

# Mechanism controlling hydrochemisty and water quality assessment of a tropical river system, Kerala, India

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## ABSTRACT

This study aims to assess the mechanism controlling hydrochemical characteristics and water quality of the surface water source of the Thuthapuzha River Basin (TRB), one among the major tributaries of Bharathapuzha River—the largest west-flowing river in Kerala, India, and its suitability for drinking. Surface water samples (15) collected during the premonsoon from the Thuthapuzha River were analysed for 18 parameters. The water samples from Thuthapuzha are slightly alkaline. Almost all the parameters studied were within the prescribed limits set by WHO, BIS, and ICMR. Hence, qualitatively, the water is suitable for drinking. When plotted on a Piper diagram, most water samples are of the Ca–HCO<sub>3</sub> type. From the Gibbs diagram, the majority of samples fall in the facies field between the atmospheric precipitation and rock dominance. The weathering plots indicate the dominance of silicate weathering in the study area, which contributes a substantial part of the chemical load. The correlation matrix also shows that the majority of the parameters exhibit a positive correlation (EC, TDS, Ca, Mg, Na, Cl, and HCO<sub>3</sub>). *Principal component analysis (PCA) and Hierarchical Cluster Analysis (HCA)* indicates that river water chemistry is primarily controlled by silicate weathering and secondarily reflects redox-sensitive geochemical processes and anthropogenic nutrient inputs. The Particulate Load (PL) and Dissolved Load (DL) ratio has been calculated for the drainage channel at the gauging station to be 1.31, indicating the dominance of physical weathering in these high-gradient, humid terrains. The high gradient terrain characteristics of the river basins, which offer only very short residence time for the stream waters to interact with the bed rocks and subsequent release of ions to sediment (suspended and dissolved) transport.

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## 1. Introduction

The surface water quality of rivers is driven by several natural and anthropogenic factors, and is one of the most susceptible resources across the globe (Diamantini et al., 2018). Catchment characteristics, including climate, geology, and land-use patterns, exert a strong influence on river hydrochemistry and water resources for human use. The chemistry of surface water quality is controlled by evaporation, precipitation, chemical weathering, geological composition,

inputs from its tributaries and human intervention (Pant et al., 2018; Bhat et al., 2021). Major divalent cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, along with HCO<sub>3</sub><sup>-</sup>, are primarily derived from the chemical weathering of geospheric minerals through interactions with atmospheric CO<sub>2</sub>. In contrast, ions such as Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> originate from multiple sources, including the geosphere, atmosphere, biosphere, and anthroposphere (Huang et al., 2009). Therefore, studies on the physicochemical characteristics

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of surface water and the mechanisms controlling them, especially major cations and anions, have broad implications for understanding water quality (Meybeck, 2003; Khan and Srivastava, 2008).

The geochemistry and water quality aspects of major tropical rivers are extensively discussed, and there is a wealth of literature available (Stallard and Edmond, 1981; Gaillardet et al., 1997; Sarin et al., 1992; Singh and Hasnain, 1998; Krishnaswami, 1999; Dalai et al., 2004; Sukanya et al., 2022). These studies have not only elucidated the sources and controlling mechanisms of hydrogeochemistry in major river basins but have also provided valuable insights into the rates and spatial-temporal patterns of dissolved chemical cycling within the continent-river-ocean system. However, small tropical rivers of Indian Peninsula hardly gained much attention although these rivers are the lifeline of many cities and industrial clusters located along the west coast. Lack of adequate baseline data on the source contribution and future trends of hydro-chemical signals/solutes in river systems is a major setback challenging regulatory systems and also wise management of the fresh water sources. Thus, a comprehensive river water quality monitoring is a useful mechanism not only for determining the suitability of surface water for drinking and irrigation, but also for ensuring effective water resource management and aquatic life protection (Kannel et al., 2007; Etteieb et al., 2017).

Thuthapuzha river basin (TRB) is a sixth order sub-basin. The main river and its tributaries draining from the Western Ghats are one among the major source of drinking water and agricultural use in Kerala, which is used by thousands of people for various purposes, e.g., domestic use, irrigation, hydropower, industrial and even ritual practices. Maintaining the water quality of the Thuthapuzha River, a major tributary of the Bharathapuzha River in Kerala, is essential due to its importance as a primary source of drinking water, agricultural supply, and ecological sustainability. Although the river water is generally classified as suitable for use, it remains vulnerable to increasing anthropogenic pressures, including untreated domestic and agricultural runoff, sand mining activities, and climate change-driven variability in rainfall patterns. Therefore, water quality of the TRB is a matter of great concern and it is important to understand the hydrogeochemistry and major weathering processes in the basin. Thus the present study is carried out to discuss the mecha-

nism controlling the hydrochemistry, major weathering process and suitability of the water for drinking of Thuthapuzha River Basin (TBR), draining the southern Western Ghats, Kerala, India.

## 2. Study Area

Thuthapuzha river basin (TRB) is a sixth order sub-basin ( $A = 1018 \text{ km}^2$ ) of Bharathapuzha and drains between N Lat.  $10^\circ 50' - 11^\circ 15'$  and  $76^\circ 05' - 76^\circ 40'$  E Long (Fig. 1). Thuthapuzha river originates from Sispara peak, northeast end of silent valley in Western Ghats and, flow through Palakkad, Malappuram and Thrissur districts of Kerala, before joining with Bharathapuzha at near Irimbiliyam. Thuthapuzha is about 63 km in length and has four tributaries draining to it, namely Kuntipuzha, Nellipuzha, Kanhirapuzha and Thuppanadpuzha (Fig. 1). The average annual discharge of the sub-basin is 1750 MCM (CWC, 2012). The study area falls within the midland (7.5–75 m elevation above mean sea level) and the highlands ( $>75$  m elevation above mean sea level) region of Kerala and experiences a humid tropical climate. The Silent Valley Reserve Forest is located at the north-eastern corner of the sub-basin. The average annual rainfall in Thuthapuzha Sub-basin is 3830 mm with a wide spatial variation in the rainfall ranging from 2020 mm to more than 5000 mm/year, with the higher rainfall towards the Silent Valley Reserve Forest (Unnikrishnan Warriar and Manjula, 2014). This is higher than the average annual rainfall (1822 mm) of entire Bharathapuzha River Basin (Raj and Azeez, 2011) and the average annual rainfall (2817 mm) of Kerala state (Krishnakumar et al., 2009).

The rainfall is dependent on the south-west and north-east monsoons which contributes 63% and 23%, respectively, of the total annual rainfall. The pre-monsoon showers also contribute 13% of the total annual rainfall. The study area is underlain by Precambrian crystalline rocks like charnockite, charnockitic gneiss, hornblende biotite gneiss, garnet biotite gneiss, khondalites, migmatites, etc. (Ravindrakumar and Chacko, 1994). A gabbro dyke traverses extensive lengths of the study area (CGWB, 2009). Laterite capping is observed over the major part of the study area with a maximum thickness of 20 m along the western part. Laterite is either absent or observed as a thin capping over the country rock towards the eastern part.

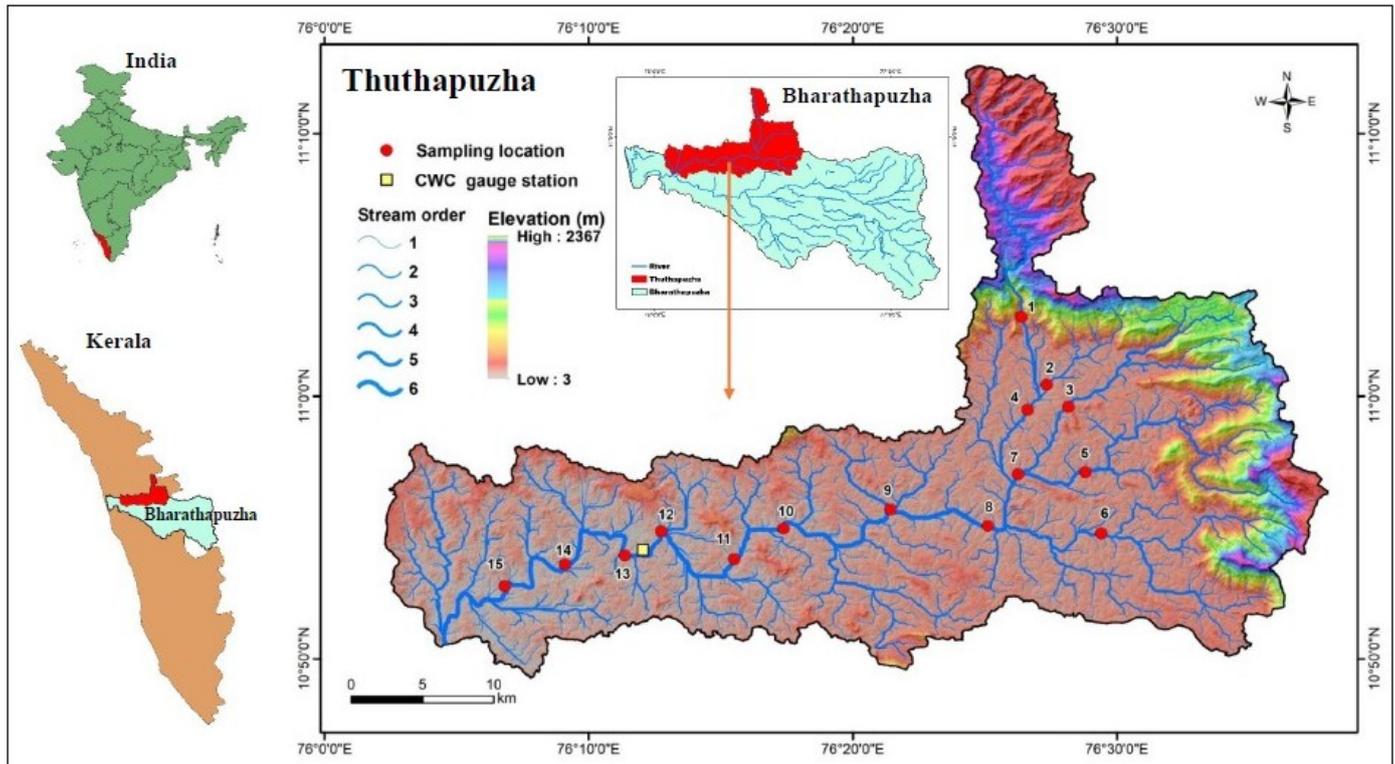


Fig. 1. Location map of the study area and water sampling locations. The terrain elevation is also depicted in the map.

### 2.1. Geological setting of the area

The TRB is underlain by Precambrian crystalline rocks like charnockite, charnockitic gneiss, hornblende biotite gneiss, garnet biotite gneiss, khondalites, migmatites, etc (Ravindrakumar and Chacko, 1994). The various geological units were delineated based on the Geological Survey of India's geological map. Based on geology, the study area is divided into nine units (Fig. 2).

The major portion of the basin is covered by charnockite group of rocks and migmatite complex (441 and 437 km<sup>2</sup> respectively) followed by basic rocks (108 km<sup>2</sup>) Peninsular Gneissic Complex (103 km<sup>2</sup>) sand and silt (sedimentary deposits) (9.9 km<sup>2</sup>) high grade metasedimentary rocks (6.8 km<sup>2</sup>) and khondalite group of rocks (1.9 km<sup>2</sup>). Pegmatite/Aplite/Quartz vein and laterite formations are very less in the study area. The precambrian crystalline rocks are well foliated at many places, striking WNW-ESE with a southward dip of 30°–50° (John and Rajendran, 2005). Laterite capping is observed over the significant part of the study area with a maximum thickness of 20 m along the western part. Laterite is either absent or observed as a thin capping over the country rock towards the eastern part.

The major lineaments in the study area trend NNW-SSE, NW-SE, and E-W. There are many minor lineaments in the study area, also trending in the NW-SE and N-S directions. Most of the lineaments in the area are found along the drainages.

### 2.2. Land use/land cover

LULC provides essential information on infiltration, soil moisture, groundwater, surface water, etc., and also indicates groundwater requirements (Ibrahim-Bathis and Ahmed, 2016). Vegetation and forest cover reduce runoff and increase subsurface infiltration, whereas bare land over impervious layers and built-up areas reduces infiltration and increases runoff (Thapa et al., 2017). The LULC of the study area is dominated by agricultural plantations (637 km<sup>2</sup>). About 149 km<sup>2</sup> of the area is covered by agriculture land, evergreen and deciduous forests covered an area of 124 km<sup>2</sup> and 64 km<sup>2</sup> respectively. Forest plantation and land with scrub forests are spread over 10 and 45 km<sup>2</sup> respectively. Build-up land, barren land, land without scrub, grass land, marshy/swampy and water bodies occupy 20, 17, 4, 1, 3 and 92 km<sup>2</sup> respectively (Fig. 3).

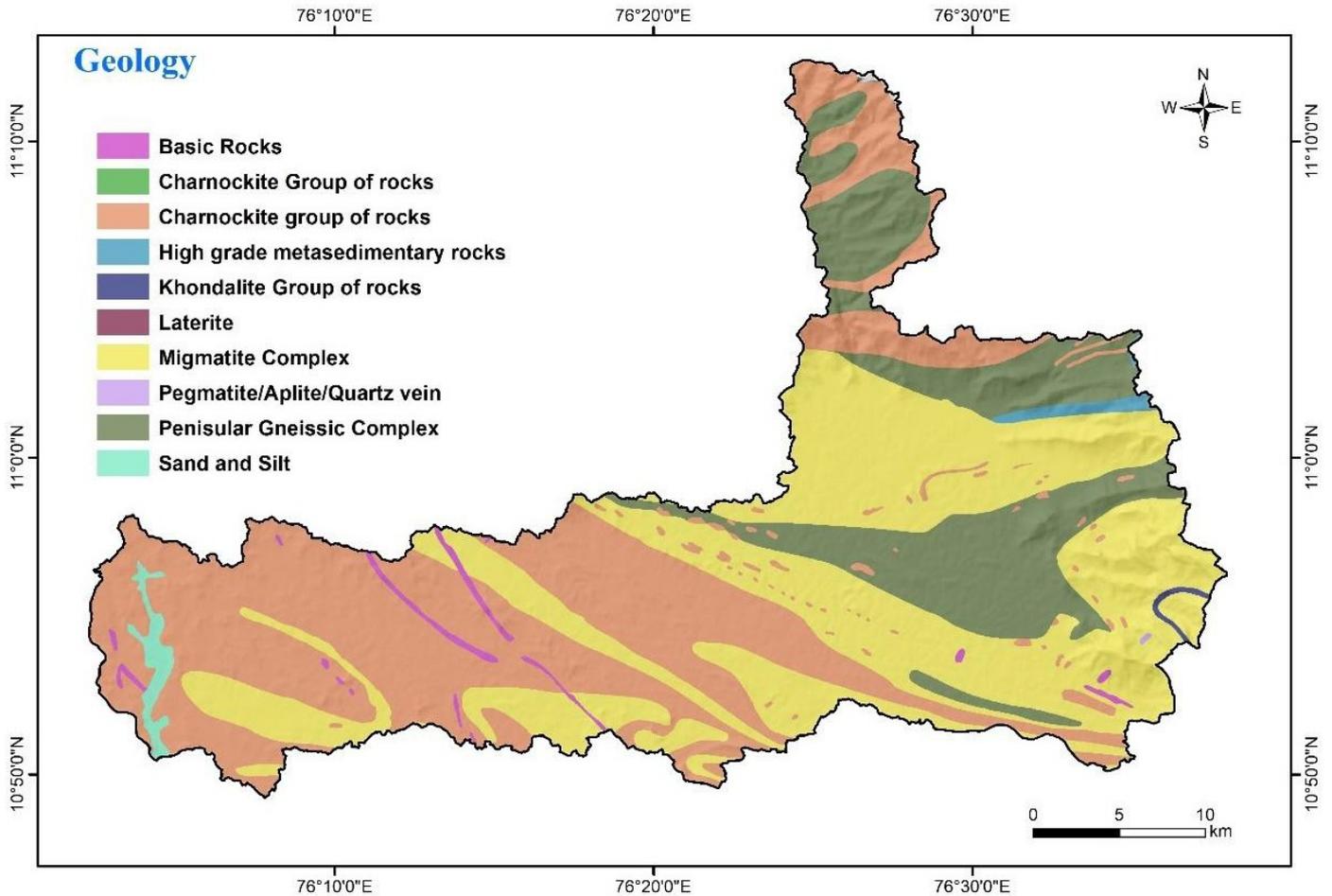


Fig. 2. Geology map of Thuthapuzha River Basin.

### 2.3. Longitudinal profile of Thuthapuzha River

The longitudinal profile of Thuthapuzha shows how a river's gradient changes as it flows from its source to its mouth (Fig. 4). The long profile shows that, in the upper stage of a river's course, the river's gradient is steep but it gradually flattens out as the river erodes towards its base level.

### 3. Materials and Methods

Fifteen river water samples of Thuthapuzha Sub-basin were collected using 1L depth water sampler during the premonsoon season. Water samples during the pre-monsoon are crucial because low flow and high temperatures concentrate pollutants, revealing baseline chemical contamination from dry season activities (like industrial/urban discharge, evaporation) and identifying potential health hazards (high TDS, heavy metals) before seasonal dilution by rain washes them away, helping assess long-term river health and

management needs. The water samples were collected (Fig. 1) at each sampling point, prewashed (with dil. HCl), and labelled in 1-L capacity narrow-mouth pre-polythene bottles. One portion of the collected samples (100 ml) was filtered on site using Millipore syringe filters (0.45  $\mu\text{m}$ ), acidified immediately with 2M  $\text{HNO}_3$ , and used for cation analysis. An additional aliquot of the samples (500 ml) was filtered through a 0.45  $\mu\text{m}$  Millipore membrane and preserved at 4 °C for further study. The water samples were analysed following the standard analytical procedures and techniques reported in the literature (APHA, 2012). The water samples were analyzed for pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), dissolved oxygen (DO), alkalinity, major cations (calcium, magnesium, sodium, potassium), major anions (chloride, bicarbonate, sulphate), nutrients (silicate-silicon, nitrite-nitrogen, nitrate-nitrogen, phosphate), ammonia-nitrogen and iron. The physico-chemical parameters,

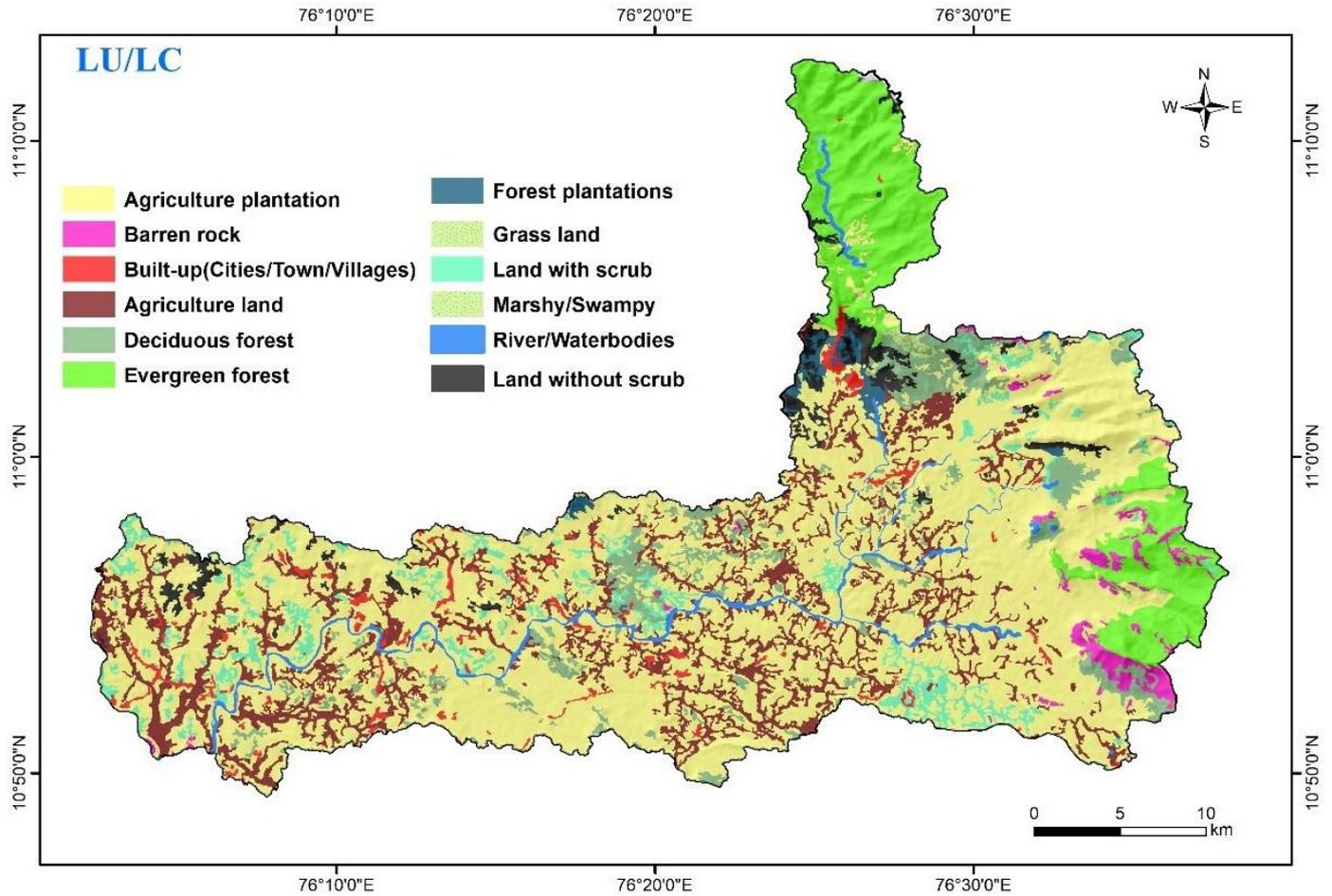


Fig. 3. LU/LC map of the study area.

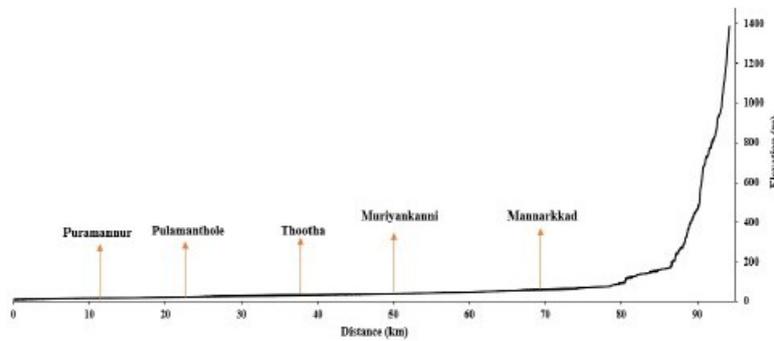


Fig. 4. Longitudinal profile of the Thuthapuzha river.

such as pH, electrical conductivity (EC), and total dissolved solids (TDS), were measured in the field using a water analyser kit (EUTECH 650). Sodium, potassium, calcium, magnesium, and iron present in the water samples were determined by Microwave Plasma Atomic Emission Spectroscopy (MP-AES), an atomic emission technique. Chloride and sulphate were estimated by the argentometric method and the turbidity method, respectively, and the nitrate using an ion-selective electrode. Continuous Flow Analyzer

(CFA) were employed to determine the silicate phosphate, nitrate, nitrite and ammonia in water samples. Bicarbonate in the water samples was calculated from measured total alkalinity values, determined by titration against a standard acid. Dissolved oxygen (DO) was measured using the Winkler method with the azide modification. All analyses were carried out in the laboratory at the National Centre for Earth Science Studies (NCESS), Thiruvananthapuram.

## 4. Multivariate Statistical Analysis

### 4.1. Pearson's correlation

Pearson's correlation analysis is an important statistical tool for assessing the degree of dependence among variables (Belkhiri et al., 2010). In fact, the correlation coefficient is used to measure the inter-relationship and extent of associations between variables. A correlation coefficient of +1 indicates a perfect relationship between the variables, -1 indicates an ideal relationship in which the variables vary inversely, and a zero value indicates no relationship between the variables (Mudgal et al., 2009) at a significant level of  $p < 0.05$ . In general, Pearson's correlation coefficient values  $r > 0.7$  are considered strong correlations, while  $r$  values between 0.5 and 0.7 are considered moderate correlations. Pearson's correlation matrix clearly shows the interdependence of the variables.

### 4.2. Principal component analysis (PCA)

Principal component analysis (PCA) is a statistical technique used to identify linear relationships among variables while retaining most of the original information (Singh et al., 2005). The first principal component (PC1) accounted for the greatest proportion of variance in the dataset. Factor loadings were categorised as strong ( $\geq 0.75$ ), moderate (0.75–0.50), or weak (0.50–0.30); however, loadings reflect a variable's relative contribution to a component rather than the component's overall importance.

### 4.3. Hierarchical cluster analysis

Hierarchical cluster analysis groups samples based on mathematical measures of similarity, using distance metrics such as Euclidean distance, angles, or vector products in multidimensional space. This method has been widely applied to classify water samples into statistically distinct hydrochemical groups, providing valuable insights into geological contexts (Belkhiri et al., 2010).

## 5. Results and Discussion

The physiochemical parameters of Thuthapuzha river basin surface water samples are summarized in Table 1. Advanced analytical and computational techniques are used to draw and interpret the results.

pH of natural waters due to geological factors as well as biological activity usually is alkaline or slightly

acidic. A low pH of below 6.5 can cause corrosion to metal pipes and gastrointestinal disorders (Rajesh et al., 2001). pH of water samples collected from Thuthapuzha river basin range from 6.99 to 8.41 with an average of 7.59. The water samples were slightly alkaline in nature. Water from majority of the stations record pH values higher than neutral pH (i.e. 7.0). The pH shows almost a linear trend along the main channel of the Thuthapuzha river. Out of the 15 river water samples studied, none of the samples showed exceeding value than the drinking water quality standards set by BIS and WHO. The desirable limit of pH of water for drinking purpose prescribed by Bureau of Indian Standards (BIS, 2012) is 6.5–8.5. A low pH of below 6.5 can cause corrosion to metal pipes and gastrointestinal disorders (Rajesh et al., 2001).

Electrical conductivity (EC) is a measure of the concentration of ions in water. In the present study, the electrical conductivity of river water samples ranges from 30.00  $\mu\text{S}/\text{cm}$  to 140  $\mu\text{S}/\text{cm}$ , with an average value of 88.07  $\mu\text{S}/\text{cm}$ . The conductivity values show almost a linear trend. Samples showed lower conductivity values than the prescribed limit (800  $\mu\text{S}/\text{cm}$ ) set by BIS and WHO (Table 1). The TDS value ranges from 23 mg/L to 91 mg/L, with an average of 56.33 mg/L. Gaillardet et al. (1999) emphasised that the majority of the world's rivers have TDS less than 500 mg/L, and that exceptions are due to either pollution (i.e., anthropogenic interference) or aridity (i.e., climate). However, several studies showed that small rivers in tropical mountainous regions have relatively significantly lower TDS values (i.e., less than 100 mg/L; e.g., Lewis Jr. et al., 1987; McDowell and Asbury, 1994; Harmon et al., 2009).

Dissolved oxygen content of river water samples varies from 5.6 mg/l to 9.57 mg/l, with an average value of 7.73 mg/l. The WHO and the BIS have set limits of 5 mg/L for DO. DO values for all the river samples are in agreement with the WHO/BIS standards. Concentrations below 5 mg/l may adversely affect the functioning and survival of biological communities. DO remains almost constant throughout the river profile. The Total hardness ranges from 8.95 mg/L to 50.85 mg/L in water samples from the Thuthapuzha River, with an average of 27.55 mg/L. Hardness also shows a linear trend towards the downstream part. Total hardness values at all stations are below the standard limit (200 mg/l) prescribed by WHO (1984) and BIS (300 mg/l). The water

Table 1. Concentration of water quality parameters estimated for the water samples of the Thuthapuzha river.

Sampling station	pH	EC	DO	TH	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	Na	K	Fe	SiO <sub>4</sub>	PO <sub>4</sub>	NO <sub>2</sub>	NO <sub>3</sub>	NH <sub>3</sub>	TDS
1	7.70	30.0	8.12	8.95	12.00	4.55	0.07	2.03	0.94	1.70	1.17	0.12	4.25	6.47	3.98	8.16	7.94	23.00
2	7.15	140.0	5.60	50.85	48.00	14.75	0.23	10.67	5.87	4.61	2.54	0.5	9.51	13.03	0.19	3.52	8.04	91.00
3	7.26	124.0	6.64	40.29	44.00	15.80	0.70	8.88	4.39	4.09	2.12	0.32	10.30	7.71	0.01	2.99	9.66	80.00
4	7.02	47.00	6.91	16.36	18.00	6.20	0.09	3.92	1.59	0.37	1.75	0.44	4.42	22.48	0.91	4.16	19.83	32.00
5	7.25	79.00	7.50	23.09	22.00	11.20	0.53	5.64	2.18	2.17	2.66	0.31	6.02	7.21	2.75	4.72	25.88	51.00
6	7.27	91.00	7.53	27.46	30.00	7.10	0.27	7.28	2.24	1.89	3.16	0.48	6.55	6.27	0.61	8.38	24.08	58.00
7	7.30	94.00	7.13	27.22	30.00	12.20	0.57	6.58	2.61	2.23	3.67	0.36	5.78	5.51	1.87	6.89	35.14	63.00
8	7.52	79.00	7.81	24.13	24.00	10.40	0.25	5.76	2.36	1.71	2.68	0.18	5.54	6.11	1.43	5.11	34.66	53.00
9	7.75	76.00	7.76	22.84	26.00	8.65	0.32	5.23	2.37	1.73	1.89	0.17	5.11	5.25	0.36	2.42	13.48	50.00
10	8.23	84.00	8.81	24.71	24.00	11.75	0.38	5.73	2.52	2.04	1.83	0.06	5.53	7.68	0.76	3.71	14.63	55.00
11	8.38	90.00	8.93	26.57	30.00	10.75	0.67	6.34	2.60	2.28	1.86	0.22	4.97	5.67	0.22	2.30	10.44	57.00
12	8.04	103.0	7.98	28.94	30.00	12.20	0.57	6.76	2.92	2.12	1.97	0.18	4.77	6.26	0.04	3.24	7.13	67.00
13	8.41	87.00	8.16	30.70	26.00	12.60	0.60	6.94	3.24	2.05	2.01	0.15	3.87	3.93	0.01	2.39	35.26	56.00
14	6.99	102.0	9.57	28.61	28.00	15.10	0.62	6.48	3.01	3.03	1.77	0.18	4.99	7.99	1.73	2.65	25.92	66.00
15	7.57	95.00	7.50	32.60	32.00	14.20	0.70	7.22	3.53	2.67	2.09	0.13	4.39	5.53	0.37	1.56	17.57	43.00

EC-Electric conductivity( $\mu\text{S}/\text{cm}$ ), DO-Dissolved oxygen( $\text{mg}/\text{l}$ ), TH-Total hardness( $\text{mg}/\text{l}$ ), HCO<sub>3</sub>-Bicarbonate( $\text{mg}/\text{l}$ ), Cl-Chloride( $\text{mg}/\text{l}$ ), SO<sub>4</sub>-Sulphate( $\text{mg}/\text{l}$ ), Ca-Calcium( $\text{mg}/\text{l}$ ), Mg-Magnesium( $\text{mg}/\text{l}$ ), Na- Sodium( $\text{mg}/\text{l}$ ), K-Potassium( $\text{mg}/\text{l}$ ), SiO<sub>4</sub>-Silicate( $\text{mg}/\text{l}$ ), PO<sub>4</sub>-Phosphate( $\mu\text{g}/\text{l}$ ), NO<sub>2</sub>-Nitrite( $\mu\text{g}/\text{l}$ ), NO<sub>3</sub>-Nitrate( $\mu\text{g}/\text{l}$ ), NH<sub>3</sub>- Ammonia( $\mu\text{g}/\text{l}$ ), TDS-Total dissolved solids( $\text{mg}/\text{l}$ ).

samples from Thuthapuzha fall into the soft category.

Among major cations, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup> show relatively higher variability compared to K<sup>+</sup> (Table 1). Ca<sup>2+</sup> in the river water ranges from 2.03 to 10.67 mg/L, with an average of 6.36mg/L. Ca<sup>2+</sup> in river water is mainly controlled by the weathering of various silicate minerals and by reactions in the carbonate system. The primary source of magnesium (Mg) in water is igneous rocks that contain ferromagnesian minerals such as olivine, pyroxenes, amphiboles, and various dark-coloured micas (Hem, 1985). Major natural sources of Ca<sup>2+</sup> in TRB are weathering of chain silicates (pyroxenes and amphiboles) and plagioclase feldspars, as well as dissolution of carbonate minerals. The concentration of Ca in the river water samples ranged from 2.03 mg/L to 10.67 mg/L, with an average of 6.36 mg/L. The maximum desirable limit of calcium in drinking water is 75 mg/l (WHO/BIS). All the samples exhibited concentrations well below the WHO/BIS standard limits. Mg<sup>2+</sup> in the stream waters is supplied by weathering of ferromagnesian minerals, including pyroxenes and amphiboles, as well as dark coloured micas (e.g., biotite), which are abundant in the host lithology (Fig. 2). The values of Mg were found to vary from 0.94 mg/l to 5.87 mg/l with an average of 2.82 mg/l. The concentration of Mg at all sampling stations is below the prescribed limit suggested by BIS/WHO. Both Ca and Mg show an almost linear trend towards the river mouth. In addition, Na<sup>+</sup> content in TRB ranges from 1.70 mg/l to 4.61 mg/l with an average of 2.31 mg/l. The main source of sodium (Na) in water is plagioclase feldspars, feldspathoids and clay minerals (Hem, 1985). Sodium is released

into natural water during chemical weathering of minerals such as plagioclase feldspar, nepheline, sodalite, glaucophane, clay minerals, and sodium-bearing pyroxenes and amphibolites. Even though potassium is widely distributed in rocks, its concentration in natural waters is usually low because potassium minerals are resistant to weathering and dissolution (Hem, 1985). Potassium concentrations ranged from 1.17 to 3.67 mg/l, with an average of 2.21 mg/l. Both Na and K showed a fluctuating trend throughout the TRB.

HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> are the dominant anions in the water samples of TRB, whereas SO<sub>4</sub><sup>2-</sup> has only secondary significance (Table 1). The HCO<sub>3</sub><sup>-</sup> concentration in this study ranges from 12 to 30 mg/L, with an average of 28.27 mg/L. At the same time, the chloride content ranges from 4.55 to 15.80 mg/L, with an average of 11.16 mg/L. Dominant sources of Cl in river water include contributions from cyclic salts, soil salt dissolution (Stallard and Edmond, 1981), and anthropogenic inputs (agricultural, industrial, and domestic activities). However, HCO<sub>3</sub><sup>-</sup> in river water is predominantly derived from silicate- and carbonate-weathering reactions (Mortatti and Probst, 2003). Alkalinity resulting from naturally occurring ions such as CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> is not considered a health hazard. Alkalinity values in the present study vary from 12 mg/l to 48 mg/l, with an average value of 28.27 mg/l. Alkalinity values at all stations are within the limit prescribed by WHO/BIS. A linear trend is observed for alkalinity. Unlike alkalinity, chloride showed an increasing trend downstream in the main river. The concentration of sulphate in this study ranges from 0.07 mg/l to 0.7 mg/l, with an average value of 0.44 mg/l. According to WHO standards, the limit for sulphate in drinking water is

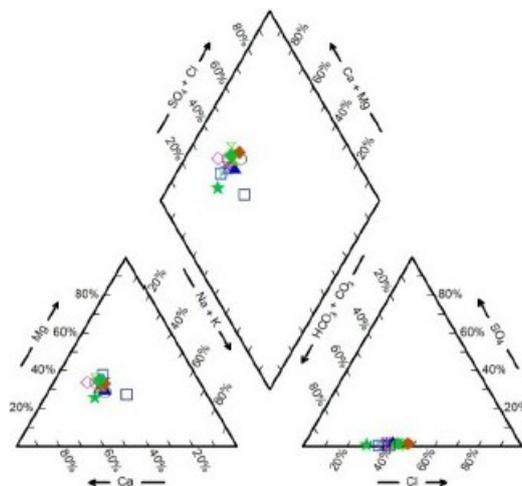


Fig. 5. Piper diagram showing the water chemistry in the river sample.

200 mg/L. Sulphate shows a fluctuating trend throughout the river basin.

Dissolved inorganic phosphorus, inorganic nitrogen as nitrate and ammonia, silica and iron are generally regarded as critical nutrients to the aquatic ecosystem functioning (Dodds, 2002; Allan and Castillo, 2007). Nitrogen and phosphorus are the major nutrients, and their sources and supplies vary considerably with geology, soil, climate and vegetation (Dodds, 2006). Nitrogen and phosphorus concentrations are often elevated due to anthropogenic inputs (Carpenter et al., 1998). Significant anthropogenic inputs of nitrogen and phosphorus to streams include agricultural fertilisers, atmospheric deposition, nitrogen-fixing crops and human and animal wastes (Boyer et al., 2002). Anthropogenic sources include municipal and industrial wastewaters, termed point source pollution, because they enter surface waters at a point, usually through a pipe; fertilizers and manure from farm fields, referred to as nonpoint sources because of their diffuse entry into streams via surface and subsurface runoff (Edwards et al., 2000; Goller et al., 2006). The inorganic phosphorus values of river water samples ranged from 3.93 µg/L to 22.48 µg/L, with an average of 7.81 µg/L.

The silicate values for river water samples in the present study ranged from 3.87 mg/L to 10.30 mg/L, with an average of 5.73 mg/L. The entire set of river water samples exhibited lower silicate concentrations than the WHO potability standards, and showed a decreasing trend towards the river mouth. Nitrite (NO<sub>2</sub>-N) ranges between 0.01 µg/l and 3.98 µg/l, whereas Nitrate (NO<sub>3</sub>-N) of TRB ranges between 1.56 µg/l and 8.38 µg/l, with an average value of

4.15 µg/l. The concentration of ammonia ranges from 7.13 µg/l to 35.26 µg/l with an average of 19.31 µg/l. The occurrence of iron in an aquatic ecosystem is dependent on oxidation and reduction. Iron occurs as ferric and ferrous ions in oxic and anoxic habitats, and the process is strongly influenced by microbiological activity. It also appears as a metal pyrite (FeS) in anoxic habitats and a flocculent precipitate (Fe(OH)<sub>3</sub>) in oxic conditions (Hem, 1985). In TRB, Fe concentration ranges from 0.06 to 0.5 mg/l, with an average of 0.25 mg/l. Iron shows a fluctuating trend towards the river mouth basin.

The observed hydro-chemical parameters are subjected to advanced statistical computational procedures, including correlation matrix analysis. To understand the processes that control the chemistry of river water, theoretical and graphical models proposed by various scientific groups/agencies were explored. The significant sources of hydrochemical constituents in the Thuthapuzha are a) weathering, b) precipitation, and c) anthropogenic activities. The overall changes in water quality of the study area can be explained in light of the natural and anthropogenic effects to which the region has been subjected over the years.

### 5.1. Piper Diagram

The chemical composition of the TRB river water is also illustrated by plotting the major cations and anions in the Piper (1944) diagram (Fig. 5).

The diamond-shaped area of the Piper diagram is divided into four major parts, each part representing and explaining a particular type of variation or domination of cations and anions. The four

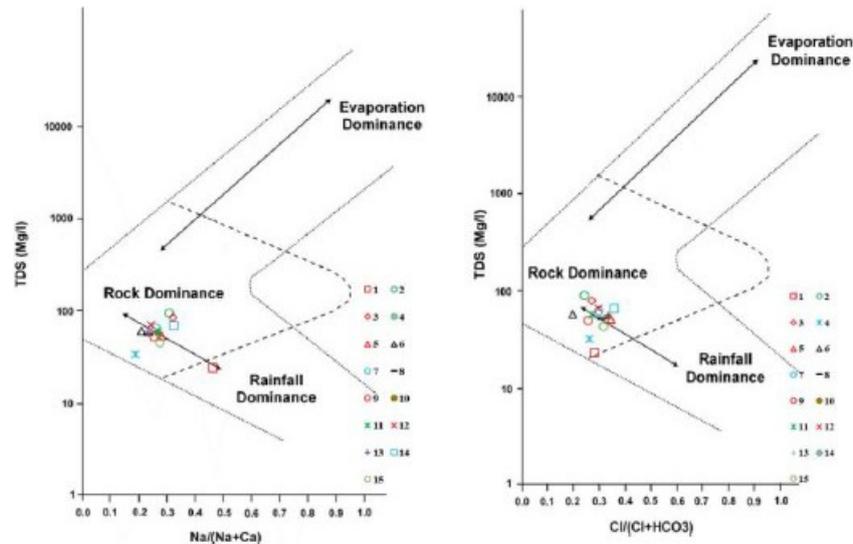


Fig. 6. Variation of the weight ratio of (a)  $\text{Na}/(\text{Na} + \text{Ca})$  and (b)  $\text{Cl}/(\text{Cl} + \text{HCO}_3)$  as a function of total dissolved salts (TDS) of the Thuthapuzha River.

parts are (1)  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-\text{-SO}_4^{2-}$ , (2)  $\text{Na}^+\text{-K}^+\text{-Cl}^-\text{-SO}_4^{2-}$ , (3)  $\text{Na}^+\text{-K}^+\text{-HCO}_3^-$  and (4)  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ . The majority of the samples of this study fall in the category (4)  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ , representing a dominance of calcium, magnesium and carbonate ions in the water (Fig. 5). The sources of this type of water may be typical shallow freshwaters (Guettaf et al., 2017).

## 5.2. Gibbs Diagram

Gibbs (1970) proposed a simple water chemistry model in which he discriminated three primary controls for the chemical composition of natural waters: (i) atmospheric precipitation dominance, (ii) soil and rock dominance, and (iii) evaporation-chemical precipitation dominance. The Gibbs plot for the Thuthapuzha river waters (Fig. 6) was drawn using the weight ratio of  $\text{Na}/(\text{Na} + \text{Ca})$  vs total dissolved solids (TDS) as well as  $\text{Cl}/(\text{Cl} + \text{HCO}_3)$  vs total dissolved solids (TDS). It is observed that in the Thuthapuzha River, both rock-water interactions and precipitation significantly alter river water chemistry. Water samples from the Thuthapuzha show TDS concentrations exceeding 30 mg/L, indicating the influence of rocks in the catchment on river water chemistry. The plots of  $\text{Na}/(\text{Na} + \text{Ca})$  and  $\text{Cl}/(\text{Cl} + \text{HCO}_3)$  against TDS reveal a marked clustering in the higher regime of the Gibbs diagram (Fig. 6), characterised by the dominance of rock weathering, except for one sample influenced by precipitation.

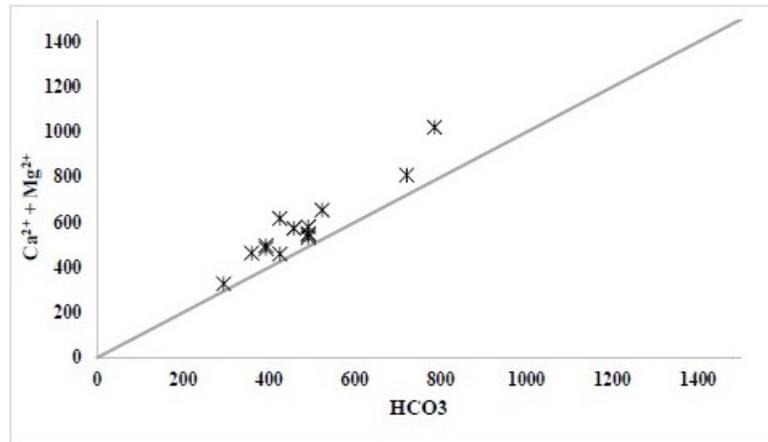
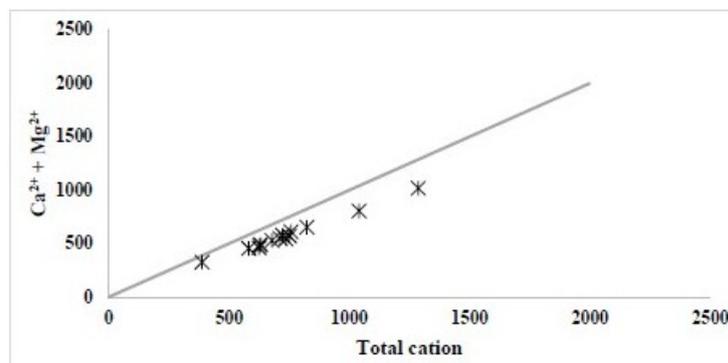
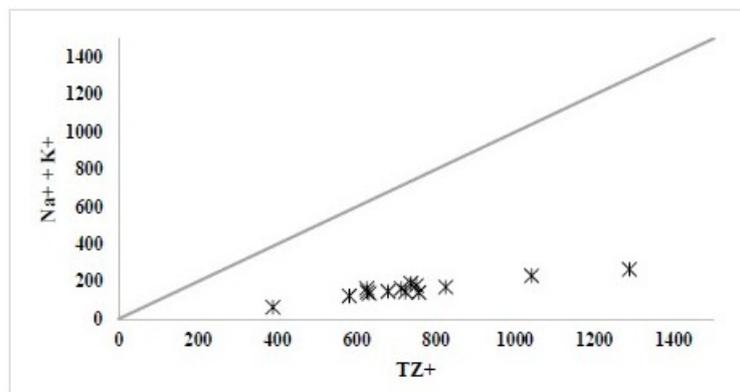
## 5.3. Plots of $\text{HCO}_3^-$ vs $\text{Ca} + \text{Mg}$ , Total cations vs $\text{Ca} + \text{Mg}$ and Total cations vs $\text{Na} + \text{K}$

A plot of  $\text{HCO}_3^-$  vs  $\text{Ca} + \text{Mg}$  was drawn (Fig. 7), indicating that the data points lie just above the equiline, suggesting that carbonate weathering could not be a major contributor of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  in the Thuthapuzha basin. Fig. 8 shows the plot of total cations vs  $(\text{Ca} + \text{Mg})$ . All the points are slightly below the equiline, indicating that, in addition to  $(\text{Ca} + \text{Mg})$ , other cations, such as Na and Mg, also strongly affect the cationic groups that determine the water chemistry. The deviation of plotted points from the equiline indicates the increasing contribution of Na and K from silicate weathering or alkaline soil. Plot of  $\text{Na}^+ + \text{K}^+$  vs TZ+ ratio (0.2-0.3), suggesting the contribution of  $\text{Na}^+$  and  $\text{K}^+$  to the dissolved ions from the weathering of silicates (Fig. 9).

## 5.4. Sediment transport

The time series analysis of the average daily discharge of the Thuthapuzha River is depicted in Fig. 10. The Pulamanthole gauging station on the Thuthapuzha River is mainly fed by the southwest monsoon. It exhibits an unimodal pattern, with peak discharges in June-August. The annual average discharge of Thuthapuzha is around 1700 MCM (million cubic meters).

The sediment (suspended and dissolved) transport of the Thuthapuzha River was calculated using the long-term discharge, sediment and major ion

Fig. 7. Scatter plots between (Ca + Mg) vs  $\text{HCO}_3^-$ .Fig. 8. Scatter plots between  $\text{TZ}^+$  vs (Ca + Mg).Fig. 9. Scatter plots between  $\text{TZ}^+$  vs (Na + K).

chemistry data from the Pulamanthole gauging station in Thuthapuzha, obtained from the Central Water Commission (CWC) via the surface water module of the India–WRIS (Water Resources Information System).

The total suspended solids (TSS) recorded at Pulamanthole station in the Thuthapuzha River showed an annual particulate content of 25 mg/l. The annual particulate sediment transport in the Thuthapuzha River is estimated at 0.088 million tonnes. At the

same time, the Thuthapuzha River showed a concentration of dissolved solids (43 mg/l) as it flows through high-gradient, forested, rocky terrain that is less susceptible to chemical weathering. The annual chemical load carried by the Thuthapuzha come to about 0.067 million tonnes.

The Particulate Load (PL) and Dissolved Load (DL) ratio has been calculated for the drainage channel in the gauging station. The PL/DL ratio of 1.31 in the Thuthapuzha River (Table 2) indicates

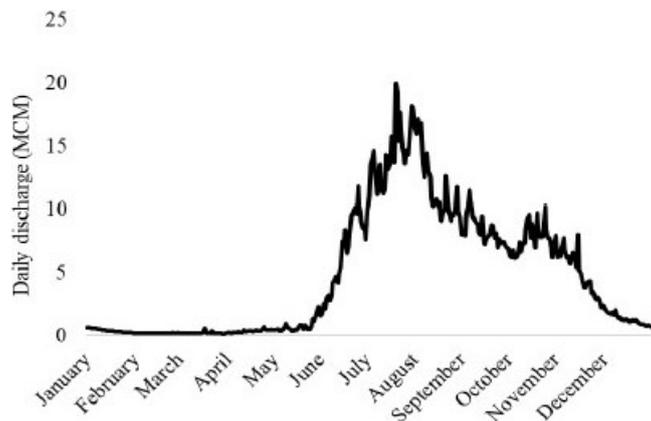


Fig. 10. Time series of the average daily discharges in the gauge station of the Thuthapuzha River for the period of 1980 to 2015.

Table 2. Comparison of sediment load of the Bharathapuzha River with that of the major rivers of India.

River	Drainage area ( $\times 103 \text{ km}^2$ )	Particulate	Sediment load ( $\times 10^6 \text{ ty}^{-1}$ )		Erosion rate ( $\text{t}/\text{km}^{-2} \text{ y}^{-1}$ )	PL/DL
			Dissolved	Total		
Thuthapuzha(a)	1.03	0.088	0.067	0.16	155.3	1.31
Bharathapuzha(b)	6.20	0.32	0.38	0.70	113.0	0.84
Cauvery(c)	88.00	0.04	3.50	3.54	40.5	0.01
Krishna(c)	251.00	4.00	10.40	14.40	57.0	0.39
Mahanadi(c)	142.00	1.90	9.60	11.50	80.9	0.19
Ganges(c)	750.00	329.00	84.00	413.00	549.0	3.90

a: Present study b: Padmalal et al. (2018); c: Subramanian and Ramanathan (1996).

Table 3. Correlation matrix for the different hydro-chemical parameters.

Variables	pH	EC	TDS	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	SiO <sub>4</sub>	NO <sub>3</sub>
pH	1											
EC	-0.125	1										
TDS	-0.138	<b>0.956</b>	1									
Ca	-0.145	<b>0.970</b>	<b>0.911</b>	1								
Mg	-0.134	<b>0.917</b>	<b>0.855</b>	<b>0.937</b>	1							
Na	-0.197	<b>0.855</b>	<b>0.818</b>	<b>0.818</b>	<b>0.887</b>	1						
K	-0.344	0.387	0.402	0.441	0.204	0.146	1					
HCO <sub>3</sub>	-0.185	<b>0.952</b>	<b>0.900</b>	<b>0.961</b>	<b>0.939</b>	<b>0.866</b>	0.350	1				
Cl	-0.049	<b>0.853</b>	<b>0.764</b>	<b>0.779</b>	<b>0.810</b>	<b>0.782</b>	0.182	<b>0.746</b>	1			
SO <sub>4</sub>	0.252	<b>0.537</b>	0.409	0.446	0.371	0.414	0.121	0.419	<b>0.747</b>	1		
SiO <sub>4</sub>	-0.424	<b>0.695</b>	<b>0.749</b>	<b>0.712</b>	<b>0.702</b>	<b>0.769</b>	0.339	<b>0.794</b>	0.453	0.059	1	
NO <sub>3</sub>	-0.294	-0.408	-0.283	-0.357	-0.482	-0.292	0.391	-0.358	<b>-0.618</b>	<b>-0.566</b>	0.023	1

the dominance of physical weathering in these high-gradient, humid terrains. Higher PL/DL ratios indicate a larger particulate fraction relative to dissolved solutes, consistent with stronger physical weathering/erosion in humid, high-relief catchments (Padmalal et al., 2018). The high-gradient terrain characteristics of the river basins, which offer only very short residence time for stream waters to interact with bedrock and for subsequent release of ions to sediment (suspended and dissolved) transport.

### 5.5. Correlation Matrix

Pearson correlation matrices were generated using XLSTAT 2016 software for the water quality parameters to evaluate relationships among the vari-

ables. The physico-chemical parameters were subjected to Pearson correlation analysis to examine the interrelationships among the various parameters of the TRB water samples (Table 3). TDS shows a robust correlation with EC ( $r = 0.956$ ). A strong correlation among EC, HCO<sub>3</sub>, Cl, Ca, Mg, Na, and K indicates that these ions dominate in the TRB. Calcium exhibits a strong positive correlation with TDS ( $r$  value: 0.911), magnesium ( $r$  value: 0.937 and bicarbonate ( $r$  value: 0.961) and a moderate positive correlation with sodium ( $r$  value: 0.818) and chloride ( $r$  value: 0.779). Magnesium exhibits very strong positive correlations with EC ( $r$  value: 0.917), bicarbonate ( $r$  value: 0.939), and Ca ( $r$  value: 0.937), and a moderate correlation with TDS ( $r$  value: 0.855) and

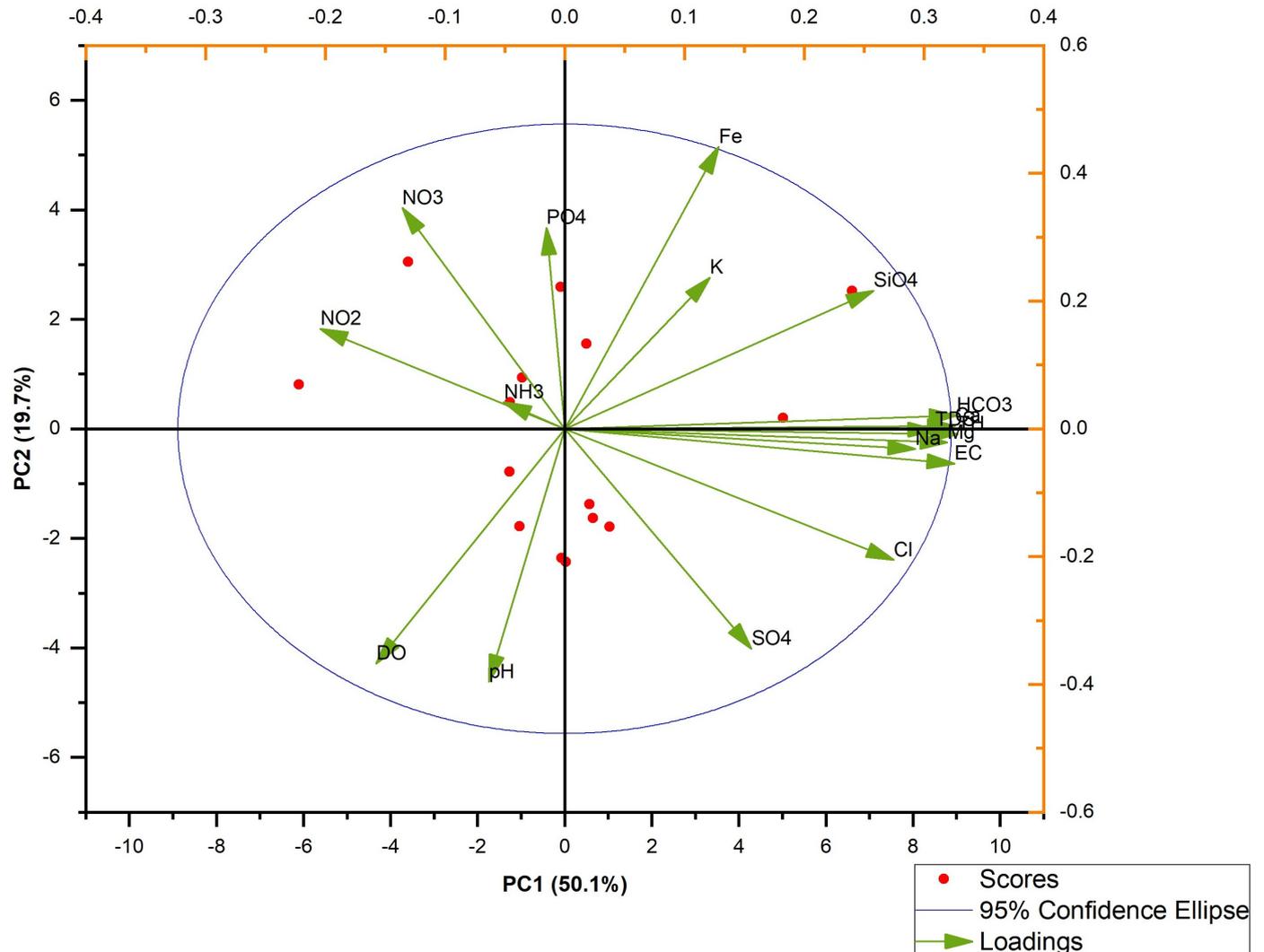


Fig. 11. PCA biplot.

Na ( $r$  value: 0.887). Sodium shows strong positive correlations with TDS, EC, Ca, Mg, and bicarbonate. Calcium, magnesium, sodium, and bicarbonate show a positive correlation with SiO<sub>4</sub>, indicating silicate weathering. This suggests that the parameters change in direct proportion to each other. Some parameters showed a fair negative correlation, suggesting they change in inverse proportion.

### 5.6. Principal Component Analysis

Principal component analysis (PCA) was applied to identify the latent factors controlling surface-water quality in the TRB. PCA was performed to classify the sources affecting stream water chemistry and address the mutual dependence among variables (Koh et al., 2009). The PCA biplot (Fig. 11) shows parameter loadings, sample scores, and a 95% confidence ellipse, with the first two components explaining 69.8%

of the total variance (PC1 = 50.1%; PC2 = 19.7%). Vector orientation and length reflect parameter influence and interrelationships, while sample clustering indicates spatial and process-based controls on river-water chemistry.

PC1 is characterized by strong positive loadings of EC, TDS, Na<sup>+</sup>, Cl<sup>-</sup>, and HCO<sub>3</sub><sup>-</sup>, indicating increasing mineralization driven mainly by silicate weathering of Precambrian crystalline rocks (charnockite, gneiss, and migmatite). Elevated EC and TDS reflect cumulative solute enrichment during prolonged water–rock interaction, while the alignment of Cl<sup>-</sup> also suggests contributions from evaporative concentration and localized anthropogenic inputs. The clustering of most samples along positive PC1 confirms silicate weathering as the dominant basin-scale geochemical process.

PC2 reflects redox-sensitive and nutrient-related processes, with positive loadings of Fe, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>,

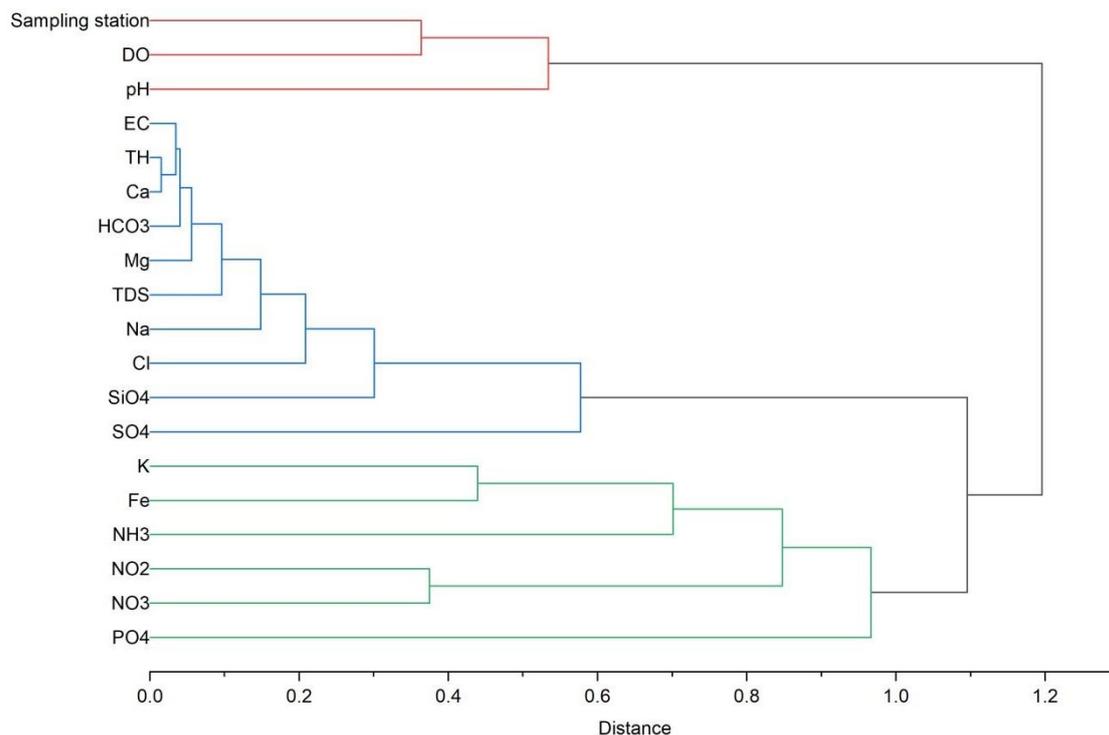


Fig. 12. HCA dendrogram.

$K^+$ , and  $SiO_4$ . The association of  $SiO_4$  and  $K^+$  indicates continued feldspar and mica weathering. In contrast, elevated Fe and its close relationship with  $PO_4^{3-}$  suggest reductive dissolution of iron oxides under sub-oxic to reducing conditions. High  $NO_3^-$  and  $K^+$  further indicate anthropogenic inputs from agriculture and domestic wastewater. Negative loadings of pH, DO, and  $SO_4^{2-}$  on PC2 imply that nutrient enrichment is due to anthropogenic input.

Overall, the PCA demonstrates that river-water chemistry in the basin is primarily controlled by silicate weathering (PC1), with secondary modification by anthropogenic nutrient inputs (PC2).

### 5.7. Hierarchical Cluster Analysis

Surface water quality data from the TRB were initially subjected to hierarchical cluster analysis to understand the geochemical characteristics better. HCA was performed on 18 hydrochemical variables. The dendrogram (Fig. 12) delineates three main clusters: geogenic mineralisation processes, redox and nutrient dynamics, and in-stream physicochemical conditions influenced by anthropogenic activity.

The first cluster groups dissolved oxygen (DO) and pH with sampling stations, indicating strong control by in-stream processes and hydrological conditions. This reflects spatial variability in river-

water chemistry primarily driven by localised anthropogenic pressures, such as domestic effluent discharge and land-use practices, rather than lithological factors alone. The second and most prominent cluster comprises EC, TDS, TH,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $HCO_3^-$ ,  $Na^+$ , Cl,  $SiO_4$ , and  $SO_4^{2-}$ , suggesting a common geogenic origin linked to water-rock interaction and mineral weathering (Belkhiri et al., 2010).  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $HCO_3^-$  are mainly derived from silicate weathering of charnockite, gneiss, and migmatite, while  $Na^+$  and  $SiO_4$  primarily originate from feldspar and mica weathering. EC and TDS reflect the overall dissolved ionic load, whereas Cl and  $SO_4^{2-}$ , although partly geogenic, may also indicate evaporative concentration and minor anthropogenic inputs. This cluster confirms the dominant influence of geology on baseline river-water chemistry and corresponds to PCA-derived PC1. The third cluster, characterised by nutrients ( $NH_3$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ),  $K^+$ , and Fe, reflects the combined effects of anthropogenic inputs and redox-controlled geochemical processes. Nutrient species are indicative of agricultural runoff, sewage discharge, and organic matter decomposition, while the association of  $PO_4^{3-}$  with Fe suggests release under reducing conditions.  $K^+$  shows mixed geogenic and anthropogenic sources, and Fe mobilisation reflects reducing micro-environments within lat-

Table 4. Comparative evaluation of observed values of the present study against various drinking water quality standards.

Sl. No	Parameters	WHO*	BIS*	ICMR*	Range of concentration (Present study)	Average
1	pH	6.5–8.5	6.5–8.5	7–8.5	6.99–8.41	7.59
2	Conductivity, $\mu\text{s}/\text{cm}$	800	800	-	30–140	88.07
3	DO, mg/l	5	5	-	5.60–9.57 mg/l	7.73
4	Alkalinity, mg/l	20	20	-	12–48 mg/l	27.55
5	Chloride, mg/l	250	250	200	4.55–15.80 mg/l	11.16
6	Sulphate, mg/l	200	200	200	0.07–0.70 mg/l	0.44
7	Hardness, mg/l	200	300	300	8.95–50.85 mg/l	27.55
8	NO <sub>2</sub> -N, $\mu\text{g}/\text{l}$	-	-	-	0.01–3.98 $\mu\text{g}/\text{l}$	1.02
9	Inorganic P, $\mu\text{g}/\text{l}$	-	-	-	3.93–22.48 $\mu\text{g}/\text{l}$	7.81
10	SiO <sub>4</sub> -Si, $\mu\text{g}/\text{l}$	-	-	-	3.87–10.30 $\mu\text{g}/\text{l}$	5.73
11	Na, mg/l	-	-	-	0.37–4.61 mg/l	2.31
12	K, mg/l	-	-	-	1.17–3.67 mg/l	2.21
13	Ca, mg/l	75	75	75	2.03–10.67 mg/l	6.36
14	Mg, mg/l	30	30	50	0.94–5.87 mg/l	2.82
15	Fe, $\mu\text{g}/\text{l}$	1	0.3	0.1	14–99 $\mu\text{g}/\text{l}$	43
16	TDS, mg/l	500	500	500	23–91 mg/l	56.33

BIS: Bureau of Indian Standards; ICMR: Indian Council of Medical Research; WHO: World Health Organization.

eritic soils, sediments, and low-flow river zones. This cluster corresponds closely to PC2, highlighting areas or periods of nutrient enrichment and potential water-quality degradation. Hierarchical cluster analysis indicates that river water chemistry is primarily governed by silicate weathering of crystalline rocks, with secondary modification by redox-sensitive nutrient dynamics and anthropogenic inputs.

## 6. Water quality assessments

### 6.1. Drinking water quality

A comparative evaluation of the observed values in the present study against various drinking water quality standards is presented in Table 4. The study found that all 15 water samples fall within the potable limit of drinking water quality standards.

## 7. Conclusions

The following are the major conclusions drawn from the present study during the pre-monsoon season. The pre-monsoon sampling is crucial because low flow and high temperatures concentrate pollutants, revealing baseline chemical contamination from dry season activities (like industrial/urban discharge, evaporation) and identifying potential health hazards (high TDS, heavy metals) before seasonal dilution by rain washes them away, helping assess long-term river health and management needs. The Thuthapuzha watershed has unique terrain characteristics and a geo-environmental setting, as it links the forested upper catchments and the populated downstream stretches. The long profile of TRB shows

that in the upper stage of a river's course, the river's gradient is steep and gradually flattens out as the river erodes towards its base level. Hydrochemical studies show that the water samples are slightly alkaline. All the other parameters are well within the prescribed limit set by WHO and BIS. Hydro-chemically, the water is suitable for drinking. The water samples fall into the Ca–HCO<sub>3</sub> type. The plots of Cl/(Cl + HCO<sub>3</sub>) against total dissolved solids (TDS) and of Na/(Na + Ca) against TDS reveal a marked clustering in the zone between atmospheric precipitation and rock dominance on the Gibbs diagram. This indicates the combined effects of precipitation and rock-water interactions in contributing to the solute load in the Thuthapuzha. Bivariate plots HCO<sub>3</sub> vs (Ca + Mg), total cations vs (Ca + Mg), and total cations vs (Na + K) point to the role of silicate weathering taking place in TRB. Further, the Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA), and Pearson correlation matrix substantiate that river water chemistry is primarily governed by silicate weathering of crystalline rocks, with secondary modification by redox-sensitive nutrient dynamics and anthropogenic inputs. The Particulate Load (PL) and Dissolved Load (DL) ratio has been calculated for the drainage channel at the gauging station to be 1.31, indicating the dominance of physical weathering in these high-gradient, humid terrains. The high-gradient terrain characteristics of the river basins, which offer only very short residence time for stream waters to interact with bedrock and for the subsequent release of ions to sediment (suspended and dissolved) transport.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

## Credit author statement

Shabna Sherin: Methodology, Data Curation, Resources, Software, Investigation, Writing - Original draft preparation. K S Arunkumar: Conceptualization, Supervision, Writing - Reviewing and Editing. Samreena Mohammed: Writing - Reviewing and Editing.

## Data Availability

The complete datasets cannot be shared publicly; however, processed data and analytical outputs used in the study are available from the corresponding author upon reasonable request.

## AI-Assistance Disclosure

No AI tool was used for data analysis, interpretation, or conclusion. All responsibility for the content rests with the authors.

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