	3.2	5.2	151.5	240.5	7.0
	14	7.5	2.2	11.4	2.2	35.6	31.0	1.6	66.6	2.6	5.3	158.1	250.9	7.1
	15	10.0	2.4	15.0	2.7	85.4	26.6	2.0	112.0	1.9	5.5	256.1	406.6	7.6
	16	11.0	5.4	9.5	3.2	91.5	39.9	0.1	131.4	1.9	3.6	292.0	463.5	7.5
Downstream	17	12.0	8.4	21.9	4.0	97.6	53.2	0.2	150.8	1.8	4.0	348.1	552.6	7.8
	18	18.0	4.8	25.3	5.2	115.9	79.8	0.2	195.7	4.3	4.6	444.7	706.1	7.9
	19	20.5	5.3	85.5	108.2	120.5	129.6	0.1	250.1	2.9	3.3	719.8	1142.6	8.0
	20	23.6	6.4	90.6	158.5	118.7	150.7	0.1	269.4	2.7	3.1	818.0	1298.4	7.9

*Refer Fig 2.1 for sampling locations

In the river basin are dominant anions (SO_4^{2-} , HCO_3^- and Cl^-). On an average, these anions account 73.6% of the total major ions compositions and increases gradually to increasing river order. The sulphate was observed in higher concentration particularly at Tenkasi (S7) location during postmonsoon (115 mg l^{-1}) and summer (362.6 mg l^{-1}) in the upstream region is due to agriculture runoff consequence fertilizer input from dual agriculture practices. Similarly, high bicarbonate concentration observed in the same location during premonsoon (176.9 mg l^{-1}) and summer (256.2 mg l^{-1}) is due to increase in the dissolution rates of soil organic matters where root respiration and oxidation of organic carbon produces higher levels of carbonic acid (Bluth and Kump 1994). For rivers with prevailing silicate weathering in their basins have the anions present in the form of $\text{H}_4\text{SiO}_4 > \text{HCO}_3^- + \text{Cl}^- + \text{SO}_4^{2-}$ (Zhang et al 1990). In this present study does not occur with such a situation from the results. On the other hand for river basin in which carbonate weathering prevails, has a characteristic feature of predominance in Ca^{2+} and Mg^{2+} cations and high $(\text{Ca}+\text{Mg}):(\text{Na}+\text{K})$ ratio. On a ternary anion diagram, figure 3.1(a) relating SiO_2 , HCO_3^- , SO_4^{2-} and Cl^- most of the data cluster falls towards the alkalinity side of the field. A similar cations diagram relating to Ca^{2+} , Mg^{2+} and (Na^++K^+) shows that most of the data point towards left corner of the triangle figure 3.1(b). The HCO_3^- concentration increases towards downstream during all the four season (1.2 fold during monsoon and pre-monsoon; 1.3 fold during summer). Downstream variations of major ions have been reported for a number of other rivers (Gibbs 1967; Subramanian 1983; Gupta and Subramanian 1994; Zhang 1995; Datta and Subramanian 1998).

Chloride is the third major anions of about (20.2%) after HCO_3^- in the river water. Its concentration ranged from 8.9 to 106.4 mg l^{-1} during pre-monsoon, 15.1 to 109.8 mg l^{-1} during monsoon, 8.9 to 260.5 mg l^{-1} during post monsoon and 7.6 to 150.7 mg l^{-1} during summer season. An annual average of 43.2 mg l^{-1} has been observed in this study which is comparable with other South Asian rivers and World rivers (Table 3.1). Berner and Berner (1987) estimated that 55% of the Cl in the river is derived from rock formation and the remaining 45% is recycled through the atmosphere. In general,

a very high positive correlation of Cl^- has been observed with Na during all seasons (Table 3.6).

The Box-Whisker plot was used as an exploratory data tool. These plots are called five members summary for the variable displayed, generally shown on actual concentration units. The plot is based on the medium, quartiles, and extreme values. The box represents the inter-quartile range, which contains the 50% of values. The Whisker is lines that extend from the box to the highest and lowest values, excluding outliers. A line across the box indicates the medium and a triangle indicates the arithmetic mean. The Box and Whisker plots showed that seasonal variation in EC, TDS and HCO_3^- were high concentration during postmonsoon and low during premonsoon Figures 3.2 (a) & (b). This strongly suggests that the flow of river during postmonsoon and summer seasons are reduced to its maximum level and there are significant seasonal changes in concentration of river water during dry season due to low fresh water discharge and evaporation processes. The level of pollutants in stream water rises to its maximum. The total TDS of the surface water was reduced levels in premonsoon and monsoon season is because of the heavy rains during the months of June-September, October-December in the catchment area. Heavy rainfalls during monsoon act as a dilution factor which results in the dilution of contaminants intensity. The main source of the HCO_3^- in surface water is due to the rock weathering processes.

The concentration of dissolved silica fluctuates widely throughout the river basin. In pre-monsoon, the concentration varied from 2.7 to 18.8 mg l^{-1} . The possible source of dissolved silica is kaolinisation of silicates such as feldspar, augite and biotite. The temperature of the river basin always exceeds 38 °C during summer and immediately followed by the rainfall during the southwest monsoon in the catchments areas, which enhances the weathering of the country rocks such as charnockites, granitic gneiss, calc gneisses, calc granulites, and quartzites resulting in high concentration of silica (18.8 mg l^{-1}) in the premonsoon season. The alkaline nature of the river further enhances the solubility of amorphous silica and also the mineral-water

interaction responsible for the dissolved silica concentration of the river basin (Gupta and Subramanian 1994). At the earth surface temperature, quartz has a solubility of 6.5 mg/l where as other forms of silica have solubility up to 115 mg l⁻¹ (Garrels and Mackenzie 1971). Meybeck (1979) suggested that the dissolved silica content of river water is controlled by the average temperature and geology of the basin.

3.2.3 Major cations

An analytical study of major cations of the river has been carried out to assess the weathering processes within the basin. Calcium and potassium in river water are entirely from weathering processes. Calcium constitutes about 5 % of the average chemical composition and Mg²⁺ about 1.8 % of the total dissolved solids of the river basin. This is probably derived from the dissolution of Kanker, limestone's, plagioclase feldspar and other ferromagnesian minerals. On the other side, magnesium is derived from the hydrolysis of olivine bearing rocks in the sources area. In summer, the Ca²⁺ concentration range from 2 to 38 mg/l in the upstream and 12 to 23.6 mg l⁻¹ in the downstream. Similarly, premonsoon season, the calcium concentration ranged from 4.4 to 38 mg l⁻¹ and magnesium concentration ranges of 1.2 to 16.2 mg l⁻¹. The ratio of (Ca²⁺+Mg²⁺) : (Na⁺+K⁺) indicates that the carbonate weathering could be the primary source of the major ions to this water. Wide seasonal and spatial variations are observed in the total dissolved solids (TDS) concentration in the river basin. The ratio (>1) of (Ca²⁺+Mg²⁺) : (Na⁺+K⁺) in the Tamiraparani river suggests that the contribution of these ions by silicate weathering is less significant. Gaillardet et al (1997) computed Ca²⁺/Na⁺; HCO₃⁻/Na⁺ and Mg²⁺/Na⁺ ratios to differentiate between the carbonate and silicate weathering in the Amazon river basin. In the upstream region of river basin, high values of Ca²⁺/Na⁺ (0.61-7.3) has been observed when compare to the downstream region (0.07-4.48) indicating the predominance of carbonate weathering in the catchment region.

Sodium is the dominant cations in the river system and accounts to 9% of the average TDS. The catchment silicate weathering and atmospheric inputs are the major

sources of the Na^+ in river water. The sodium concentration is lower than chloride values from upstream to downstream for all the seasons. This indicates that the atmospheric recycling is the main source for sodium and is less influenced by physical weathering (Subramanian et al 1987). In premonsoon season, an average sodium concentration was higher (598.9 mg l^{-1}) in comparison to the monsoon season (308.2 mg l^{-1}). Potassium concentration is lower by about two times when compared to Na in all the four seasons possibly due to low mobility of potassium than sodium. Based on the environmental factors that influence river water chemistry, Gibbs (1970) suggested a three fold classification of rivers:

- i) Low total dissolved solids (TDS) and high $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ water controlled by rainfall
- ii) Intermediate TDS and low $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ water controlled by rock weathering
- iii) High TDS and high $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ water controlled by evaporation

The Gibbs ratio I, $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ for anion and ratio II, $\text{Na}^+ + \text{K}^+ / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ for cations in water samples were plotted separately against the respective values of total dissolved solids. Ratios I and II range from 0.14 to 0.6 and 0.22 to 0.93 for postmonsoon and from 0.31 to 0.55 and 0.19 to 0.84 for premonsoon seasons. This gives a characteristic boomerang shaped plot, depicting the major factors operating behind the water chemistry. From the figs 3.3 and 3.4, it can be observed that the points fall in the region of rock dominance, consistent with the observation that the dissolution of various minerals is a prime factor operating the water chemistry of the Tamiraparani basin. A plot figures 3.3 and 3.4 of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs Total cations and $(\text{Ca}^{2+} + \text{Mg}^{2+}) / (\text{Na}^+ + \text{K}^+)$ shows that the river basin is dominated by rock weathering. One of the unifying factors is the excellent relationship between the major parameters calcium and magnesium. All the rivers, in general, show high carbonate alkalinity independent of local lithology; rock weathering involving atmospheric CO_2 and minerals in different lithology uniformly releases Ca^{2+} , Mg^{2+} and HCO_3^- to the river

water (Berner and Berner 1996). Correlation coefficient matrix for the post monsoon and premonsoon major ions is given in the (Table 3.6). The correlation between Ca^{2+} and other parameters except nitrite is significantly negative, whereas HCO_3^- , Cl^- , Mg^{2+} , Na^+ , PO_4^{3-} is significantly positive for both premonsoon and postmonsoon seasons.

In the river basin, Ca^{2+} and Mg^{2+} together constitute 36.4% of the total cations and HCO_3^- contribute about 32.7% to the total anionic balance. Carbonate and silicate weathering and evaporite dissolution can supply Ca^{2+} and Mg^{2+} in water, whereas the source for Na^+ and K^+ are atmospheric deposition, evaporite dissolution and silicate weathering. The sodium concentration in the analysed water is significantly in less over chloride and $(\text{Cl}^-/\text{Na}^++\text{K}^+)$ i.e. 1.8 suggesting that much of the alkaline in these water originated from a source other than precipitation and probably from the weathering of silicate minerals. On an average (Na^++K^+) contributes 63.8% of the total cationic balance and relatively high concentration of dissolved silica and $(\text{Na}^++\text{K}^+)/\text{TZ}^+$ ratio of (1.6) suggests that silicate weathering could be the major source of alkalis. However, this is an upper limit of silicate weathering, as there could be other evaporite sodium/potassium minerals and/or contribution from alkaline soil and groundwater. The evaporite encrustations of sodium/potassium salts developed in some part of the drainage area due to cyclic wetting and drying during high and low flow period. This aids the formation of alkaline/saline soils, which may also serve as a source of sodium and potassium (Sarin et al 1989).

The $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ ratio marks the upper limit of bicarbonate input from the weathering of carbonate rock (Stallard and Edmond 1983). The variation diagram between $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs HCO_3^- for the reservoir water samples show that in many samples, $(\text{Ca}^{2+}+\text{Mg}^{2+})$ contents is in excess of alkalinity explains kanker, limestones, plagioclase feldspar and other ferromagnesian minerals in the rock type in the catchment area i.e. pre-monsoon $(\text{Ca}^{2+}+\text{Mg}^{2+}/\text{HCO}_3^-=3.6)$ and post-monsoon $(\text{Ca}^{2+}+\text{Mg}^{2+}/\text{HCO}_3^-=5.8)$. The excess of $\text{Ca}^{2+}+\text{Mg}^{2+}$ over bicarbonate in these water indicated some extra source of Ca^{2+} and Mg^{2+} and demanding that part of the excess

positive charge has to be balanced by other anions like SO_4^{2-} and/or Cl^- (Fig 5.5 (a)). The excess of bicarbonate over $\text{Ca}^{2+}+\text{Mg}^{2+}$ requires that part of the alkalinity should be balanced by alkalis (Na^++K^+). A plot of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ versus $(\text{HCO}_3^-+\text{SO}_4^{2-})$ shows better correlation throughout the data range (Fig 5.5 (b)); most of the plotted points fall below the 1:1 equiline requiring a portion of the $(\text{HCO}_3^-+\text{SO}_4^{2-})$ to be balanced by the alkalis (Na^++K^+). Further, the plot of $(\text{Ca}^{2+}+\text{Mg}^{2+})$ vs Total Cations (TZ^+) shows that the plotted points fall far below the equiline, the departure being more pronounced at high concentration and during lean flow period (pre-monsoon), reflecting an increasing contribution of Na^+ and K^+ with increasing dissolved solids (Fig 5.5 (c)).

3.3 FACTOR ANALYSIS

FA / PCA, a multivariate statistical technique for pattern recognition, attempts to explain the variance of a large set of inter-correlated variables and transforming into a smaller set of independent (uncorrelated) variables (principal components). Principal components (PCs) are obtained by multiplying the original correlated variables with the eigenvector, which is a list of coefficients (loadings and weightings) and are thus, weighted linear combinations of the original variables. PCs provide information on the most meaningful parameters, which describe whole data set affording data reduction with minimum loss of original information (Helena et al 2000; Wunderlin et al 2001). The general purpose of the factor analysis is to find a way of condensing the information contained in a number of original variables into a smaller set of new composite dimensions with a minimum loss of information. The PCs/FA was performed on normalized variables (13 nos) after sorting out the highly correlated variables from the data sets. The data matrix of 13 variables (pH, EC, Cl^- , NO_2^- , SO_4^{2-} , HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , H_4SiO_4 , PO_4^{3-} and TDS) and 20 observations has been used in the present factor analysis. Three factors with eigenvalue >1 have been extracted from the principal factor matrix after varimax rotation (Table 3.7)

Table 3.6 Correlation matrix for water quality parameters in premonsoon and postmonsoon seasons

Variable	Premonsoon season												
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	H ₄ SiO ₄	SO ₄ ²⁻	NO ₂	PO ₄ ³⁻	TDS	EC	pH
Ca ²⁺	1.00												
Mg ²⁺	0.53	1.00											
Na ⁺	0.55	0.78	1.00										
K ⁺	0.30	0.61	0.62	1.00									
HCO ₃ ⁻	0.63	0.76	0.98	0.55	1.00								
Cl ⁻	0.64	0.75	0.97	0.55	0.99	1.00							
H ₄ SiO ₄	0.24	-0.29	-0.03	-0.15	0.00	0.02	1.00						
SO ₄ ²⁻	0.21	0.17	0.26	0.30	0.19	0.20	0.16	1.00					
NO ₂	-0.19	-0.35	-0.66	-0.32	-0.63	-0.61	-0.25	-0.51	1.00				
PO ₄ ³⁻	0.27	0.44	0.76	0.29	0.70	0.68	0.30	0.52	-0.89	1.00			
TDS	0.66	0.77	0.98	0.62	0.98	0.98	0.05	0.36	-0.67	0.74	1.00		
EC	0.66	0.77	0.98	0.62	0.98	0.98	0.05	0.36	-0.67	0.74	1.00	1.00	
pH	0.51	0.62	0.89	0.53	0.88	0.86	0.10	0.37	-0.81	0.82	0.90	0.90	1.00
Variable	Postmonsoon season												
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	H ₄ SiO ₄	SO ₄ ²⁻	NO ₂	PO ₄ ³⁻	TDS	EC	pH
Ca ²⁺	1.00												
Mg ²⁺	0.95	1.00											
Na ⁺	0.31	0.39	1.00										
K ⁺	0.40	0.47	0.65	1.00									
HCO ₃ ⁻	0.93	0.96	0.57	0.61	1.00								
Cl ⁻	0.52	0.58	0.95	0.69	0.75	1.00							
H ₄ SiO ₄	-0.36	-0.37	-0.45	-0.41	-0.46	-0.49	1.00						
SO ₄ ²⁻	0.43	0.41	0.21	0.07	0.47	0.35	-0.32	1.00					
NO ₂	0.83	0.81	0.16	0.15	0.77	0.37	-0.23	0.71	1.00				
PO ₄ ³⁻	0.29	0.29	0.31	0.46	0.39	0.37	-0.46	0.47	0.38	1.00			
TDS	0.71	0.76	0.87	0.71	0.89	0.96	-0.52	0.46	0.56	0.43	1.00		
EC	0.71	0.76	0.87	0.71	0.89	0.96	-0.52	0.46	0.56	0.43	1.00	1.00	
pH	0.45	0.40	0.46	0.50	0.47	0.46	-0.38	0.19	0.20	0.53	0.51	0.51	1.00

Correlation significant at $P < 0.05$

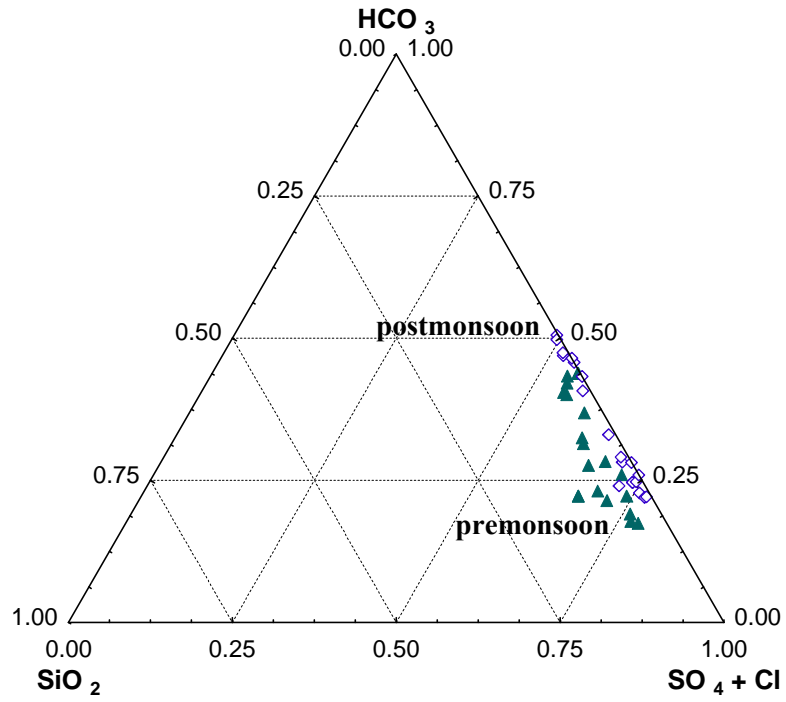


Figure 3.1 (a) Ternary diagram for anion relationship

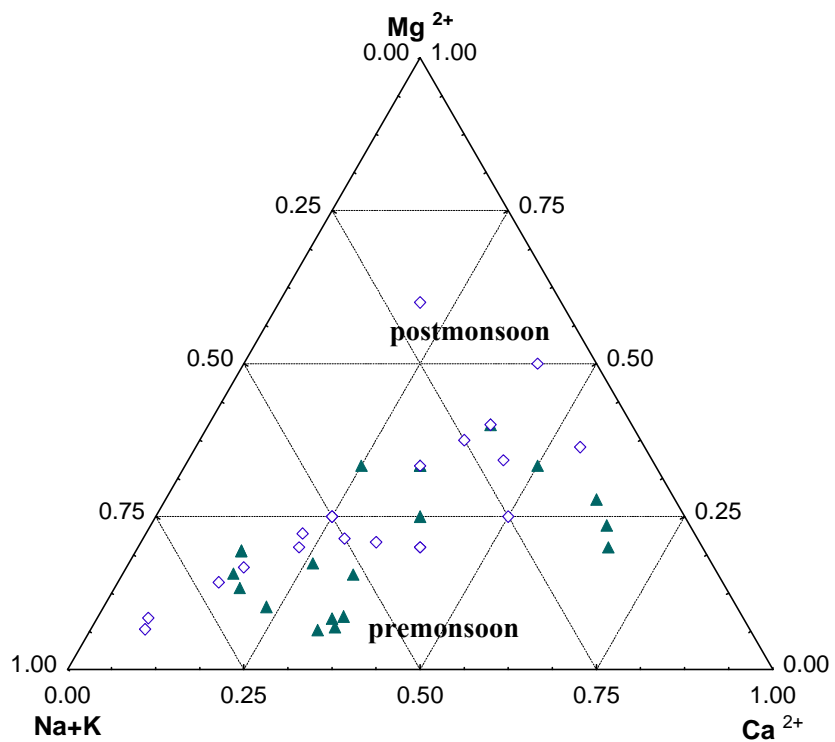
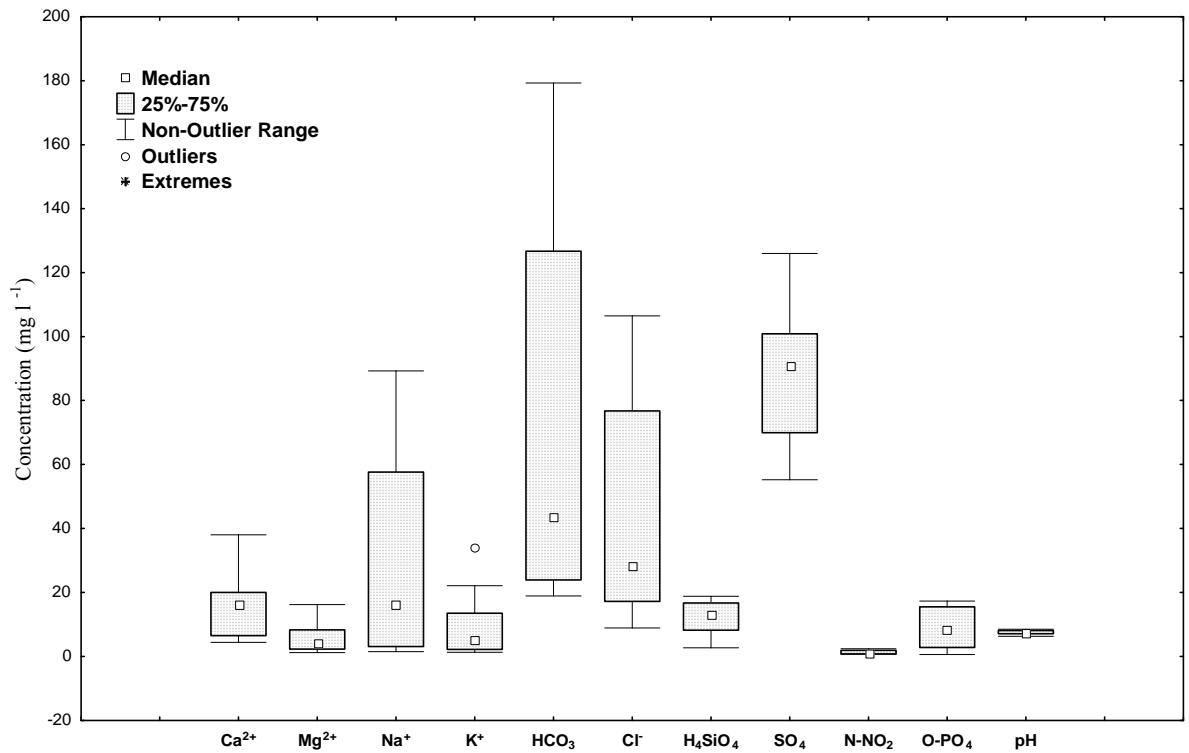
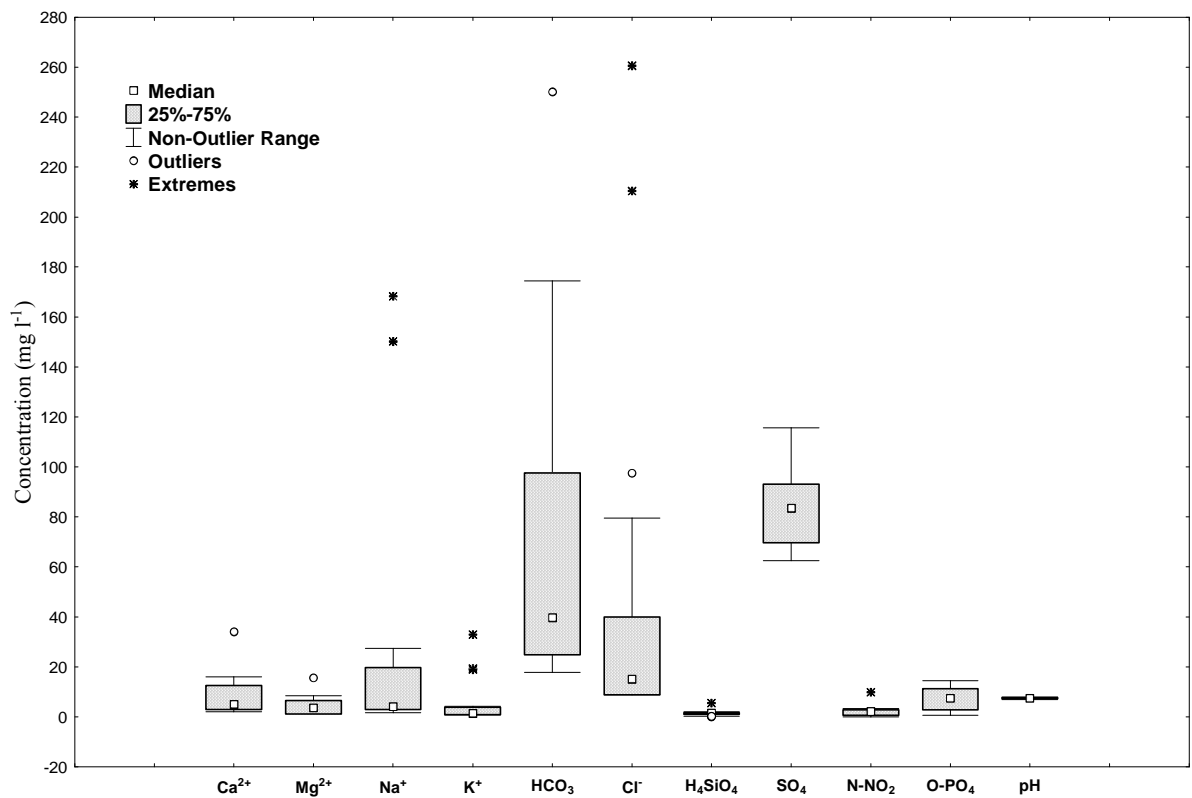


Figure 3.1 (b) Ternary diagram for cation relationship



(a)



(b)

Figure 3.2 Box-Whisker plot showing variation of physiochemical parameters during (a) premonsoon and (b) postmonsoon season.

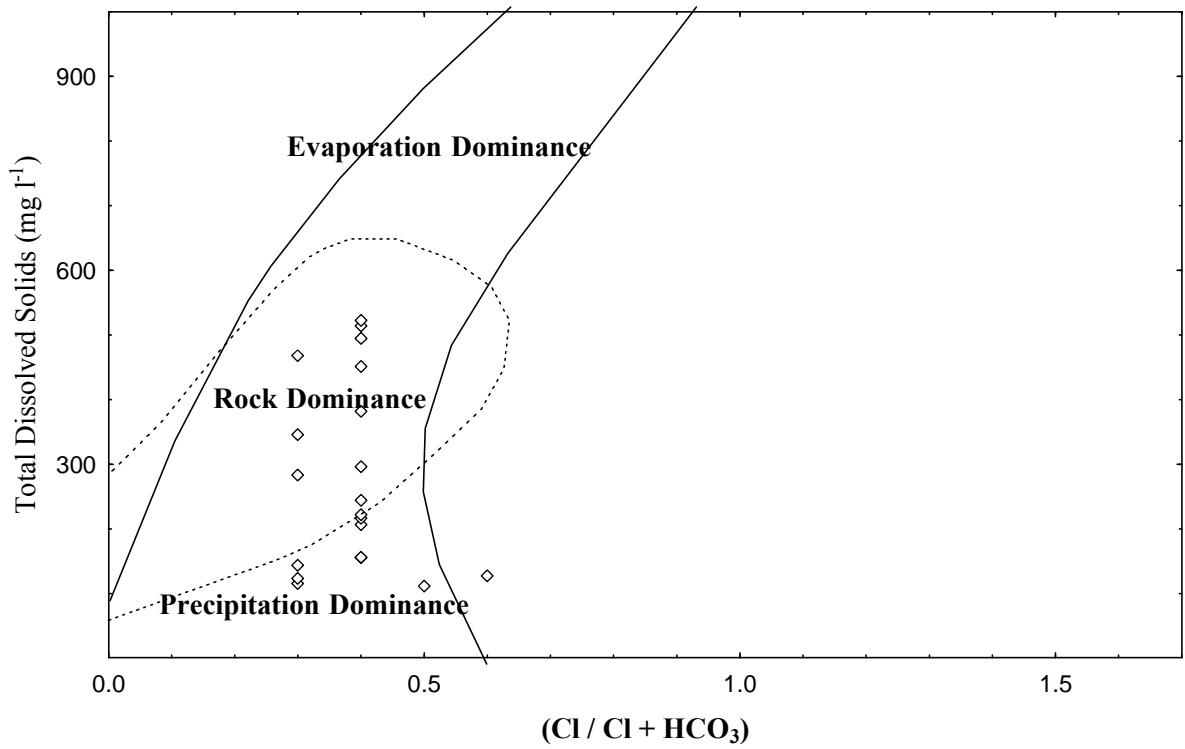
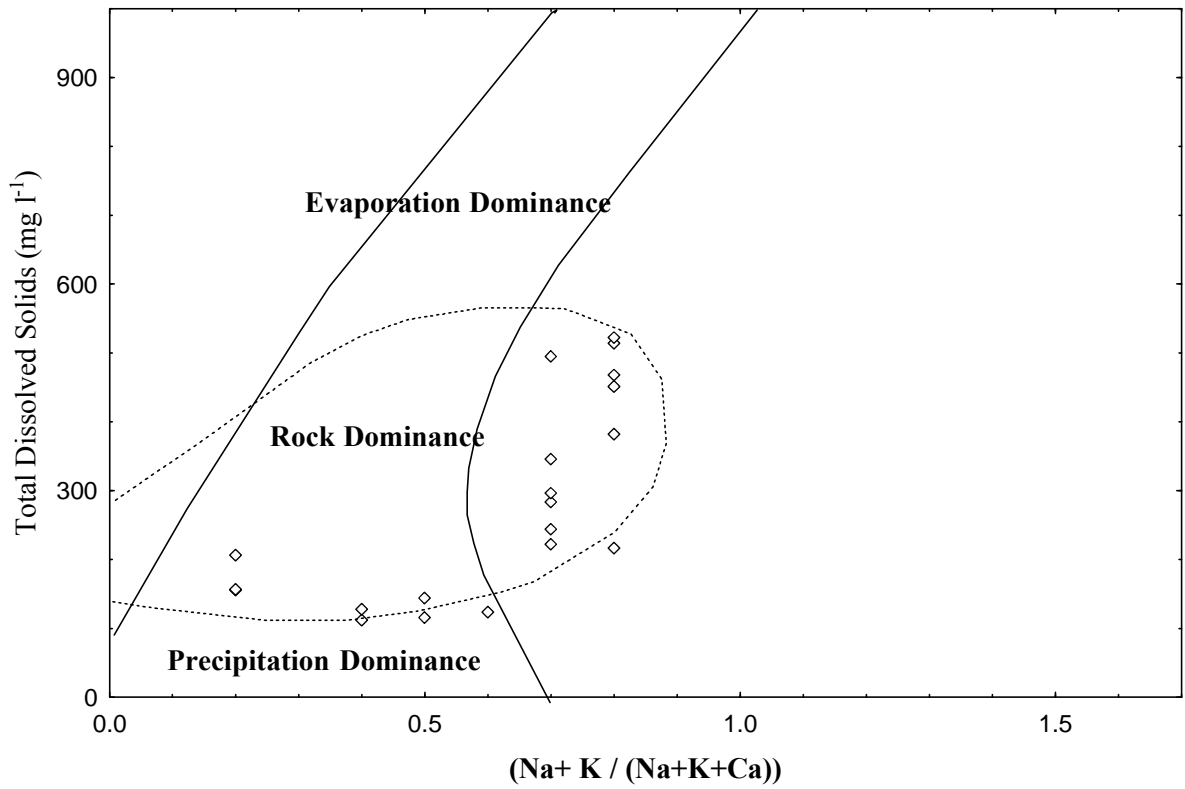


Figure 3.3 Mechanism controlling chemistry of river water during premonsoon season (after Gibbs 1970)

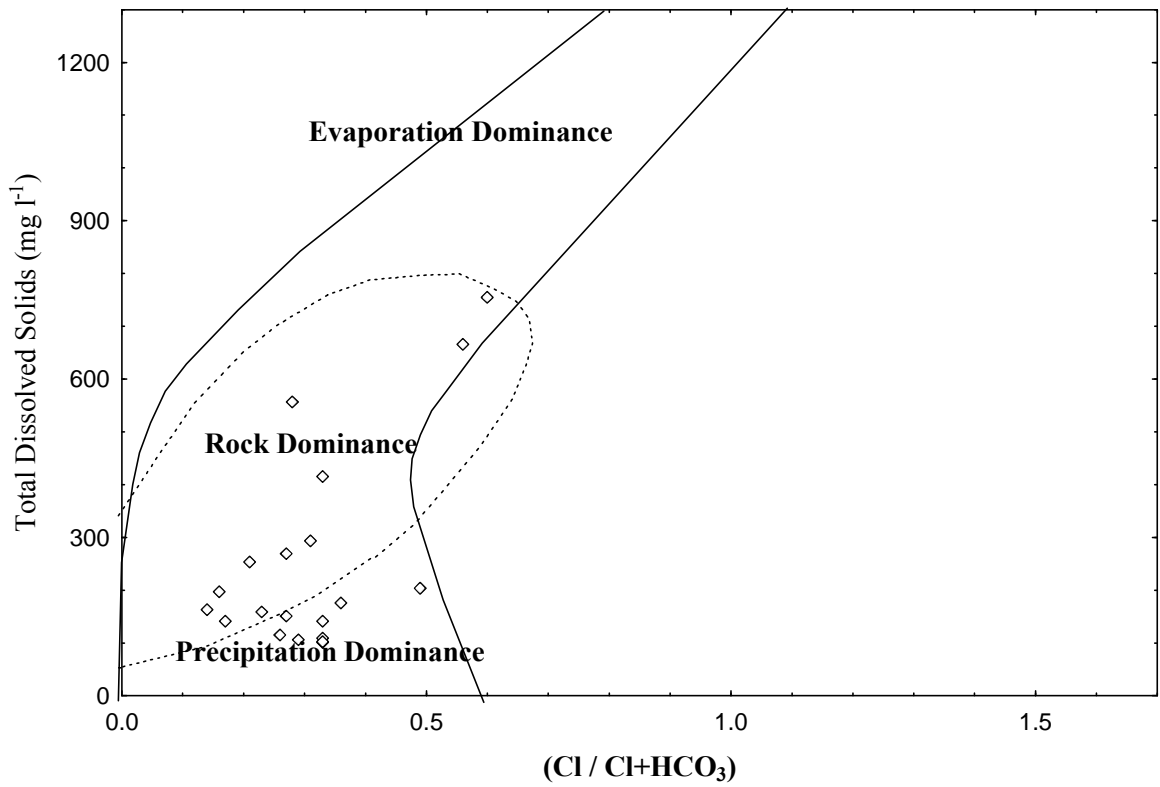
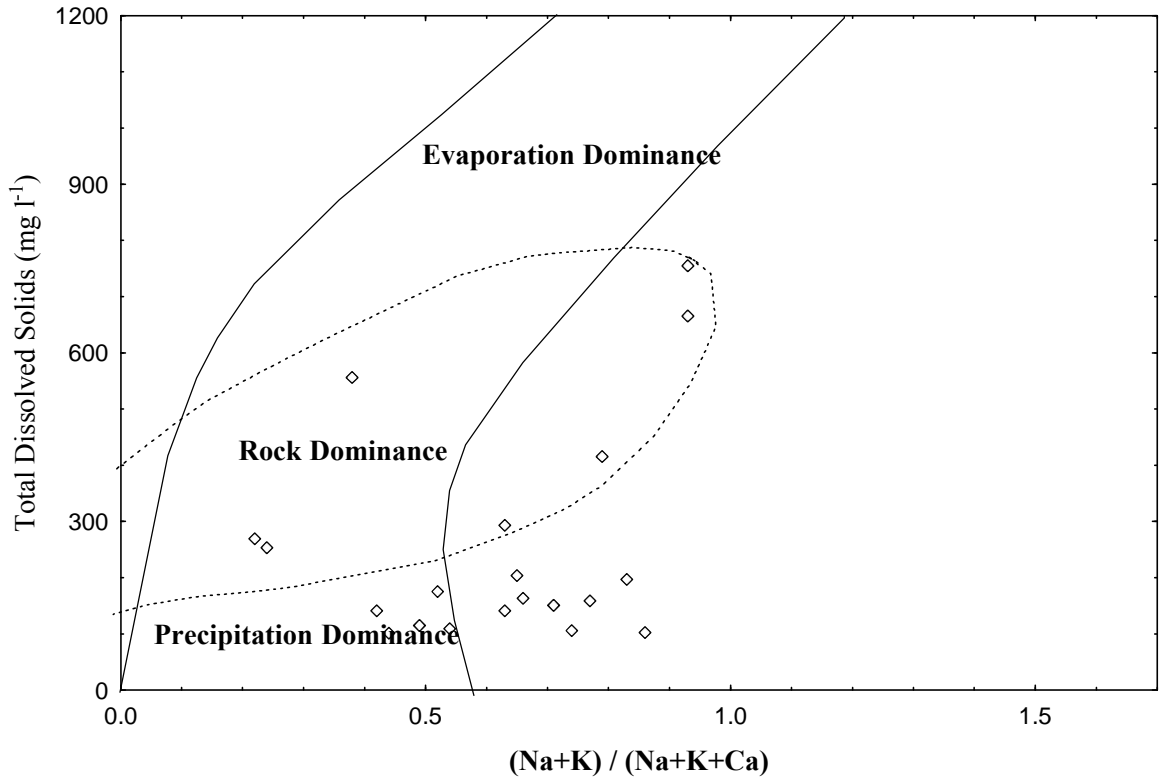
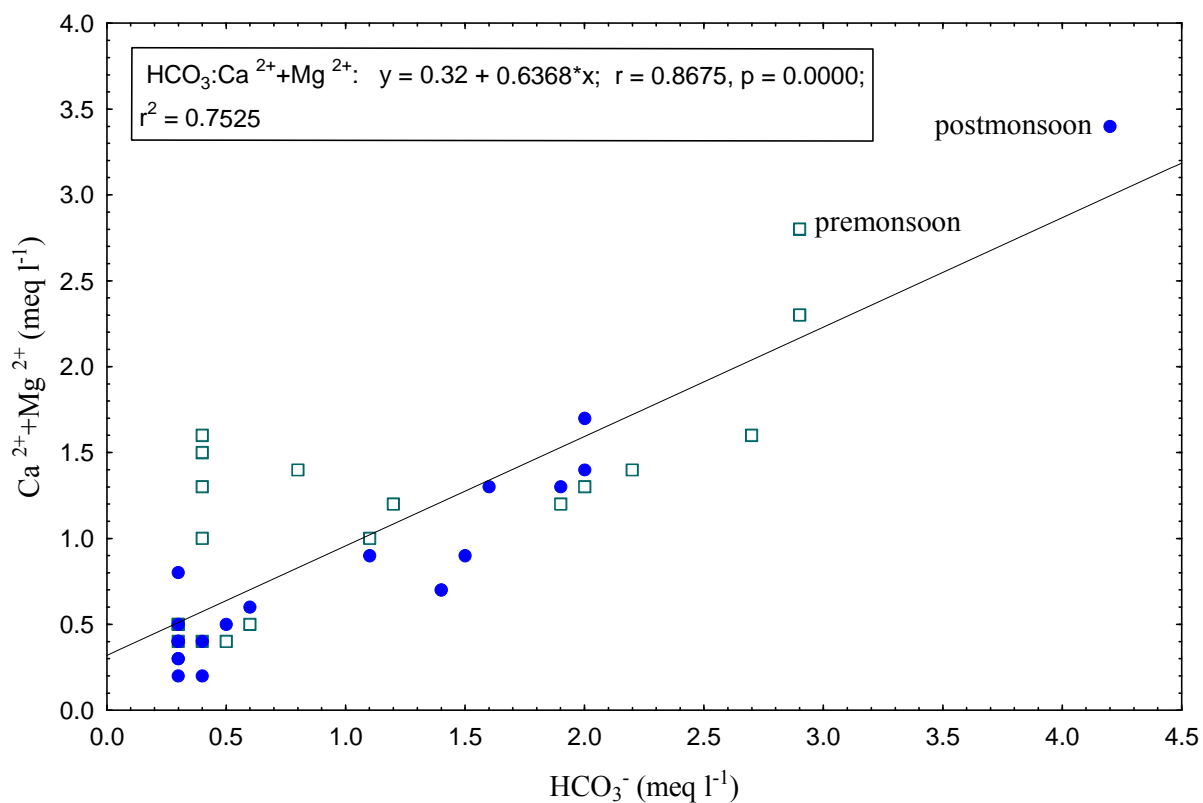
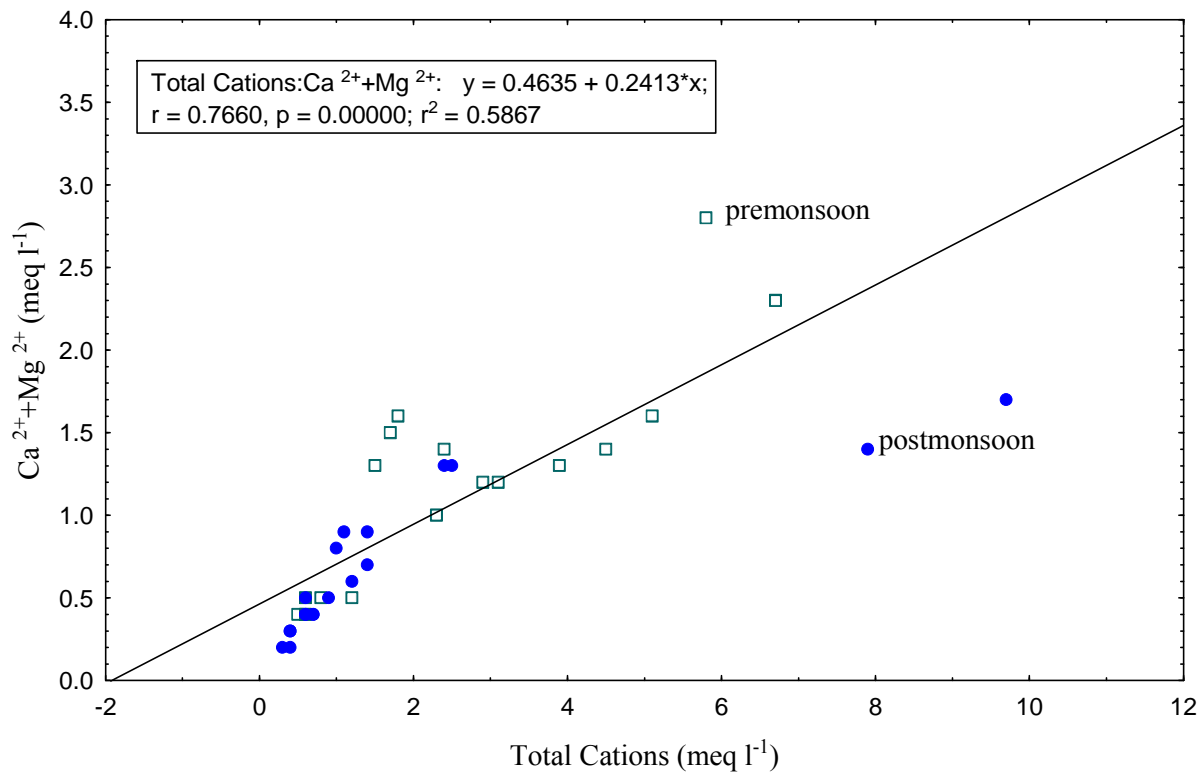


Figure 3.4 Mechanism controlling chemistry of river water during postmonsoon season (after Gibbs 1970)



(a)



(b)

Figure 3.5 (a) & (b) Scatter plot for major ion chemistry

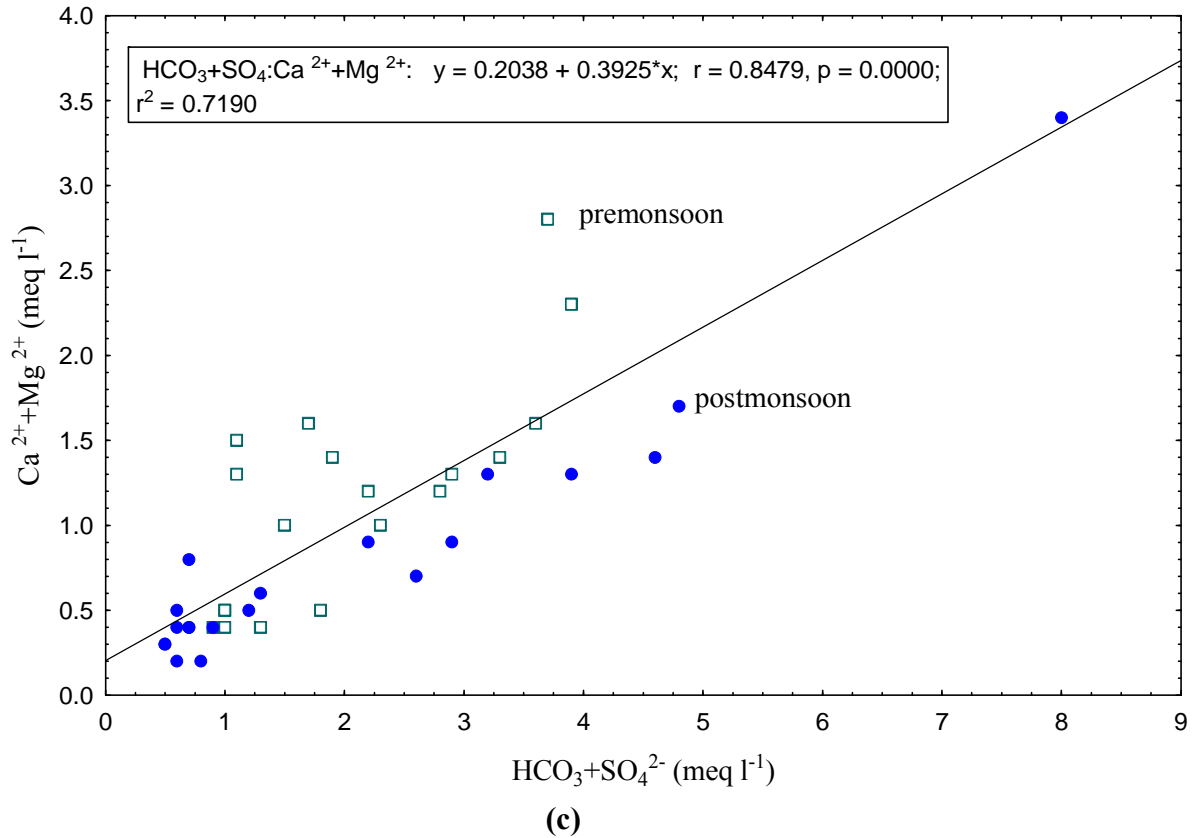


Figure 3.5 (c) Scatter plot for major ion chemistry

3.3.1 Factor- I

Factor analysis was applied to the normalized data to compare the compositional patterns between the analysis of water samples and identified factors that influence each one. Factor analysis evolved six factors with eigenvalues >1 explaining about 96% of the total variance in the hydro-chemical dataset. The first factor accounting for 55.5% of the total variance showed high positive loading (>0.78) on magnesium, phosphate, chloride, bicarbonate, and sodium, whereas, moderate loading (>0.58) on silicate, calcium and potassium during pre-monsoon and post-monsoon season. Thus, the factor I contains hydro-geochemical variables (Mg^{2+} , PO_4^{3-} , Cl^- , HCO_3^- , and Na^+) originating, at a first glance, from mineralization of the geological components of the soils. The contribution of Na^+ , K^+ and Mg^{2+} to this factor can be considered as a result of cation exchange processes at soil water interface (Guo and Wang 2004) and dissolution of sodium bearing minerals, which are found in the region

as kanker, limestones, plagioclase feldspar and other ferromagnesian minerals in the rock type is involved in the geographical weathering. The accounts for 55% of variance in the data matrix and hence factor-I dominates the water chemistry of Tamiraparani and bicarbonate coexists with Ca^{2+} , Na^+ , K^+ , Cl^- and SO_4^{2-} explaining the ‘precipitation factor’ and the interaction of hydrosphere-lithosphere coupled with chemical weathering process.

3.3.2 Factor-II

The second factor accounting for 17.5 % of total variance showed high negative loading on silicate, moderate positive loading on nitrite. (postmonsoon and premonsoon seasons) Factor-II accounts for 17.5% variance in the data matrix and consists of variables NO_2 , Ca^{2+} , H_4SiO_4 and K^+ are the least dominated cations in the analysed samples. During the course of continental weathering, sodium turns out to be more mobile than potassium and dominate the natural solution (Milliot 1970). Only 15% of the river transport of potassium is in the dissolved form (Berner and Berner 1987). The high loading of H_4SiO_4 and NO_2 may be attributed to anthropogenic input from the intense fertilizer discharge from agricultural lands and domestic sewage into the river basin. A high negative score of Silicate can be attributed to the weathering of kanker, limestones, plagioclase feldspar and other ferromagnesian minerals in the rock type are involved in the geographical weathering.

3.3.3 Factor -III

The third factor capturing 11.1% of variance was moderate positive loading on phosphate and sulphate whereas, negative loading on calcium and silicate in premonsoon season. This factor is mainly represented by sulphate and orthophosphate. These third factors taken together explains about 84% of the total variance in the data matrix, The fourth and fifth factor capturing 7.9% and 5.7% of variance was moderate positive loading on sulphate and potassium indicating that the determined variables,

which control the water chemistry are rock weathering with minor contribution from anthropogenic and atmospheric sources.

3.4 CLUSTER ANALYSIS

Hierarchical cluster analysis is a powerful tool for analysis water chemistry data and this method groups samples into distinct populations that may be significant in the geologic/hydrologic context, as well as from a statistical point of view (Piper 1994). Data standardization is preferred in cluster analysis since it gives equal weight to each variable in the multivariate analysis. Otherwise, the Euclidean distances calculated will be influenced most strongly by the variable that has the greatest magnitude (Güler et al 2002). Cluster analysis is an unsupervised learning procedure that group names and number of groups are not known in priori. Classification differs from clustering since it is a supervised learning procedure in which group names and numbers of groups are known. Since the purpose of cluster analysis is to organize observed data into meaningful structures, it combines data objects into groups (clusters) such that objects belonging to the same cluster are similar as those belonging to different clusters are dissimilar (Anderberg 1973; Everitt 1993; Karaca et al 2000). R-mode hierarchical cluster analysis (HCA) was then applied to the standard z-scores using squared Euclidean distance as a similarity (dissimilarity) measure and the Ward's linkage algorithm. The statistical package for Statistica six sigma software packages was used for both the R-mode HCA and factor analysis. A combination of squared Euclidean distance and the Ward's linkage algorithm produces optimal results in R-mode cluster analysis. R-mode cluster analysis places a set of variables into distinct groups on the basis of their similarity or dissimilarity with each other in the field. The classification is based on the similarity of object attributes.

The clusters are characterized by similarity within the cluster and high dissimilarity between clusters. Cluster analysis Backer (1994) was performed on the

mean values of the parameters for each of the stations. Standardization of the data using Euclidean distance coefficients with the average linkage method of clustering was used (Fig 3.6) to segregate the stations according to the concentration values of water parameters. The results separated two different clusters along with the Tamiraparani river consist of all the measured values. The first cluster was made up of major concentration of sodium and chloride, where the level of pollution was moderate. In this cluster chloride in surface water may be from diverse sources such as weathering and leaching of sedimentary rocks and soils, domestic and industrial waste discharges, municipal effluents and the followed by other parameters as potassium, calcium, nitrite, silicates, orthophosphates, pH and magnesium. The second cluster was comprised of the bicarbonate and sulphate, which could be regarded as the least pollutants in the river water increasing due to the natural weathering processes and effluent from certain industries may also be a major source of sulphate to receiving the water. As we conclude from cluster results, the river Tamiraparani basin is not polluted from anthropogenic activities.

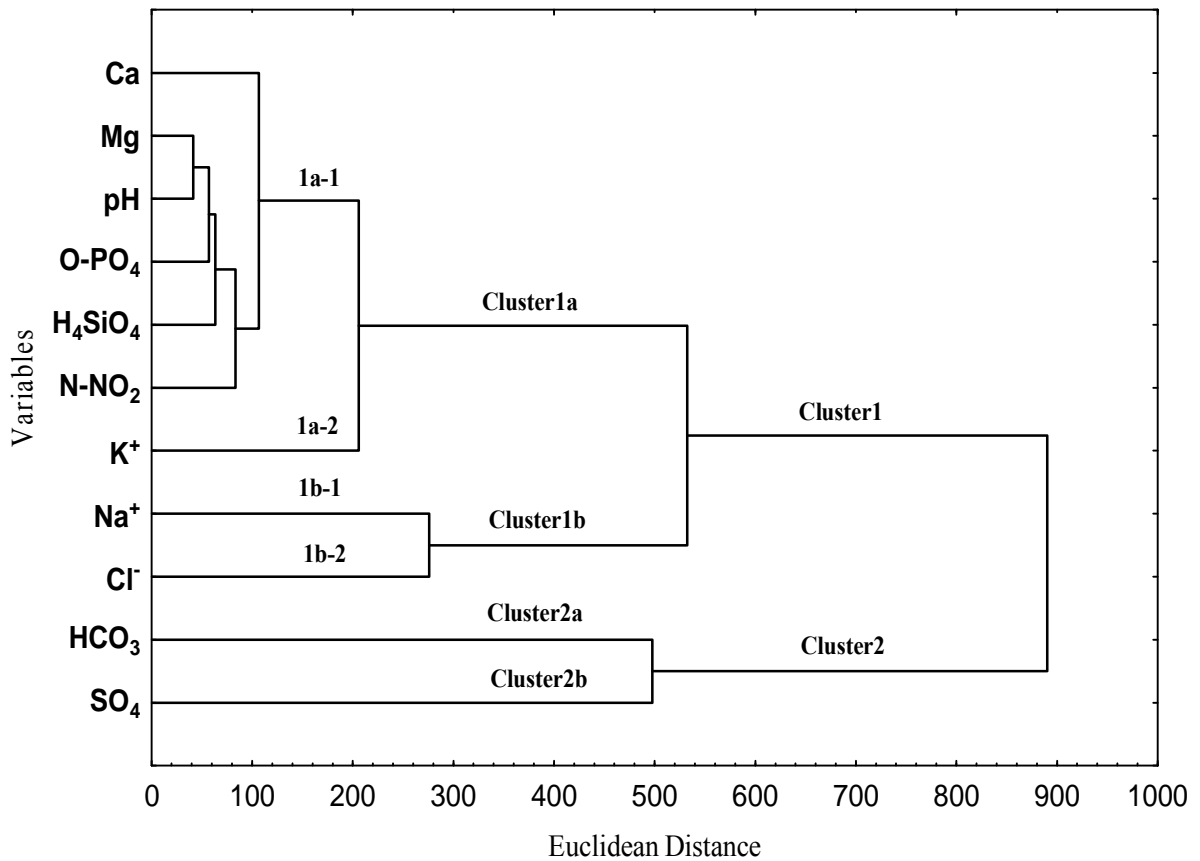


Figure 3.6. Dendrogram for chemical parameters in water samples

3.5 DISTRIBUTION OF DISSOLVED INORGANIC NUTRIENTS

3.5.1 Nitrogen

The occurrence of nitrite in surface water is closely connected with the nitrogen cycle and the main nitrite source is the oxidation of ammonia and organic nitrogen. Microorganisms play an important role in these processes, although nitrite can also be produced on photo-degradation of dissolved organic matter (DOM) (Kieber et al 1999). The fast oxidation of nitrite to nitrate by different pathways limits the concentration of nitrite in surface water. Accordingly, nitrite concentration is usually considerably lower than that of nitrate. The higher absorption rate of solar UV radiation by nitrite compared to nitrate and the higher photolysis quantum yield makes nitrite a competitive photo reactant (Boule et al 1999). Nitrate pollution usually originates from diffused sources, like intensive agriculture and un-sewered sanitation or point sources, such as irrigation of land by sewage effluent (Eckhardt and Stackelberg 1995; McLay et al 2001).

It may also originate from industrial effluents, including paper and munitions manufacturing, septic tanks and human and animal wastes, due to biochemical activity of nitrifying bacteria. The distribution of nitrifying activity along this transects; a peak in potential nitrifying activity (pNA) is invariably observed in the upper freshwater estuary together with a minimum oxygen concentration (Garnier et al 2001; Ce'bron et al 2003). Nitrification is a two-step process performed by two different functional bacterial groups. The oxidation of ammonia into nitrite by ammonia-oxidizing bacteria (AOB) has been extensively studied in the lower Seine river (Ce'bron et al 2003 & 2004). As the AOB present in freshwater environments belong to a monophyletic group from the β subclass of proteobacteria, it is possible to investigate the whole ammonia oxidizing population with molecular tools by targeting part of the ammonium monooxygenase (*amoA*) gene (Rotthauwe et al 1997). However, the nitrite oxidizing bacteria, which are responsible for the second step in the nitrification process (oxidation of nitrite into nitrate), have been less studied. The genus *Nitrobacter* was previously thought to be the main nitrite oxidizer (Bock and Koops 1992). However, a variety of recently developed techniques made it possible to explore the composition of the nitrite-oxidizing community in the environment and to enhance our knowledge of its functioning (Daims et al 2001; Dionisi et al 2002; Maron et al 2003).

Table 3.7 Varimax rotated factor analysis for water samples

	Premonsoon							Postmonsoon					
Variable	Communality	Factor I	Factor II	Factor III	Factor IV	Factor V	Variable	Communality	Factor I	Factor II	Factor III	Factor IV	Factor V
Ca ²⁺	0.97	0.62	0.11	-0.61	0.39	-0.22	Ca ²⁺	0.97	-0.85	0.37	-0.27	-0.15	0.05
Mg ²⁺	0.85	0.79	0.46	0.05	0.08	-0.11	Mg ²⁺	0.98	-0.88	0.29	-0.30	-0.14	0.03
Na ⁺	0.98	0.97	0.12	-0.01	-0.14	0.02	Na ⁺	0.97	-0.67	-0.62	-0.08	0.36	0.02
K ⁺	0.99	0.64	0.31	0.28	0.36	0.53	K ⁺	0.90	-0.66	-0.54	-0.11	-0.27	-0.29
HCO ₃ ⁻	0.98	0.96	0.14	-0.14	-0.16	-0.01	HCO ₃ ⁻	0.99	-0.96	0.11	-0.22	-0.05	-0.00
Cl ⁻	0.96	0.95	0.14	-0.16	-0.13	-0.01	Cl ⁻	0.99	-0.82	-0.45	-0.11	0.31	0.00
H ₄ SiO ₄	0.97	0.07	-0.75	-0.55	0.09	0.31	H ₄ SiO ₄	0.99	0.58	0.29	-0.37	0.27	-0.60
SO ₄ ²⁻	0.99	0.41	-0.51	0.42	0.57	-0.24	SO ₄ ²⁻	0.93	-0.58	0.39	0.53	0.40	-0.00
N-NO ₂	0.92	-0.74	0.50	-0.25	0.24	-0.01	N-NO ₂	0.96	-0.75	0.61	0.05	0.08	-0.06
O-PO ₄ ³⁻	0.96	0.80	-0.48	0.15	-0.23	-0.06	O-PO ₄ ³⁻	0.95	-0.56	-0.12	0.66	-0.27	-0.34
Eigenvalue		5.54	1.67	1.06	0.79	0.50	Eigenvalue		5.55	1.75	1.11	0.66	0.57
%Total Variance		55.35	16.71	10.62	7.95	5.00	%Total Variance		55.49	17.49	11.11	6.58	5.74
Cumulative %		55.35	72.07	82.68	90.63	95.63	Cumulative %		55.49	72.98	84.09	90.67	96.40

3.5.2 Nitrite

In living organisms, nitrogen cycle is considered to be most important after carbon cycle. Nitrogen occurs in the form of nitrogen gas, oxides (N_2O , NO and NO_2) and reduced nitrogen (NH_4). The major forms of nitrogen occurring in river water are nitrite (NO_2), nitrate (NO_3^- - most oxidized), ammonium (NH_4^- - most reduced) and organic nitrogen. The occurrence and distribution of these forms of nitrogen are governed by the chemistry of the subsoil, land use pattern, geology, vegetation, river water quality etc. The formation of nitrates assumes great importance in an aquatic ecosystem since, it is utilized by phytoplankton or lost from the environment through denitrification. Many agricultural practices affect soil aeration and enhance mineralization of organic nitrogen in soil. In the upstream region of the Tamiraparani river basin, the landscape is dominated by forested area, resulting in significant amount of nitrogen fixation (i.e. the conversion from N_2 gas to organic nitrogen) from the atmosphere. Due to death and decay of leaves and other organic matter in the environment, and through microbial activity, the NH_3 is first converted to the assimilable form of NO_3 and NO_2 termed 'nitrification'. In the downstream region, because of the high organic input from agricultural runoff, the NO_3 is converted to N_2 by the process of 'denitrification' resulting from an oxygen stress in the environment. The seasonal variations of NO_2 -N concentration in the surface water Tamiraparani river basin are presented in (Tables 3.2–3.5). In the summer season, the high concentration was observed particularly at S7 (Tenkasi) $47.1 \mu g l^{-1}$ and S3 (Papanasam) location was obtained $10.2 \mu g l^{-1}$ in the upstream region, and location 18 (Athoor) in the downstream region ($4.6 \mu g l^{-1}$), High concentrations of NO_2 -N were observed in the same location $9.8 \mu g l^{-1}$ during post-monsoon season. The upstream region is dominated by Western Ghats region, containing dense evergreen forests. The death and decay of leaves, twigs, plankton, etc., results in the degradation of organic matter and an enrichment of nitrogenous nutrients particularly NO_2 -N suggesting that intense in primary productivity (James 2000). In the midstream region by contrast, the NO_2 -N 0.71 - $1.9 \mu g l^{-1}$ and 1.4 - $3.2 \mu g l^{-1}$ concentrations were low both pre-monsoon and post-monsoon

seasons (Tables 3.2 to 3.5) This is due to the fact that in the midstream region, the river water is diverted through eight weirs and channels, for agricultural and other uses, resulting in the trapping of nutrients. In the upstream Tamiraparani river basin located in an agricultural region nitrite concentration ($\text{NO}_2\text{-N}$) however, this upstream river water contain high quantities of nitrate presumably resulting from the fertilization of agricultural soils; these values are even higher than those found in the lower downstream region after nitrification of the ammonium. The Tenkasi (S7) site has obtained nitrite concentration ranges ($47.1 \mu\text{g l}^{-1}$) during summer season due to untreated municipal sewage waste mix with river water.

The Western Ghats, containing dense evergreen forests, dominates the upstream region. The death and decay of the leaves, twigs, plankton, etc., results in the degradation of organic matter and an enrichment of nitrogenous nutrients particularly $\text{NO}_3\text{-N}$ suggesting that intense nitrification occurs in this region. This is a characteristic feature of vegetation dominant terrain with a high annual rainfall resulting in a consequent increase in primary productivity. In the midstream region by contrast, the $\text{NO}_2\text{-N}$ concentrations was very low, due to the fact that in the midstream region, the river water is diverted through eight weirs and channels, for agricultural and other uses, resulting in the trapping of nutrients. However, a distinct loading of $\text{NO}_2\text{-N}$ has been observed in the downstream region during summer, suggesting that anthropogenic input contributes significantly to nutrient enrichment in the surface water.

3.5.3 Phosphorus

Phosphorus is a very important element in biogeochemical cycling and mass transfer in the continent-ocean interface, because of its occurrence and involvement in the inorganic and biological processes. Unlike transfers in the global N cycle, the major transfers in the global cycle of P are not driven by microbial reactions. Nearly, all the phosphorus on land is originally derived from the weathering of calcium phosphate minerals, such as apatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$]. The main flux of P in the global cycle is

carried by rivers, which transport about 21×10^{12} g P yr⁻¹ to the sea (Meybeck 1982). This flux may be slightly higher since prehistoric times as a result of erosion, pollution and fertilizer runoff. The present day flux of phosphorus provides a clue regarding the sources of phosphorus for the formation of phosphorites (Subramanian 1984). The amount of phosphorus transported by rivers depends on the natural processes (climate and rock type), man's influence (deforestation, agriculture and population) and biological removal processes. The phosphorus forms discussed here includes orthophosphate (PO₄-P) and total dissolved phosphorus (TDP). Orthophosphate levels in natural water are normally low, ranging between 1 to 24 µg l⁻¹ with an average concentration of 12 µg l⁻¹ in the tropical rivers (Meybeck 1982). Of the inorganic forms, the complex commonly referred to as PO₄-P is important; being the only form of phosphorus that is capable of being taken up by autotrophic organisms (Vaithiyanathan et al 1989).

3.5.2.1 Orthophosphate

Eutrophication is one of the most serious problems facing the ecology of freshwater in the India and elsewhere. The nutrient status of many lakes and rivers has increased dramatically over the past 30 years in response to increased collection and discharge of domestic wastes, increased loadings to collection systems (including the use of phosphate detergents) and widespread agricultural intensification. Phosphorus is delivered to the river system from a range of sources, varying in its bioavailability from source to source. The load from point sources (which are dominated by sewage treatment works) is typically highly bioavailability and is delivered along with considerable loads of readily degradable organic material. The delivery of diffuse loads is more complicated and highly seasonal, but is largely dictated by the strong affinity of phosphorus for particulates. The majority of the diffuse annual load is, therefore, generally delivered in surface run-off attached to soil particles. However, much higher proportions of soluble phosphorus occur when livestock excreta in forms such as slurry and 'dirty water' or soluble inorganic fertilizers are washed off the land soon after

application. Sub-surface drainage and leaching may be important pathways under certain conditions, particularly if the soil is overloaded with phosphorus. Sandy soils and underlying sandstone geology are particularly vulnerable since they have a very low adsorption capacity for phosphorus. Other soils and geologies are less vulnerable, but may be more at risk than supposed due to macropores and fissure flow within the soil/rock structure for more detail on phosphorus losses from soil to water) Of the major plant nutrients, phosphorus is typically in shortest supply in rivers and other freshwater and so generally has the greatest potential to limit plant growth (Heathwaite 1997). Whether nitrogen or phosphorus availability actually limits plant growth in a river depends on many factors, including light intensity, current velocity and the availability of other major and trace plant nutrients. However, an assessment can be made of which of these two major nutrients may be limiting growth purely from consideration of their relative and absolute availabilities in the environment. Similarly, the dissolved phosphorus in many types of water in the entire region is primarily governed by excess fertilizer run-off from agricultural fields (Tariq et al 1996; Datta and Subramanian 1997; Subramanian 2000). Firmly held phosphorus deep within the particle matrix can diffuse slowly into the water column, which is most likely to be an important mechanism for the river once particulates have settled as bed sediments. Soluble phosphorus can be incorporated into inorganic phosphate minerals by precipitation, particularly in association with calcium (in hard water rivers), iron and aluminum (in soft water rivers). The precipitation of soluble phosphorus with calcium is particularly likely to occur below sewage treatment works in rivers with calcareous water where both calcium and soluble phosphorus concentrations are very high (House and Denison 1997). Colloids of calcium phosphate minerals can be generated in the water column, whilst algal biofilms are thought to be involved in the co-precipitation of calcite and phosphorus onto bed sediments and plants (Hartley et al 1997).

The orthophosphate concentration ranges from 0.6 to 16.7 $\mu\text{g l}^{-1}$, 2.1 to 12.4 $\mu\text{g l}^{-1}$, 0.6 to 17.3 $\mu\text{g l}^{-1}$ and 0.6 to 14.4 $\mu\text{g l}^{-1}$ during monsoon, summer, premonsoon and

postmonsoon seasons, respectively. The orthophosphate was observed higher concentrations at ($17.3 \mu\text{g l}^{-1}$) Agaram (S19) during premonsoon and $16.7 \mu\text{g l}^{-1}$ at Tirunelveli (S13) during monsoon season in the midstream province. The lowest values of orthophosphates were measured in post-monsoon and summer season. Cause of these is utmost masculation of agricultural soil (mountain and field) from rains which fall down this time.