

Assessment of Water Quality of a Tropical River with Special Reference to Ions

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Authors' contributions

This work was carried out in collaboration among all authors. Author RVS designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors AMS, S. Jaya and S. Joseph managed the analyses of the study and managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The role of ions in a tropical river water (Neyyar, Kerala) was assessed. Rock weathering is the dominating mechanism controlling the major ion chemistry of Neyyar river. The dominance of Cl-HCO₃-Na during monsoon indicates that geology plays a major role in controlling water chemistry. The presence of mineral varieties of quartz, feldspars, pyroxene, biotite, etc., in the Pre-Cambrian crystalline namely Khondalite and Charnockites, could be the source of major ions. The major ion chemistry of Neyyar river waters show that Na is the dominant cation with lower proportions of Mg and Ca, with HCO₃ and Cl as the dominant anions. It belongs to the HCO₃ group with significant amounts of Na and Ca cations. The dominance of Cl-HCO₃-Ca and Ca-HCO₃-Cl during post monsoon and pre monsoon respectively indicates that besides geology, the land drainage and anthropogenic activities also control river water. The change in water type observed during monsoon from Na-Cl-HCO₃ to Na-Ca-Cl-HCO₃ almost from the middle portion may be attributed to anthropogenic pollution. Hence attention is to be paid to take the control measures to prevent the pollution in this stretch of the river.

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1. INTRODUCTION

Mineral substances contained in natural waters in the dissolved state (ions) determine water chemical type. The concentration of all minerals is related to the abundance of chemical elements in earth's crust and the solubility of their compounds (<http://www.eolss.net/Sample-Chapters/C07/E2-03-04-02.pdf>). The ions transported by rivers are the most important source of most elements to the ocean (http://webcache.googleusercontent.com/search?q=cache:http://ocean.stanford.edu/bomc/chem/lecture_12.pdf). The major chemical composition of river water can reveal the nature of weathering, patterns, and linkages between evaporation and anthropogenic processes on a basin-wide scale [1].

Water derives some of the dissolved chemicals such as HCO_3^- , Na^+ , Ca^{2+} , Mg^{2+} , SiO_2 , SO_4^{2-} , and several others due to chemical interaction between water and soil mineral matter and also rocks below the soil [2]. The solute load of the water determines the total dissolved solids that in turn affect the quality of water. Thus, it has been recognized that weathering plays an important role in buffering of surface waters [3,4] and results in the production of soluble basic cations (Ca, Mg, K and Na), aluminum and silica. The estimates of weathering rates of elements such as Ca and Na, which remain largely in solution, are likely to be most accurate [5].

The important patterns in river water can be recognized using methods such as a). Gibb's diagram, b). Box plots, c). Ludwig-Langelier plots, d) Piper (Trilinear) diagram and e) Durov diagram and can thus delineate the seasonal variations in chemical constituents of water bodies. Gibbs(1970) suggested that a simple plot of TDS versus the weight ratio of $\text{Na}/(\text{Na}+\text{Cl})$ would provide meaningful information on the relative importance of three major natural mechanisms controlling surface water chemistry: 1) atmospheric precipitation dominance 2) rock weathering dominance and 2) evaporation and fractional crystallization dominance. It is a simple tool to identify rivers that are dominated by precipitation or rock weathering or evaporation – crystallization.

A box plot is a very useful and convenient tool to provide summaries of a dataset and is often used in exploratory data analysis. The box represents

interquartile range and either end of the line indicates the minimum and maximum values. Langelier & Ludwig proposed a diagram in which rectangular coordinates are used representing patterns [6] and correlations between major cations and anions for multiple samples [7]. Such groups of cations and anions are selected and plotted as percentages.

Hydrochemical facies analysis using Piper diagram [8] is an excellent way to place a series of water quality analyses into a spatial context. It has become a common method in understanding and describing the chemical evolution of water which depends on pattern recognition techniques. The major parameters which regulate the water quality are HCO_3^- , Ca^{2+} and Mg^{2+} . All these three ions control the precipitation or solution of carbonate phase. Being the major constituents in most fresh water, HCO_3^- holds the key to the levels of a number of other ions such as Ca and Mg, as well as some other ions such as Fe, Mn, Cu, Pb, Zn and Cd. TDS typically increases as the length of water flow paths increase and in coastal areas is often used to determine the influence of salt water on water quality.

A review of Durov's classification was published [9]. In general, classification procedures are a basis for grouping waters that are closely related to each other. Usually, classification is done by simple inspection of a group of chemical analyses and separating them into obviously interrelated subgroups. The values of cations and anions are plotted in the appropriate triangular and projected into the square of the main field. The advantage of this diagram is that it displays some possible geochemical processes that could affect the water genesis. In general, classification procedures are a basis for grouping waters that are closely related to each other. Usually, classification is done by simple inspection of a group of chemical analyses and separating them into obviously interrelated subgroups.

The study was conducted to delineate the seasonal variation of chemical constituents of a tropical river (Neyyar) using Gibb's diagram, b). Box plots, c). Ludwig-Langelier plots, d) Piper (Trilinear) diagram and e) Durov diagram. The variation in water quality characteristics in three seasons was also discussed.

1.1 Study Area

The Neyyar river basin embodies three major physiographic divisions, viz., the highland (>600 m) representing the high hill ranges and the catchment area of the Neyyar river which constitute about 6.1% of the total area (Fig. 1). From the highland, the river descends so fast in the form of rapids and falls, due to steep westerly slope of the highlands. In the midland(600 - 300

m) the highly resistant rock outcrops with laterite cappings are observed. The low lands (10 - 300 m) represent a region of low relief and subdued topography, indicating a mature stage of the river. About 85.67% of the basin area comes under lowland. In the northern side, the basin is bounded by Neyyattinkara and Nedumangad taluk. The western side of the basin is bounded by Arabian Sea and eastern side is covered by Tamil Nadu.

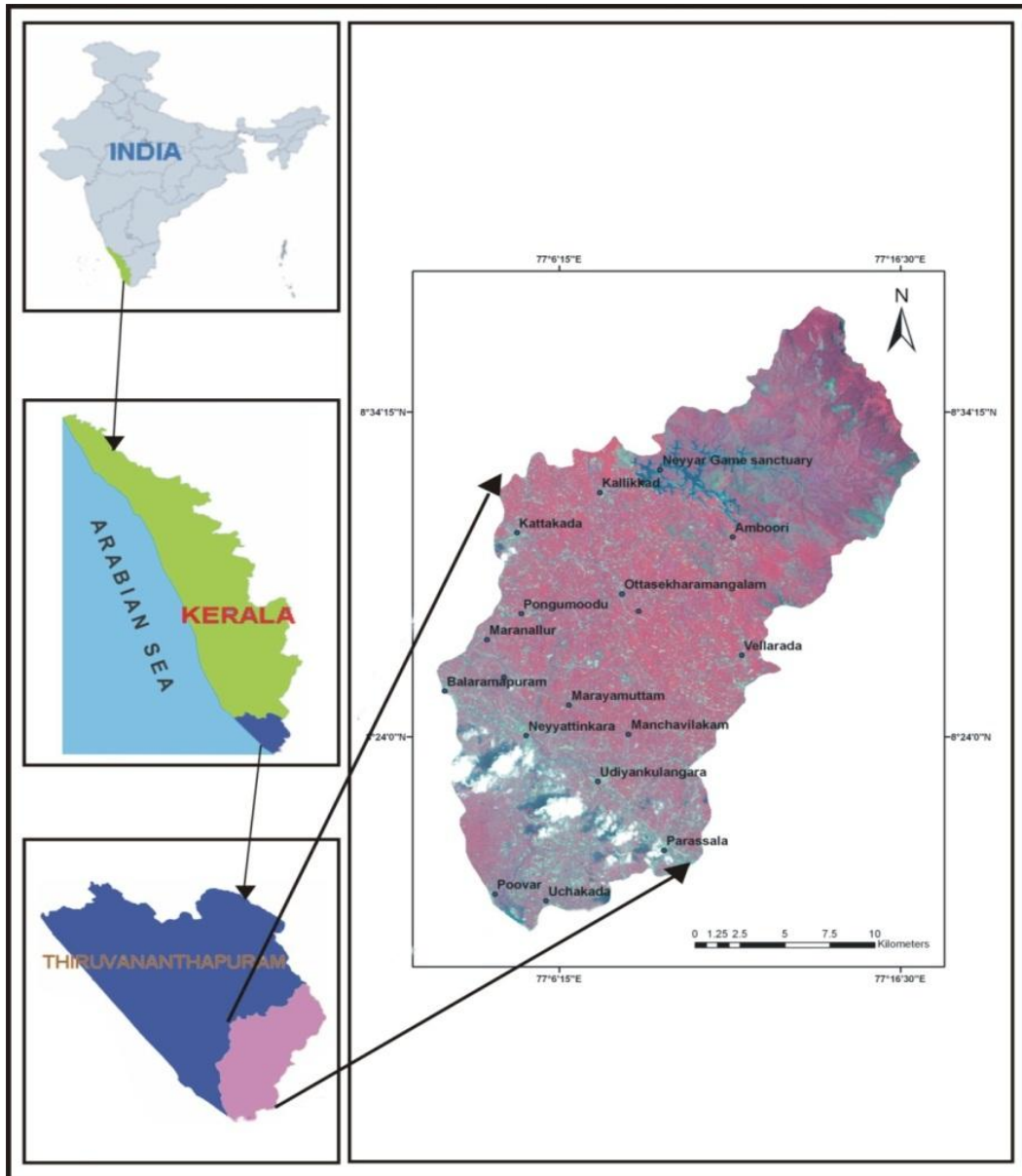


Fig. 1. Neyyar river basin

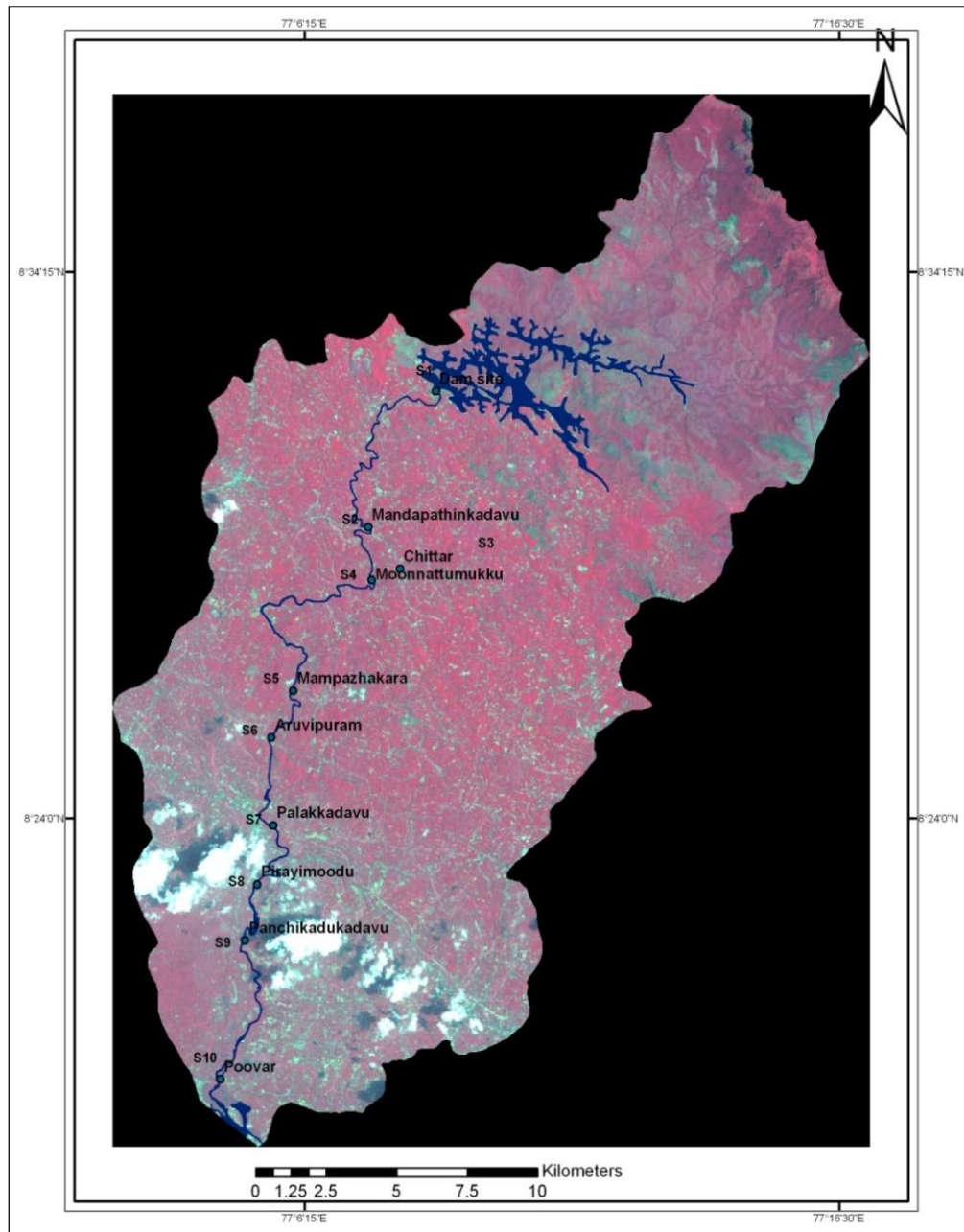


Fig. 2. Location of sampling stations in Neyyar river

2. MATERIALS AND METHODS

The surface water samples (total no.= 30) were collected from 10 stations of NRB viz., Neyyar dam (S1), Mandapathinkadavu (S2), Chittar (S3), Moonnattumukku (S4), Mampazhakkara (S5), Aruvippuram (S6), Palakkadavu (S7), Pirayimmood, (S8), Panchikadukadavu (S9) and Poovar (S10) covering the three seasons viz.,

monsoon (MON), postmonsoon (POM) and premonsoon (PRM) from September 2006 to October 2007 (Fig. 2). The samples (~2 litres) were brought to laboratory and kept in chilled storage till the analytical work was carried out. The quantitative estimation of various physico-chemical parameters like Temperature, pH, Conductivity, Turbidity, Total Dissolved Solids (TDS), Dissolved Oxygen (DO), Biochemical

Oxygen Demand (BOD), Total Alkalinity (TA), Total Hardness (TH), Calcium (Ca), Magnesium (Mg), Salinity, Chloride (Cl⁻), Total Nitrogen (TN), Nitrate, Total Phosphorus (TP), Phosphate, Potassium (K), Sodium (Na) and Sulphate were carried out according to the procedures in APHA (1987). Total Hardness (TH), Ca, Mg were estimated by titration with standard EDTA solution. Total Alkalinity (TA). TA, Carbonates (CO₃) and Bicarbonates (HCO₃) were measured by titration using standard sulphuric acid solution. Flame photometry was employed for measuring Sodium (Na) and Potassium (K). Chloride (Cl) was determined by argentometric titration, and Nitrate (NO₃), Phosphate (PO₄) and Silicate (SiO₂) by colorimetry with UV-visible spectrophotometer.

The methods used for the recognition of patterns are 1) Gibb's diagram, b). Box plots, c). Ludwig-Langelier plots, d). Piper (Trilinear) diagram and e). Durov diagram. Durov (1948) diagram for the major cations and anions of Neyyar river water is plotted by Aquachem software. The fields and lines on the diagram show the classifications of Lloyd and Heathcoat (1985).

3. RESULTS AND DISCUSSION

3.1 Variation of Water Quality

The variation of water quality during premonsoon, monsoon and post monsoon is given in Tables 1, 2, 3.

3.1.1 pH

pH value ranges from 6.5 to 7.9 (ave. = 6.9) for premonsoon, 6.6 to 7.0 (ave. = 6.7) for monsoon and 6.6 to 6.9 (ave. = 6.8) for postmonsoon in the present study. In normal unpolluted water, the pH is slightly alkaline. Blum (1956) observed that majority of flowing waters are neutral to alkaline in nature. In the study area, the season wise value of pH shows a slight increase from monsoon to premonsoon (Tables 1, 2, 3). Relatively high pH in the premonsoon can be ascribed to low precipitation, and relatively low pH in monsoon can be ascribed to heavy rainfall and consequent land runoff experienced in that region. It had encountered a similar finding in relation between rainfall and river discharge with pH from the Ramgarh reservoir area [10].

3.1.2 Total dissolved solids (TDS)

The lowest and highest content of TDS are 90 and 445 mg/l respectively and the values

decrease in the postmonsoon season. The season wise variation of TDS shows a minimum in postmonsoon (ave. = 190.2 mg/l) and a maximum in premonsoon (ave. = 254 mg/l). TDS shows higher value in the downstream station (S10) during all seasons and comparatively lower TDS is noticed in upstream station (Tables 2, 3 and 4). TDS in a stream depends on various parameters such as geology of watershed, rainfall and amount of surface runoffs [2]. TDS show relatively lower values during monsoon and post monsoon owing to influx of more water from catchment areas and subsequent dilution of dissolved salts. Concentrations decline as annual precipitation and runoff increase, initially gradual and then rapidly [11]. It was reported a concentration range of total ions from 25 to 650 mg/l, resulting from small-scale shifts between igneous and sedimentary formations [12].

3.1.3 Dissolved oxygen (DO)

DO level is a good indicator of pollution status of the system. The solubility of oxygen in water is a function of temperature, pressure and concentration of ions in water. The season wise average value of DO ranges from 3.95 mg/l in postmonsoon to 6.22 mg/l in monsoon. The observed values indicate that there is not much spatial variation in terms of DO, during different seasons (Tables 1, 2, 3). The river shows almost similar DO levels for various stations and no definite trend is present, and also there are hardly any symptoms of anoxic conditions in this river. However, relatively higher DO is observed in monsoon. Similar conditions have been earlier reported by Venkateswarlu (1969) for different systems elsewhere.

3.1.4 Biochemical oxygen demand (BOD)

BOD is an excellent indicator of the strength of domestic and industrial contaminants in aquatic environments (APHA, 1998). The season wise values of BOD in the surface water of the study stations ranges from 1.37 (monsoon) to 2.99 mg/l (postmonsoon). Generally the BOD of Neyyar recorded low values during the period of study. It was also observed that the peak values of BOD are recorded in premonsoon season at all the stations and it may be due to the flushing of organic pollutants from river catchment areas through the lean discharge of river water. High human activity also influences the BOD values of surface water bodies.

Table 1. Physico-chemical characteristics of Neyyar during Premonsoon

Parameters	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	Average	SD
Water Temp (0°C)	28	28	29	29.00	29.00	30.00	30	30	31	32	29.60	1.26
pH	7.01	6.51	6.54	7.09	6.72	6.57	6.82	6.55	6.8	7.89	6.85	0.42
Conductivity (mS/cm)	0.12	0.1	0.04	0.08	0.07	0.05	0.09	0.1	0.3	0.1	0.11	0.07
Turbidity (NTU)	3	3	4	4.00	5.00	6.00	6	7	8	15	6.10	3.54
TDS (mg/l)	120	110	200	240.00	245.00	250.00	250	300	312	513	254.00	112.78
DO (mg/l)	6.4	5.73	4.6	4.03	5.05	5.50	4.94	4.55	4.71	4.94	5.05	0.68
BOD (mg/l)	0.5	1.2	2.2	2.50	2.70	3.10	3.2	2.2	3.6	3.8	2.50	1.04
Bicarbonates (mg/l)	17.08	17.08	18.3	24.40	24.40	25.62	24.4	30.5	30.5	48.8	26.11	9.35
Hardness (mg/l CaCO ₃)	14	14	12	12.00	12.00	10.00	15	15	32	22	15.80	6.55
Alkalinity (mg/l)	14	14	15	20.00	20.00	21.00	20	25	25	40	21.40	7.66
Ca (mg/l)	10.2	8.8	5.6	6.20	5.90	5.40	10.9	9.9	11.6	10.98	8.55	2.51
Mg (mg/l)	2.8	2.4	2.02	1.96	1.30	1.02	2.03	1.98	2.13	2.2	1.98	0.51
Salinity (ppt)	0.63	0.34	0.72	0.42	0.43	0.40	0.41	0.45	0.45	7.8	1.21	2.32
Chlorides (mg/l)	10	10	9.8	11.20	11.00	11.50	13	15	15.5	35	14.20	7.58
Total Nitrogen (mg/l)	0.4	0.3	0.2	0.80	0.40	0.30	0.5	0.6	0.2	0.9	0.46	0.24
Nitrates (mg/l)	0.18	0.21	0.18	0.27	0.26	0.22	0.31	0.36	0.33	0.41	0.27	0.08
NH ₄ -N (μ mole/l)	0.049	0.075	0.049	0.06	0.07	0.07	0.136	0.056	0.051	0.093	0.07	0.03
Phosphates (mg/l)	0.27	0.09	0.05	0.09	0.05	0.04	0.06	0.09	0.05	0.06	0.09	0.07
Sulphates (mg/l)	0	2	3	3.20	3.20	3.00	3.5	2.89	5	20	4.58	5.56
Potassium (mg/l)	0.5	0.57	0.75	0.90	0.90	1.00	1	2	1.2	3.5	1.23	0.90
Sodium (mg/l)	1.5	1.5	1.67	1.62	1.90	2.00	2.3	2.2	27	65.8	10.75	20.90
Copper (ppm)	0.01	0.003	0.01	0.01	0.04	0.03	0.033	0.004	0.02	0.015	0.02	0.01

Table 2. Physico-chemical characteristics of Neyyar during monsoon

Parameters	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	Average	SD
Water Temp (°C)	27	27	28	29	29	29	29	29	31	30	28.80	1.23
pH	6.59	6.57	6.61	6.61	6.83	7.01	6.74	6.58	7.01	6.89	6.74	0.18
Conductivity (mS/cm)	0.06	0.08	0.09	0.08	0.9	0.9	0.9	1.00	1.27	2.34	0.76	0.73
Turbidity (NTU)	4.90	5.00	10.00	12.00	15.00	15.00	18.00	20.00	22.00	25.00	14.69	6.82
TDS (mg/l)	112.00	200.00	220.00	232.00	230.00	250.00	242.00	250.00	275.00	320.00	233.10	53.65
DO (mg/l)	7.05	6.85	5.01	5.84	6.29	6.50	6.75	5.95	5.95	5.97	6.22	0.60
BOD (mg/l)	0.20	0.85	1.40	1.20	1.09	1.50	1.12	1.90	2.00	2.40	1.37	0.63
Bicarbonates (mg/l)	9.76	12.20	12.20	10.98	10.98	12.20	13.42	21.96	24.40	24.40	15.25	5.87
Hardness (mg/l CaCO ₃)	3.20	2.40	2.50	3.00	3.25	2.70	2.78	4.00	6.50	7.00	3.73	1.66
Alkalinity (mg/l)	14.00	14.00	15.00	20.00	20.00	21.00	20.00	25.00	25.00	40.00	21.40	7.66
Ca (mg/l)	1.20	1.27	0.80	1.05	1.90	1.37	1.95	3.06	4.64	5.78	2.30	1.68
Mg (mg/l)	0.07	0.09	0.05	0.80	0.64	0.07	0.98	0.69	1.23	2.36	0.70	0.72
Salinity (ppt)	0.24	0.54	0.61	0.54	0.54	0.63	0.66	0.69	0.87	2.80	0.81	0.72
Chlorides (mg/l)	10.00	10.00	9.80	11.20	11.00	11.50	13.00	15.00	15.50	35.00	14.20	7.58
Total Nitrogen(mg/l)	0.40	0.30	0.20	0.80	0.40	0.30	0.50	0.60	0.20	0.90	0.46	0.24
Nitrate (mg/l)	0.20	0.30	0.17	0.32	0.27	0.34	0.43	0.38	0.50	0.49	0.34	0.11
NH ₄ -N (μ mole/l)	0.00	0.04	0.00	0.04	0.02	0.02	0.12	0.12	0.36	0.19	0.09	0.11
Phosphates (mg/l)	0.03	0.03	0.04	0.04	0.04	0.04	0.03	0.06	0.07	0.10	0.05	0.02
Sulphates (mg/l)	0.00	0.02	0.03	0.03	0.40	0.42	0.50	0.90	0.90	0.92	0.41	0.39
Potassium (mg/l)	1.40	1.60	0.99	1.80	1.14	1.8	2.10	2.00	1.40	4.20	1.58	0.90
Sodium (mg/l)	3.00	3.80	2.70	2.70	2.80	2.40	3.00	4.00	32.00	65.00	12.14	20.69
Copper (ppm)	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.00

Table 3. Physico-chemical characteristics of Neyyar during postmonsoon

Parameters	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	Average	SD
Water Temp(°C)	27	27	27	28	28	28	29	29	29	30	28.2	1.12
pH	6.78	6.58	6.68	6.74	6.92	6.91	6.96	6.89	6.86	6.86	6.82	0.12
Conductivity (mS/cm)	0.07	0.06	0.04	0.05	0.06	0.06	0.05	0.10	0.30	1.00	0.18	0.38
Turbidity (NTU)	4.00	5.00	8.00	9.00	9.00	10.00	12.00	12.00	16.00	18.00	10.30	4.77
TDS(mg/l)	90.00	92.00	132.00	175.00	190.00	182.00	176.00	200.00	220.00	445.00	190.20	121.86
DO(mg/l)	4.04	2.70	4.26	3.81	5.05	2.80	3.92	4.26	4.26	4.43	3.95	0.76
BOD(mg/l)	1.42	2.34	2.84	3.85	3.28	3.84	3.04	3.28	2.98	2.98	2.99	0.72
Bicarbonates (mg/l)	12.20	14.64	14.64	18.30	18.30	18.30	24.40	26.84	26.84	36.60	21.11	8.49
Hardness (mg/l CaCO ₃)	4.00	5.20	5.50	9.00	10.00	10.20	9.90	10.50	20.00	25.00	10.93	7.60
Alkalinity (mg/l)	10.00	12.00	12.00	15.00	15.00	15.00	20.00	22.00	22.00	30.00	17.30	6.96
Ca (mg/l)	2.92	3.41	3.23	5.87	7.91	8.03	8.20	8.01	12.80	13.60	7.40	4.00
Mg (mg/l)	1.03	0.95	1.10	0.90	0.90	1.00	1.00	2.00	1.20	2.00	1.21	0.47
Salinity (ppt)	0.99	0.43	0.81	0.49	0.56	0.47	0.45	0.47	0.60	0.96	0.62	0.23
Chlorides (mg/l)	11.00	11.50	12.00	12.20	12.50	13.00	20.00	23.00	25.00	50.00	19.02	14.77
Total Nitrogen(mg/l)	0.40	0.30	0.90	0.60	0.89	0.52	0.60	0.65	0.90	0.93	0.67	0.23
Nitrate(mg/l)	0.18	0.20	0.16	0.26	0.24	0.29	0.42	0.31	0.48	0.53	0.31	0.14
NH ₄ N (μ mole/l)	0.02	0.01	0.00	0.01	0.02	0.04	0.00	0.01	0.03	0.08	0.02	0.03
Phosphates (mg/l)	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.49	0.60	0.89	0.22	0.36
Sulphates (mg/l)	0.00	0.00	0.02	0.02	0.01	0.30	0.40	0.50	0.62	0.70	0.26	0.30
Potassium (mg/l)	0.70	0.90	1.10	0.90	0.90	1.00	1.00	2.00	1.20	2.00	1.17	0.50
Sodium (mg/l)	2.00	2.50	2.50	2.40	2.00	2.00	2.30	3.00	28.00	68.00	11.47	26.54
Copper (ppm)	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.00

3.1.5 Bicarbonates

Alkalinity is imparted more by the presence of CO₂ content in natural waters [13]. Alkalinity measures the sum total of the components in water that tends to elevate the pH of water above a value of 4.5 and it indicates the buffering capacity of water. Alkalinity is attributed by the presence of hydroxyl (OH⁻) ions capable of combining with hydrogen (H⁺) ions. In unpolluted water, the major anions which can neutralize the positive H⁺ ions in an acid are HCO₃⁻, CO₃⁻ and OH⁻. The primary source of carbonate and bicarbonate ions in water is the dissolved CO₂ in rain and as it enters the soil dissolves more CO₂. The decay of Organic matter may also release CO₂. Water charged with CO₂ dissolves carbonate minerals, as it pass through soils and rocks to give bicarbonates. It should be noted that in polluted waters, other negative ions like phosphates, nitrates may contribute to alkalinity [14].

The average season wise values of bicarbonate varies between 15.25 (monsoon) and 26.11 mg/l (premonsoon). The bicarbonates of river water recorded a general decline during the period of monsoon. The value shows an increasing trend during summer months.

3.1.6 Total Hardness

Total hardness of water is the sum of concentrations of alkaline earth metals present in it. Calcium and magnesium, the two principal ions, are present in many sedimentary rocks, the most common being limestone and chalk.

The hardness ranges from 10 to 32 (premonsoon), 2.4 to 7 mg/l (monsoon) and 4 to 25 mg/l (postmonsoon) during the study period (Tables 1, 2, 3). Minimal values are noted during monsoon (ave. = 3.73 mg/l). The monsoon rains are the reason behind the lower hardness prevailing at that period. The findings are similar to those reported [15].

Towards summer, the steady state of hardening of water may be attributed to evaporation of surface water and addition of Ca²⁺ and Mg- salts from detergents and soaps due to washing and ablutions. It was found [16] found mean values of total hardness between 56 and 156 mg/l in River Narmada from Amarkantak to Jabalpur. It was noted lower hardness values for Periyar waters from 7.1 to 18.2 mg/l, while lower stretches recorded higher values up to 220.1 mg/l [17].

3.1.7 Calcium

Calcium (Ca) is a major constituent of most igneous, metamorphic, and sedimentary rocks. The principal source of Ca in water resources are some members of the silicate mineral groups like plagioclase, pyroxene and amphibole among igneous and metamorphic rocks, and limestone, dolomite and gypsum among sedimentary rocks. The disposal of sewage and industrial wastes are also important sources of Ca and as such has no hazardous effects on human health.

The average season wise concentration of Ca ranges from a minimum of 2.3 (monsoon) to maximum of 8.55 mg/l (premonsoon) during the study period. The presence of calcium in water is mainly due to its passage through or over deposits of limestone, dolomite, gypsum and other gypsiferous materials [18]. Calcium and magnesium are abounding in waters which are drained mainly from calcitic / dolomitic terrains or terrains composed of plagioclase feldspar or mica rich rocks. In general, concentration of Ca in freshwaters is somewhat greater than Mg because of greater abundance of Ca in earth's crust.

Calcium shows an increasing trend towards estuarine side during all seasons. The variation may be due to gradual reduction in the incursion of seawater into estuary with increasing distance from mouth. Station 10 near the mouth of estuary, receives more saline water, which leads more calcium than other stations. Similar reports have been put forth by several workers [19,20,21].

Calcium concentrations during the study period were in the order of premonsoon>postmonsoon>monsoon. The higher concentration during premonsoon may be due to scanty freshwater discharge. Another reason may be due to recovery of calcium for gradual attainment of normal estuarine conditions. This is found to agree with [22,23]. The lower calcium concentrations observed during monsoon may be due to high influx of fresh water resulted by heavy rainfall and land drainage. More freshwater runoff leads to greater dilution, which accounts for lowering of calcium concentration than other seasons. Similar observation was also made for Gopalpur creek [24].

3.1.8 Magnesium (Mg)

Magnesium is commonly associated with Ca. The geochemical behavior of Mg is altogether

different from that of Ca. The magnesium concentration during the study period were in the order of premonsoon>postmonsoon> monsoon. Average season wise concentration of Mg ranges from a minimum of 0.70 (monsoon) to maximum of 1.98 mg/l (premonsoon) during the study period. Source rocks are the controlling factor of Mg in this riverine system.

A decrease in level of Mg in monsoon may be due to its rapid utilization by planktonic community. On the contrary, in summer and early monsoon increase in level is related to release of Mg from decaying plants. During monsoon and postmonsoon, the greater dilution will lead to a wide variation, whereas the summer may be the recovery period for magnesium.

3.1.9 Chlorides

Chloride ions have a large migration ability in connection with very high solubility of chloride salts of sodium, magnesium and calcium. Chlorides occur naturally in all types of waters. However, its concentration remains quite lower in natural unpolluted waters. Underlying alkaline rocks can also impart chloride to freshwater bodies. The other sources of chlorides are atmospheric fallouts, city drainages and ingress of salt water from the sea.

In the present study, the chloride value ranges from 9.8 to 35 mg/l for monsoon and premonsoon (ave= 14.2) while in postmonsoon it varies from 11-50 mg/ l (ave = 19.02). The chloride content does not show wide variations for different seasons. However, the chloride values in one station (S10) in the lower reaches record very higher values due to salt water ingress. Further, pollution sources of chloride viz., municipal wastewater and organic waste can modify natural concentrations greatly. Several workers [25,26] described chloride as a pollution indicator. It was also advocated that high chloride concentration are indicators of large amount of organic matter in water, which have been further supported [27,28].

3.1.10 Salinity

Upland streams are strongly influenced by hill slope processes. The properties progressively change downstream and influence the biological community. Salinity is considered to be an important parameter in the study of physico-chemical parameters of coastal water bodies. Seawater intrusion, freshwater influx,

precipitation and evaporation generally influence salinity distribution.

The season wise average value of salinity ranges from 0.62‰ in postmonsoon to 1.21‰ in pre monsoon season for the study period (Tables 1,2,3). The maximum values are noted in the premonsoon and minimum during postmonsoon indicating the high discharge of water during monsoon causing dilution of dissolved constituents in water than other seasons and seems to be the recovery period in which the values are gradually increasing with lowering of water level. Further, irrespective of seasons, it is seen that salinity values more or less same for all the stations except the river mouth zone (S10) and may be due to the ingress of saline water with freshwaters. Salinity is caused by the increase in concentration of various ionic species like Ca, Mg, Na, K, hardness and TDS. A saline intrusion component may be present in some waters.

3.1.11 Nitrate

Nitrate is the highly oxidized form of nitrogen compounds. Nitrate varies from 0.18 to 0.41 mg/l in premonsoon and 0.18 to 0.53 mg/l in postmonsoon. Monsoon and postmonsoon account for peak nitrate values. Higher nitrate was recorded in Bhavani river during winter [29]. Season wise values of nitrate show maximum values in monsoon, followed by postmonsoon and premonsoon seasons. Highest nitrate concentration for monsoon period can be attributed to heavy rainfall and land drainage or increased decomposition of organic debris in sediments.

3.1.12 Phosphates

Phosphorus occurs in natural waters almost solely as phosphates rather than free state. The most important anthropogenic sources of phosphate are discharge of domestic sewage, detergents, and agricultural runoff [30]. The phosphate content of flowing water change slightly from time to time while in stagnant water, it is more or less constant [31].

Phosphate values range between 0.04 and 0.27 mg/l for premonsoon; 0.03 to 0.89 mg/l for postmonsoon during the present study. The season wise trend shows that phosphate concentration is the maximum during postmonsoon and is due to the high concentration for the three stations towards the shoreward side.

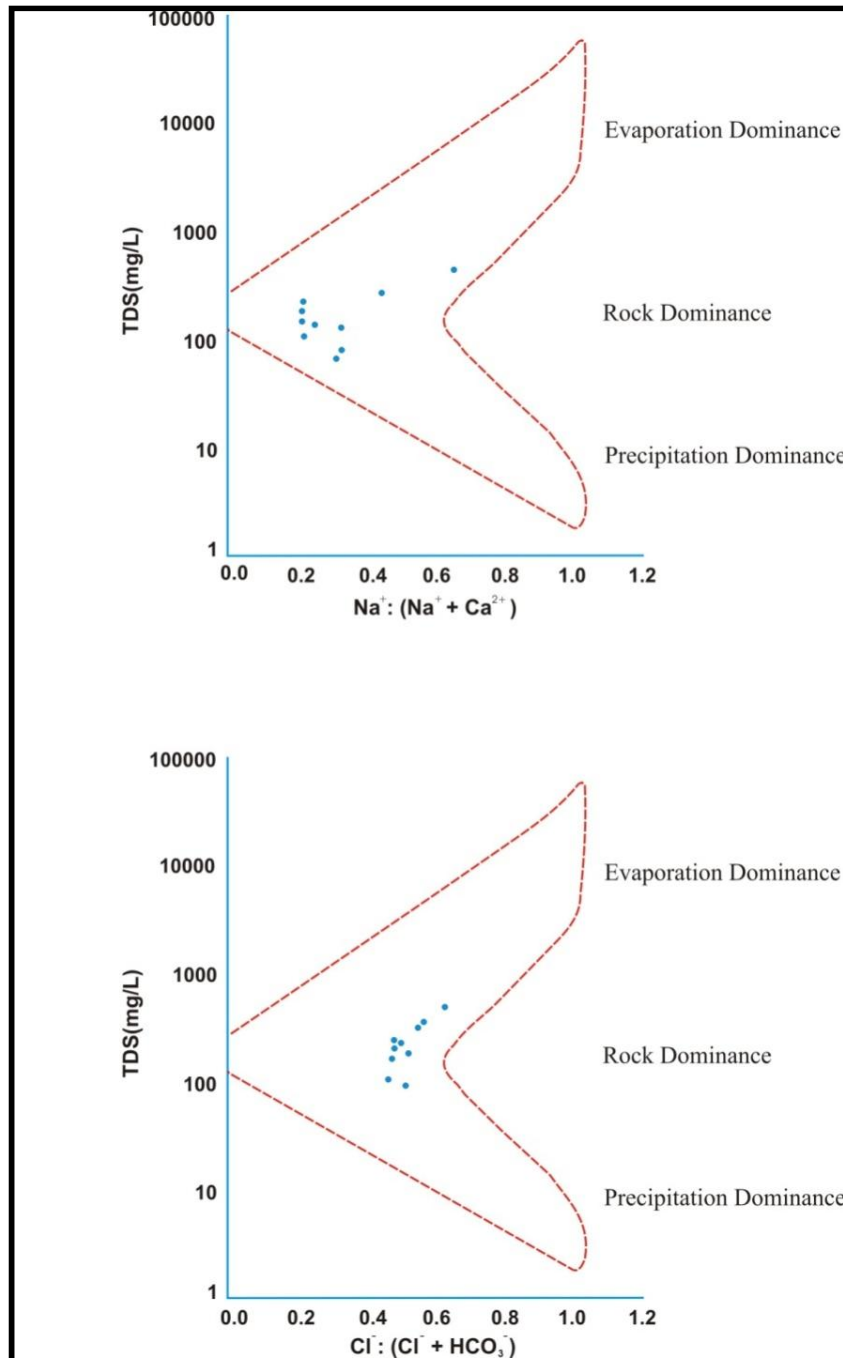


Fig. 3. Gibb's diagram for Neyyar river – Postmonsoon

3.1.13 Potassium

The common source of potassium (K) is silicate minerals such as orthoclase, microcline, nepheline, leucite and biotite in igneous and metamorphic rocks. Potassium though found in small amounts, plays vital role in metabolic

activity of freshwater organisms, and hence considered to be an important micronutrient [32]. Potassium get liberated from various feldspar bearing rocks during crustal weathering, but the residence time of this metal is low compared to sodium. Potassium recombines easily with other products of weathering and is being removed

from solution. All these phenomena lead to make K, a rare component in water than sodium, but is superior to sodium in world's rocks [2].

The concentration of K remains quite lower than the sodium, calcium and magnesium in aquatic ecosystems [30]. Although it is found in less quantity, it is also important in the ecology of blue-green algae [33].

Potassium has got a more or less similar chemistry like sodium and remains mostly in solution without undergoing any precipitation [30]. The potassium concentration in river water shows prominent seasonal variations. The seasonal average value of potassium ranges from 1.17 (postmonsoon) to 1.58 mg/l during monsoon. The highest (4.2 mg/l) value records during monsoon at S10.

3.1.14 Sodium

The main source of sodium in water resources is plagioclase feldspars, feldspathoids and clay minerals. Sodium and potassium are important alkali metals found in all freshwaters. The sodium spans between 2.4 and 65 mg/l for monsoon; 1.5 to 65.8 mg/l for premonsoon and 2 to 68 mg/l for postmonsoon. Station 9 and 10 shows higher values of Sodium. Saline ingressions might have resulted in exceptional values of sodium in those stations. Besides, various anthropogenic activities also enhance the sodium concentration in downstream portion of the river.

3.1.15 Sulphates

Most natural waters contain sulphates. A considerable amount of sulphates is added to the hydrologic cycle through atmospheric precipitation. Sulphate salts are mostly soluble and impart hardness to water. The sources of sulphate are sulphur minerals, sulphides of heavy metals which are of common occurrence in igneous and metamorphic rocks, gypsum and anhydrite found in some sedimentary rocks.

The season wise average content of sulphate ranges between 0.41 (monsoon) and 4.58 mg/l (premonsoon) during the study period (Tables 1, 2, 3). Minimum sulphate values are observed during the monsoon and postmonsoon. Two stations in lower reaches of river course exhibit comparatively higher values for premonsoon. This can be attributed to saline water ingressions in which sulphates impart permanent hardness to natural waters.

3.2 Assessment of Ion Concentration

Based on the average values of the chemical parameters, the cations were in the order of abundance in the order of Na>Ca>K>Mg during all seasons. This is in agreement with the decreasing order of abundance as noted during pre-monsoon in Meenachilriver [34]. The cations in the decreasing order of abundance include Na> Ca> K> Mg> Fe for PRM. The general dominance of anions was in the order of HCO₃>Cl>SO₄>PO₄. Rain water composition is location dependent, Na⁺ and Cl⁻ are the dominant components of coastal rains, this changes to Ca²⁺, HCO₃⁻ and SO₄²⁻ inland [34]. For cations, Na was higher than Potassium in all the seasons. The lower value of potassium is due to its lower geochemical mobility. This is in conformity with the finding [35].

3.2.1 Gibb's diagram

The dominant mechanism controlling the major ion chemistry of both surface and ground waters can be revealed by plotting the selected water quality parameters in the Gibb's diagram (Gibbs, 1970). From the plot of Na⁺ / Na⁺ + Ca²⁺ Vs. TDS and Cl⁻ / Cl⁻ + HCO₃⁻ Vs. TDS in the Gibb's diagram, it has been found that almost all the water samples for the three seasons (Fig. 3) belong to the rock dominance field, and hence the rock dominance or rock weathering is the dominating mechanism controlling the major ion chemistry of Neyyar river. Thus the source of soluble ions in the river water samples are the weathering of stones over which it flows. Based on Gibbs' diagram, the source of soluble ions in the river water samples is the weathering of stones over which water flows. This is in agreement with the finding [36].

3.2.2 Box plots

The major water quality parameters of Neyyarriver for the three seasons have been plotted in the Box plots (Fig. 4).

Cl-HCO₃-Na is the three dominating species control water quality during monsoon and geology plays a major role in controlling the water chemistry. But in postmonsoon (Cl-HCO₃-Ca) and premonsoon (Ca-HCO₃-Cl) seasons, besides geology, the land drainage and other anthropogenic activities in the river basin will contribute on the quality of water.

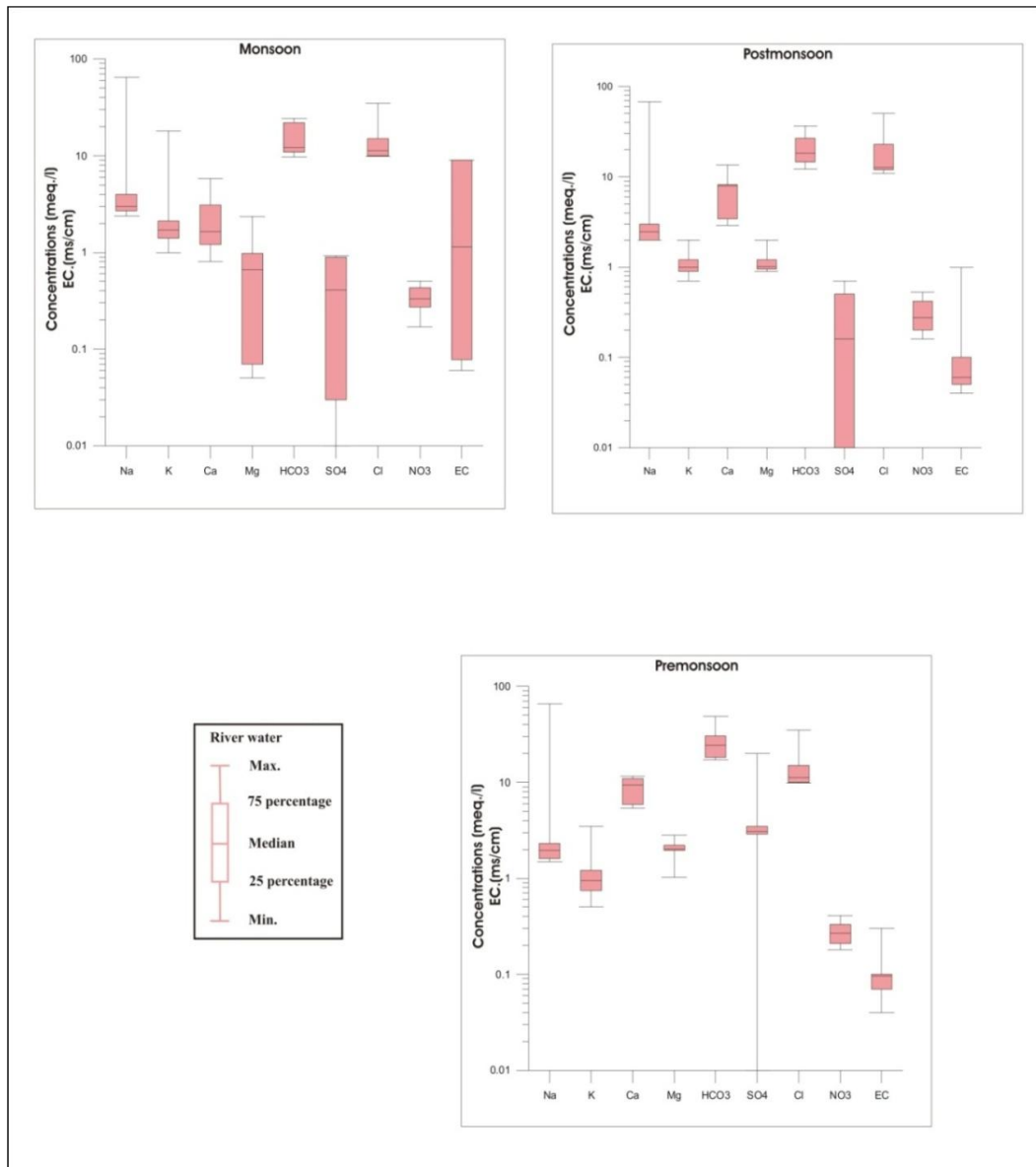


Fig. 4. Box plots showing the distribution of major ions and conductivity

3.2.3 Ludwig - langelier plots

A plot of major ion concentration on the Ludwig–Langelier [6] classification diagram (Fig. 5) indicates that the river water is of bicarbonate – alkaline earth type. The hydrochemical facies of upstream water types (Na-Cl-HCO₃/Ca-Na-Cl-HCO₃/Ca-Mg-HCO₃) with low TDS represents early stage of geochemical evolution of young meteoric or recharge area waters/ground waters that have undergone a relatively pronounced degree of groundwater chemical evolution.

The most common rock–water interaction processes (weathering of silicates and carbonates) tend to release cations (especially Ca²⁺ and Na⁺) and anions (especially HCO₃) in a rising pH condition. Subsequently, the ion-exchange reactions may modify the river water chemistry, while redox reactions lead to the dissolution of minor and trace elements [37]. The presence of mineral varieties of quartz, feldspars, pyroxene, biotite, etc., in the Pre-Cambrian crystallines (i.e., khondalites and charnockites) could be the source of major ions. The solutes which are subject to this process may be derived

from water–rock interaction or from leachates arriving in the rainfall recharge. The relative high concentration of HCO_3^- might have introduced through decay of organic matter. In the study area, evidences for chemical weathering can be explained by the relationships between major ions in water. The L-L plot between $(\text{Ca}+\text{Mg})$ vs. HCO_3^- indicates that most of the data points fall on equiline which indicates that the carbonate alkalinity is being balanced by the alkalis and there is chemical weathering in the study area. The abundance of various ions can be modelled in terms of weathering of various rock forming minerals [38]. The result is in agreement with the finding of that weathering of silicate rocks results in high sodium and potassium as reported in the hard rock regions. <http://shodhganga.inflibnet.ac.in/bitstream/10603/>

26395/11/11_chapter%206.pdf. Weathering of silicates might be the possible source of ions in the region comprising of composite gneiss and charnockite.

A plot of $(\text{Na} + \text{K})$ vs. HCO_3^- in river water shows relatively high concentration of $(\text{Na} + \text{K})$ to the HCO_3^- , indicating dissolution of alkaline earth minerals from rock/soil into river water especially during monsoon. In river water, all the $(\text{Ca} + \text{Mg})$ points on or below the equiline indicating that the dissolution rate is likely to be more in the upstream area. This is in agreement with the finding of the dominance of cations namely Ca^{2+} and Mg^{2+} and the anions namely Cl^- and HCO_3^- in the mountain river namely Muthirapuzha river (Periyar, longest tropical river in Kerala [39].

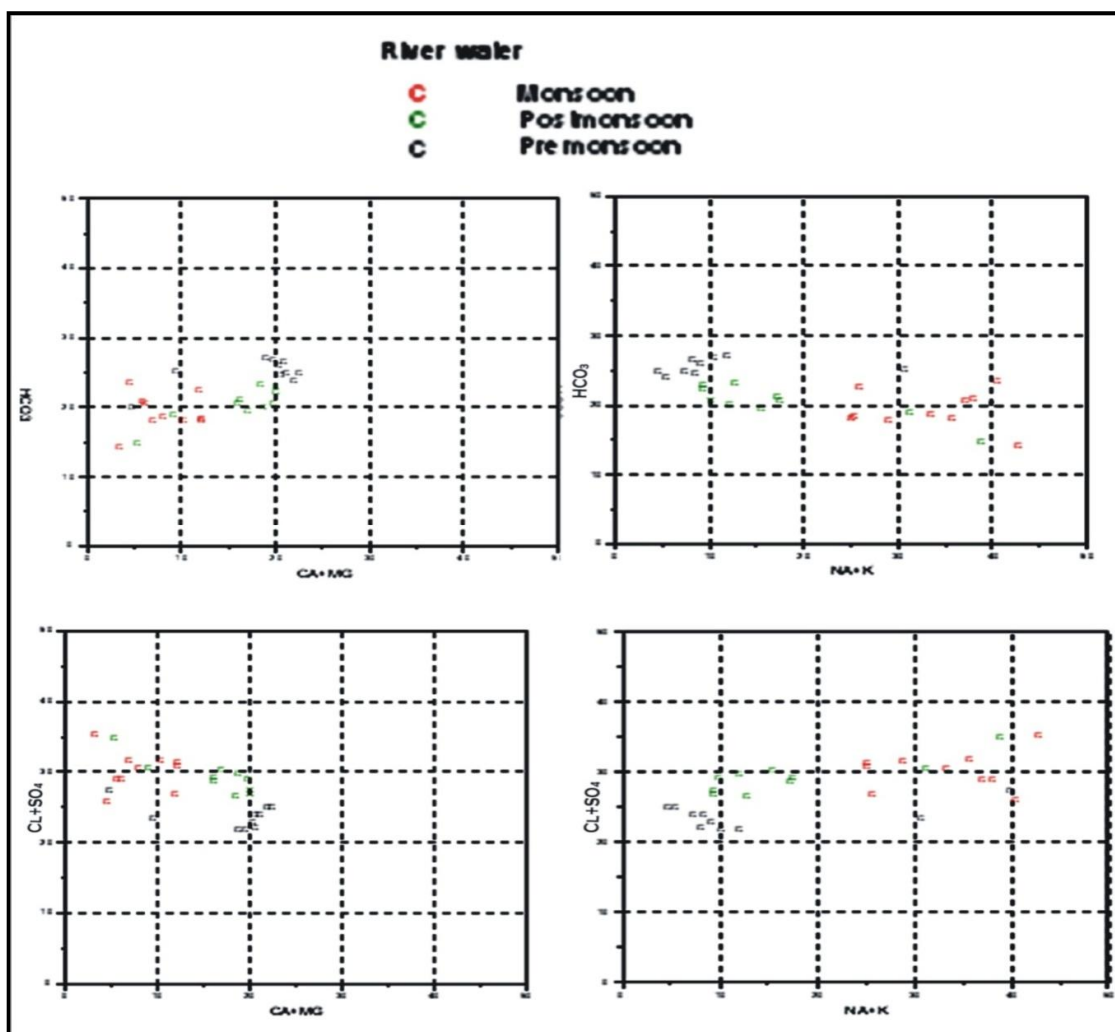


Fig. 5. Classification of river water on L-L diagram

The L-L Plots of Cl + SO₄ vs. Ca + Mg and Cl + SO₄ vs. Na + K exhibit that most of the data points fall above the equiline in view of the fact that high chloride can also be in part contributed from the salts of riverine sediments.

3.2.4 Piper (Trilinear) diagram

The observed flow pattern is summarised in Fig. 6.

The dominant water types of Neyyarriver are Na-HCO₃-Cl rich with subordinate Ca. The samples are relatively enriched in Na-HCO₃ and

characterized by water which is more or less similar to the source of highlands/provenance.

Na-Cl-HCO₃ water type is the characteristics feature of Tropical coastal Highlands. It points moderate chemical weathering processes taking place in the provenance areas of the basin. From the geological map of the study area (Fig.7), it is revealed that, the area is characterized by Feldspar bearing rocks (Orthoclase and Plagioclase), which upon chemical weathering can liberate alkali and alkaline earth elements to the feeder channels of the river [40].

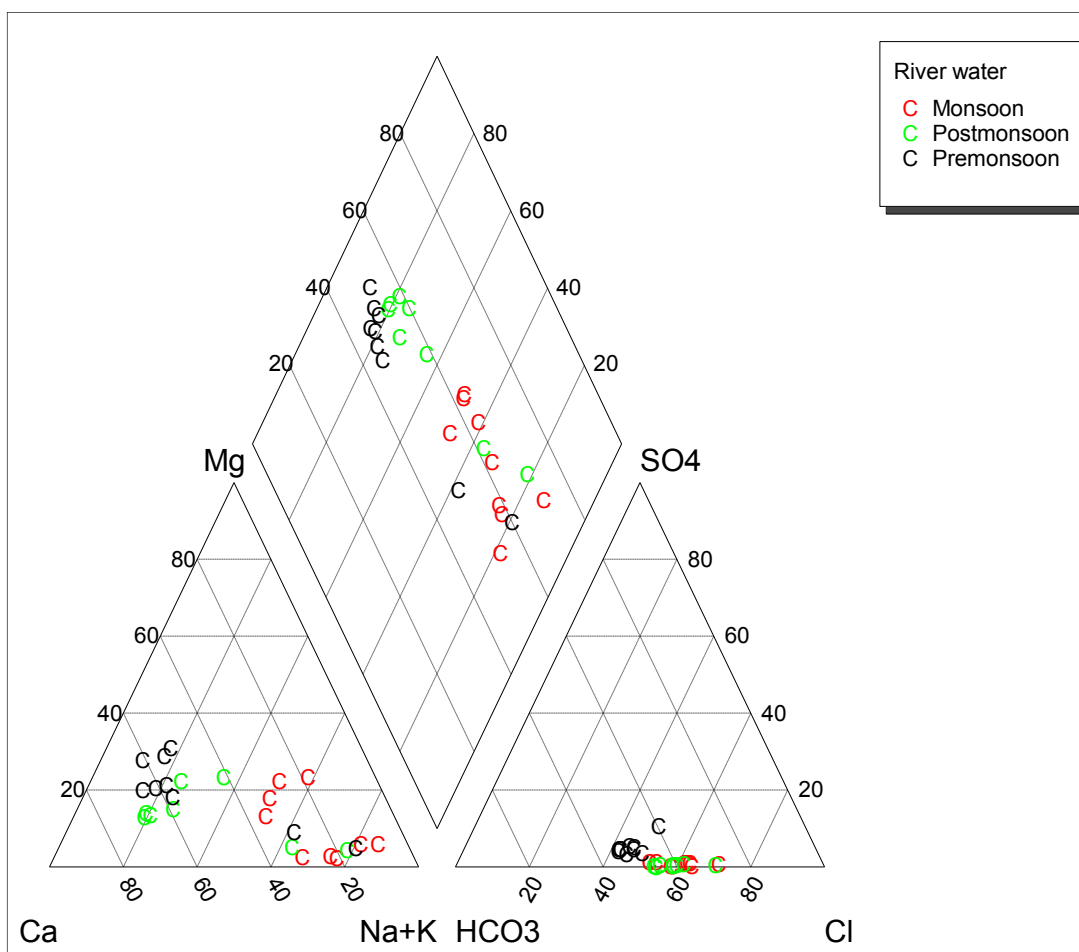
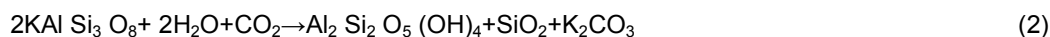
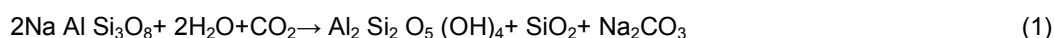


Fig. 6. Hydrochemical characterization of Neyyar river using piper diagram

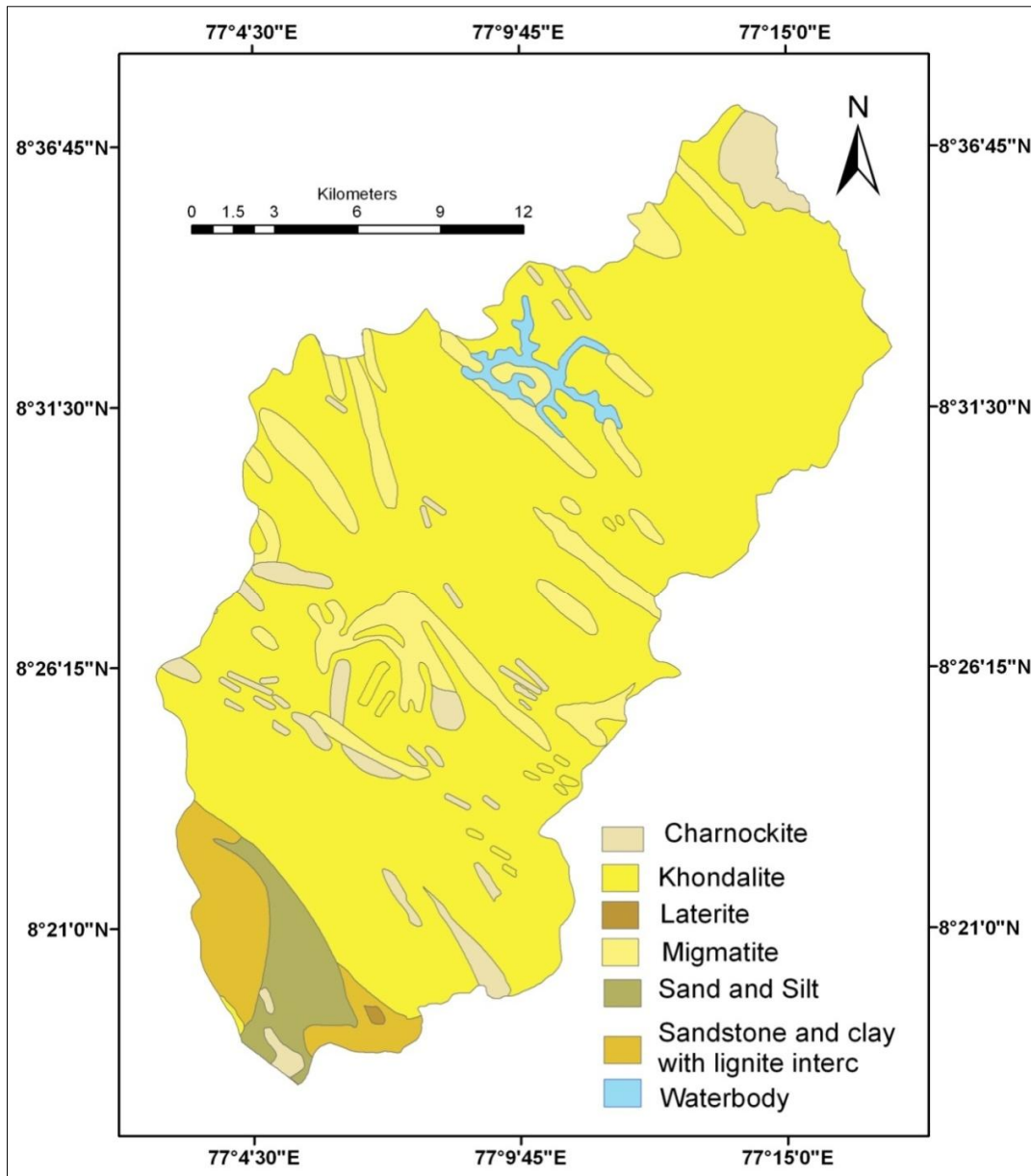


Fig. 7. Geology of the Neyyar river basin

From the equations 1-3, it is clear that chemical weathering of orthoclase (KAlSi_3O_8) and Plagioclase feldspars ($\text{NaAlSi}_3\text{O}_8/\text{Ca Al}_2\text{Si}_2\text{O}_8$) might be the source of Na^+ , K^+ and Ca^{++} ions in the overlying waters [41] of Neyyar river. The high Na^+ concentration in the upstream is probably from the mixing of two or more type of recharge area waters/groundwater from the origin [42]. Sodium ions enter the hydrologic system and remain for a long time, behave conservatively and are not used up in biological processes. The samples, relatively enriched with

HCO_3^- might naturally be considered moderately altered rocks in the provenance area and closer to the composition of meteoric water, but the meteoric signatures have mostly been obliterated. Another possibility of introduction of HCO_3^- in this riverine system is through the decay of organic matter since the catchment area is prevailing in the dense forested environments.

The water type (Na-Ca-Cl-HCO_3) with low TDS represents early stage of geochemical evolution of young meteoric waters with likely contribution

of salts from riverine deposits [43]. In the downstream reaches of Neyyar river, the dominance of Na-Cl water type with subordinate Ca and HCO₃ indicating the dissolution of Tertiary sedimentary formations (Sandstones and clay with lignite intercalations) in the coastal margin/mixture of fresh and saline water.

3.2.5 Durov Diagram

Accordingly, in Neyyar, during monsoon, most of the samples are Na-Cl-HCO₃ type; in post-monsoon the dominant water type belongs to Ca-Na-Cl-HCO₃ and the greater part of premonsoon samples are Na-Ca-Cl-HCO₃ type, whereas the water further downstream are Na-Cl with subordinate Ca and HCO₃ prevailing during all seasons (Fig. 8). This ion exchange can be explained by the occurrence of clay media in the riverine sediments. This simple dissolution of water type change from Na+HCO₃ to Na+ Cl water type distinctly matches the general flow of riverine water towards the near shore regions.

The dominance of HCO₃ is attributed by intermediate rock-water interaction processes and indicates slight alteration along the flow path. During all seasons, most of the samples are lying

in the fields 4, 5 and 6 of the diagram indicates that the water exhibiting simple dissolution or mixing influences and the dominance in Cl- and Na frequently represent the end-point waters.

The major ion chemistry of Neyyarriver waters show that Na is the dominant cation with lower proportions of Mg and Ca, with HCO₃ and Cl as the dominant anions in the majority of samples. It can be concluded from the diagram, that the water samples of Neyyarriver belong to the HCO₃ group with significant amounts of Na and Ca. The Na and Ca content may be attributed due to weathering of plagioclase feldspars from the source rocks. The clay rich sediments played a dominant role to capture these ions within the lattice layers. Under favourable conditions, the release of Na and K ions through ion-exchange process between the riverine waters and clay minerals. The dominance of HCO₃ is attributed by intermediate rock-water interaction processes and indicates slight alteration along the flow path. The dissolved constituents of river water can be very useful in indicating the geological evolution, the mode of river water origin within the hydrological cycles, soil or rock mass influences etc.

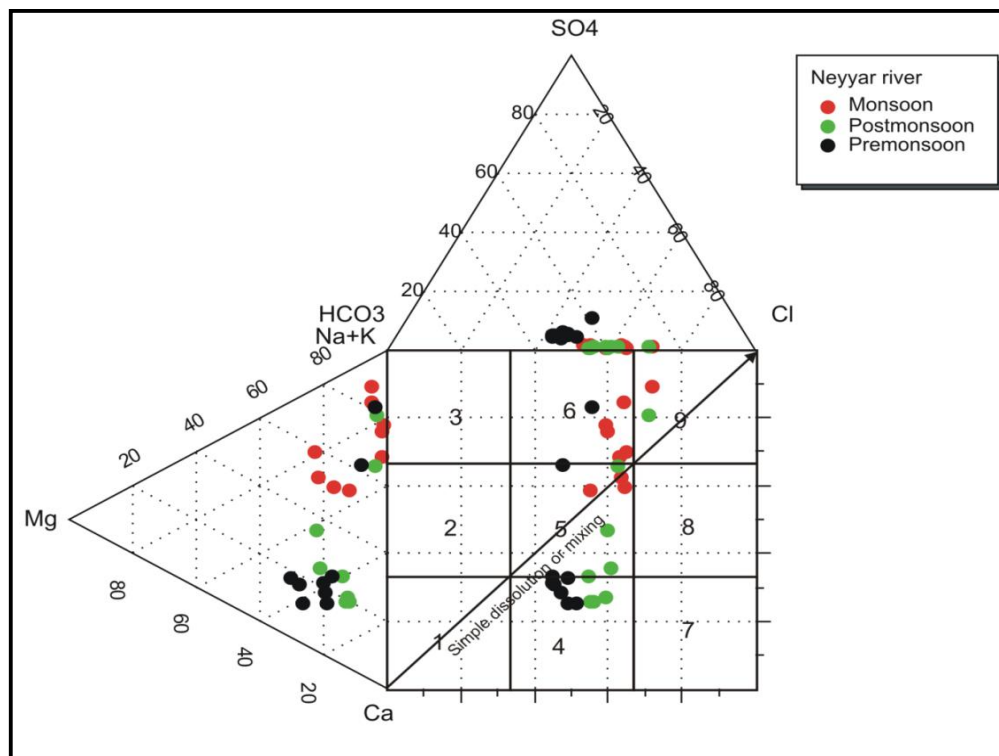


Fig. 8. Durov diagram illustrating the water type

3.3 Comparison of Major Chemistry with Other Tropical Rivers

The lithological heterogeneity and the intensity of weathering have significant effect on the river water as observed by the difference in water chemistry between the Deccan, East flowing and West flowing rivers [44]. The geomorphological settings of the Western Ghats (which brings-in the rainfall over its western slope) induce higher surface runoff which has significant effect on the weathering process and thus, on the water chemistry. The slope of the terrain has minimal effect on the water chemistry of water. The weathering of sedimentary formations in the plains leads to elevated fluxes of silica and radiogenic strontium. The weathering bedrock forms the main source of trace elements to the river water in this region. The abundance of trace elements in monsoon dominated terrain is controlled primarily by the discharge. This is in agreement with the finding that the rock dominance or rock weathering is the dominating mechanism controlling the major ion chemistry of Neyyarriver. This is also in agreement with the finding that geology plays a major role in controlling the water chemistry as $\text{Cl-HCO}_3\text{-Na}$ are the three dominating species. The secondary processes namely, redox reactions and oxidative scavenging of surface reactive metals by the oxyhydroxides of iron and manganese appears to have significant role in determining the geochemical abundance [44].

4. CONCLUSION

The study has been conducted to assess the tropic river water quality with respect to ions. The role of ions in a tropical river water (Neyyar, Kerala) was assessed. The study revealed that during premonsoon, there existed high pH, total dissolved solids, BOD, bi carbonate, total hardness, calcium, magnesium and sulphate in river water and this can be ascribed to low rainfall. But high nitrate concentration can be observed during monsoon periods which can be attributed to heavy rainfall and land drainage or increased decomposition of organic debris in sediment. High phosphate content can be observed during post monsoon especially in the downstream stretch of the river. The change in water type observed during monsoon almost from the middle portion from Na-Cl-HCO_3 to Na-Ca-Cl-HCO_3 can be observed and this may be attributed to anthropogenic pollution. Hence attention is to be paid to take the control

measures to prevent the pollution in this stretch of the river.

Rock weathering is the dominating mechanism controlling the major ion chemistry of Neyyarriver. The dominance of $\text{Cl-HCO}_3\text{-Na}$ during monsoon indicates that geology plays a major role in controlling water chemistry. The dominance of $\text{Cl-HCO}_3\text{-Ca}$ and $\text{Ca-HCO}_3\text{-Cl}$ during post monsoon and pre monsoon respectively indicates that besides geology, the land drainage and anthropogenic activities also control river water. The balancing of carbonate alkalinity with the alkali confirms chemical weathering in this hard rock study area. The Na and Ca content may be attributed due to weathering of plagioclase feldspars from the source rocks. The clay rich sediments played a dominant role to capture these ions within the lattice layers. Under favourable conditions, the release of Na and K ions through ion-exchange process between the riverine waters and clay minerals occurs. The dissolved constituents of river water can be very useful in indicating the geological evolution, the mode of river water origin within the hydrological cycles, soil or rock mass influences etc.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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