

Multivariate water quality assessment from the Tamiraparani river basin, Southern India

P. Kumarasamy · R. Arthur James · Hans-Uwe Dahms ·
Chan-Woo Byeon · R. Ramesh

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Abstract The hydrochemistry of a perennial river has been investigated with multivariate cluster analysis (CA) and principal component analysis/factor analysis (PCA/FA). The aim was to investigate parameters responsible for spatial and temporal variations of river water quality. Water quality was monitored along the river basin at 20 different sites over a period of 1 year from July, 2008 to June, 2009. Multivariate statistics revealed that Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , H_4SiO_4 , SO_4^{2-} , NO_2^- , and PO_4^{3-} were influenced by seasonal and spatial variations and that water quality was in the first place determined more by natural weathering processes than by anthropogenic activities. We could prove by (a) Box and Whisker plot, (b) matrix scatter score mean plot, (c) ternary plot, and (d) Gibbs plot that the chemistry of river water is controlled by lithogenic weathering processes. The higher concentration of dissolved silica during summer and the

pre-monsoon season is explained by natural and tropical climatic conditions of the environment.

Keywords Tamiraparani river · Factor analysis · Box and Whisker plot · Cluster analysis · Water quality

Introduction

Rivers, ponds, and groundwater are used for domestic and agricultural purposes worldwide. Rivers play a major role in integrating and organizing the landscape and molding the ecological setting of a basin. They are the prime factors controlling the global water cycle coupled with dynamic agents of transport (Garrels et al. 1975). Rivers carry elements, in suspended or in dissolved form, from their source and deposit them subsequently at different locations based on their physicochemical nature. The suspended loads in the river can act as a sink for nutrients and other elements (Horowitz 1997; Gaur et al. 2005; Yao and Xu 2013). The quality and quantity of surface waters in a river basin is influenced by natural factors such as rainfall, temperature, and weathering of rocks as well as by anthropogenic disturbances. Rivers and streams are highly heterogeneous at spatial as well as at temporal scales and several investigators have documented this heterogeneity focusing on the physicochemical dynamics of rivers. Variation in the quality and quantity of river water was studied in several rivers worldwide (Riedel et al. 2000; Koklu et al. 2010; Akbal et al. 2011; Wan et al. 2013). These studies showed that continental weathering and erosion are major components of the exogenic cycles of elements on earth. Weathering breaks down rocks and the resulting dissolved and particulate materials are transported by rivers to the sea. Physical and chemical weathering of rocks and minerals cause the dislodgement and

P. Kumarasamy · R. Arthur James (✉)
Department of Marine Science, Bharathidasan University,
Tiruchirapalli 620024, India
e-mail: james.msbd@gmail.com; marine@bdu.ac.in

R. Arthur James · H.-U. Dahms (✉)
Green Life Science Department, College of Convergence,
Sangmyung University, 7 Hongij-dong, Jongno-gu,
Seoul 110-743, South Korea
e-mail: hansdahms@smu.ac.kr; marc436@yahoo.com

C.-W. Byeon
Department of Environmental Resources, Graduate School of
Sangmyung University, Sangmyung University, 7 Hongij-dong,
Jongno-gu, Seoul 110-743, South Korea

R. Ramesh
Institute for Ocean Management, Anna University,
Chennai 600 025, India

transport of particles. The study of dissolved and particulate components of river waters is important to characterize and quantify weathering and erosion (Krishnaswami and Singh 2005). In spite of their widely ranging role, presently, rivers are under severe threat due to various anthropogenic pressures (Singh and Singh 2007; Varol et al. 2012).

Monitoring the surface runoff of a river on a regular basis provides valuable information on the eco-hydrological conditions of a river basin. Such data provide valuable insights into spatial and temporal variation of water quality, considered as a measure of river health and reliability of water quality models and their predictability (Rode and Suhr 2007). Stallard and Edmond (1983) established the dominant role of chemical weathering of calcareous rocks in the Amazon River Basin through mass balance and solution equilibria. Meybeck (1987) emphasized the effects of silicate and carbonate weathering on water quality, in an extensive study, covering a number of large watersheds in France. Ohruhi and Mitchell (1998) showed the regulation of weathering products on water chemistry of small Japanese rivers. A comprehensive review on weathering and water quality was provided by Berner and Berner (1987) and Drever (1988) for major river basins of the world. A large number of records concerning sediment mineralogy and river erosion in the major river basins are provided by Subramanian (1987) for the Indian subcontinent. An evaluation of the Mahanadi river water chemistry has been

carried out by Chakrapani and Subramanian (1990). Ray et al. (1984) and Naidu et al. (1985) have pointed out certain limitations concerning the nature and source of sediment mineralogy reported in earlier studies by Subramanian and his co-workers. Kumarasamy et al. (2012) made biogeochemical analyses in the river studied here, the Tamiraparani river basin. However, there have been very few attempts to evaluate water quality through a comparative analysis of lithology and soil formation in Indian drainage basins. Anthropogenic activities and improper management of natural resources also led to an unequal distribution of major and minor elements (Vieira et al. 2012) and microorganisms in nature (Vignesh et al. 2013).

Multivariate statistical analyses are particularly useful since they evaluate the relative importance of combinations of chemical variables. They are used as analytical tools to reduce and organize large hydro-geochemical datasets into groups with similar characteristics. Correlation analyses are widely used in geochemistry and are useful for interpreting collected river water quality data and relating them to specific hydro-geological processes (Yerel and Ankara 2012; Shah et al. 2013). The basic purpose of such an analysis is to study the hydro-geochemistry of a system with a set of factors, which can explain a large amount of the variance of the analytical results (Ruiz et al. 1990; Kannel et al. 2007; Yidana et al. 2008; Chatterjee et al. 2010). In order to evaluate river water quality and to

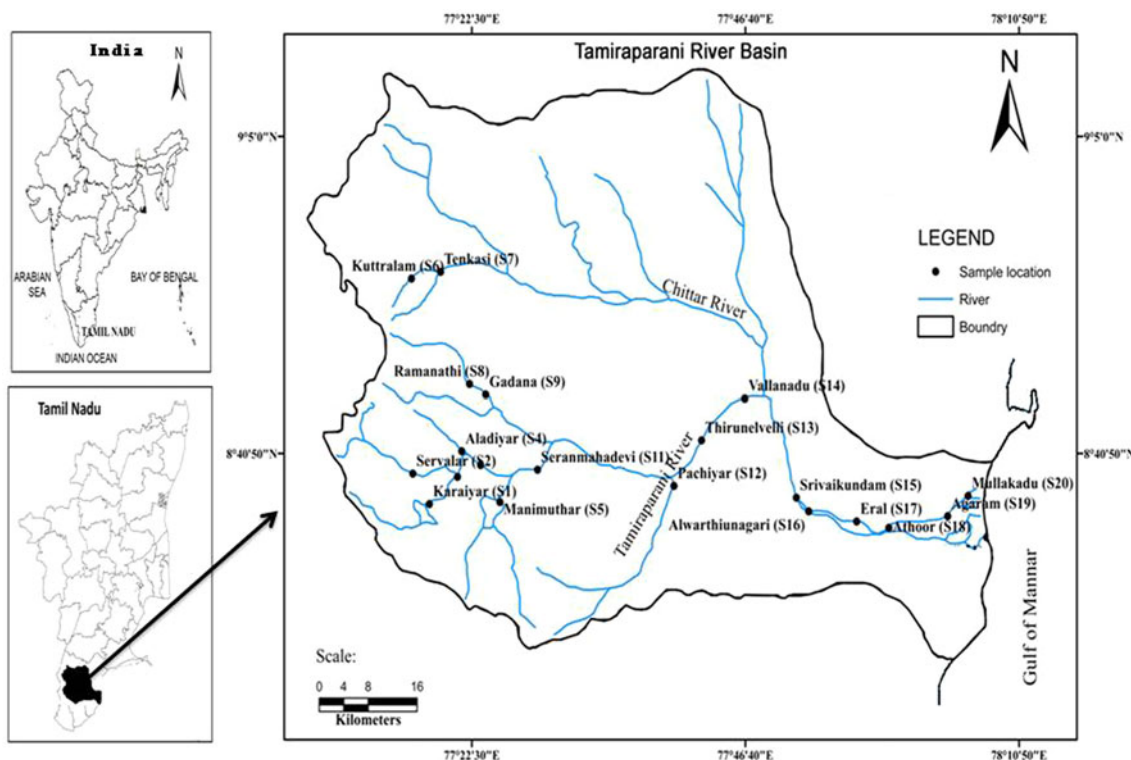


Fig. 1 Study area with sampling locations

identify the geochemical sources of diluted materials we deployed multivariate techniques to delineate the factors responsible for the Tamiraparani river basin.

Materials and methods

Study area

The Tamiraparani is a perennial river in the South of India (Fig. 1) with its basin located at 8°30' to 9°15'N latitude and

77°10' and 78°10'E longitude. The main river originates on the eastern slopes of the Western Ghats at an altitude of 2,000 m above mean sea level (MSL), travels about 125 km in the hills and plains, and drains an area of 5,869 km². The hilly slope extends only for a distance of 30 km and thereafter the land is flat and the river opens with its estuary into the Gulf of Mannar (Bay of Bengal). The southern part of the Indian subcontinent is influenced by two monsoons: the southwest and the northeast monsoons. The basin receives a rainfall of 1,100 mm during the southwest monsoon (June–September) and the northeast monsoon (October–December) and has a perennial flow

Table 1 Statistical analysis of major ions during the study period

Parameters (mg l ⁻¹)	Pre-monsoon			Monsoon		
	Minimum	Maximum	Mean ± SD	Minimum	Maximum	Mean ± SD
pH	6.3	8.5	7.46 ± 0.63	6.4	7.9	7.3 ± 0.44
TDS	111.6	522.0	278.8 ± 146.1	87.6	310.4	220.4 ± 81.4
EC (μS cm ⁻¹)	177.1	828.6	442.5 ± 231.9	139.0	493.0	342.4 ± 129.6
Ca ²⁺	4.4	38.0	15.1 ± 8.43	2.0	26.0	11.0 ± 7.9
Mg ²⁺	1.2	16.2	5.6 ± 4.4	1.2	6.0	2.7 ± 1.7
Na ⁺	1.5	89.2	30.0 ± 30.7	1.4	19.3	9.9 ± 6.6
K ⁺	1.3	34.0	8.7 ± 8.9	0.8	15.2	3.9 ± 3.9
HCO ₃ ⁻	18.9	179.3	75.3 ± 62.2	15.1	109.8	58.6 ± 32.5
H ₄ SiO ₄	2.7	18.8	12 ± 5.4	2.7	10.6	6.4 ± 1.9
Cl ⁻	8.9	109.8	44.3 ± 34.0	7.7	65.2	41.3 ± 21.0
SO ₄ ²⁻	55.2	126.0	87.9 ± 20.0	49.2	126.2	86.6 ± 22.1
NO ₂ ⁻ (μg l ⁻¹)	0.7	2.4	1.3 ± 0.6	0.3	3.5	1.3 ± 3.5
PO ₄ ³⁻ (μg l ⁻¹)	0.6	17.3	9.1 ± 6.6	0.6	16.7	8.8 ± 6.4
Ca + Mg	6.5	48.8	20.7 ± 11.4	3.2	32.0	13.7 ± 9.3
Na + K	2.8	109.0	38.1 ± 35.8	2.9	34.5	13.8 ± 9.8
Ca + Mg/Na + K	0.3	5.6	1.4 ± 1.6	0.7	2.1	1.1 ± 0.3
Parameters (mg l ⁻¹)	Post-monsoon			Summer		
	Minimum	Maximum	Mean ± SD	Minimum	Maximum	Mean ± SD
pH	6.9	7.9	7.5 ± 0.3	6.5	8.0	7.2 ± 0.5
TDS	103.0	740.0	245.3 ± 188.3	60.0	818.0	251.4 ± 253.8
EC (μS cm ⁻¹)	163.3	1174.6	389.4 ± 298.8	95.3	1298.4	399.0 ± 402.8
Ca ²⁺	2.0	34.0	8.3 ± 7.8	2.0	38.0	9.8 ± 9.1
Mg ²⁺	1.2	15.6	4.3 ± 3.8	1.2	18.0	4.1 ± 3.8
Na ⁺	1.7	168.3	23.8 ± 47.1	2.5	90.6	16.6 ± 25.6
K ⁺	0.8	32.9	5.1 ± 8.5	0.8	158.5	15.4 ± 41.2
HCO ₃ ⁻	17.8	250.1	73.0 ± 66.0	15.6	256.2	60.5 ± 60.7
H ₄ SiO ₄	0.10	5.5	1.5 ± 1.1	0.09	7.2	1.5 ± 1.5
Cl ⁻	8.9	260.5	45.9 ± 69.8	7.6	150.7	41.5 ± 42.2
SO ₄ ²⁻	62.5	115.6	83.5 ± 15.8	2.1	65.3	11.5 ± 18.1
NO ₂ ⁻ (μg l ⁻¹)	0.02	9.79	2.2 ± 2.1	1.8	47.1	7.8 ± 10.3
PO ₄ ³⁻ (μg l ⁻¹)	0.6	14.4	7.3 ± 4.9	2.1	12.4	4.8 ± 2.3
Ca + Mg	3.2	49.6	12.3 ± 11.4	3.2	56.6	13.9 ± 12.6
Na + K	3.1	187.2	28.9 ± 53.0	3.4	249.1	32.0 ± 66.0
Ca + Mg/Na + K	0.1	2.6	1.1 ± 0.6	0.1	2.2	1.1 ± 0.6

regulated through eight diversion weirs for irrigation (Ravichandran et al. 1995). The river basin is categorized as upstream (catchment areas S1–S7), midstream (urban and agricultural areas S8–S15) and downstream (estuary region S16–S20) areas which show some differences in water chemistry. The river bed contains igneous and metamorphic rock in the upper reaches, but turns sandy in the middle and lower reaches. The river has deposited extensive alluvium in the basin used for cultivation. Red soils and a mixture of red and black clay soils are the major soil types found in the basin (IWS 1988). The river water is utilized for domestic purposes and drinking water for livestock throughout its course and a water treatment plant is located near Srivaikundam at the tail end of the basin. This plant has been constructed to treat and supply 20 MLD (million liters per day) of water to the Tuticorin industrial complex and township (Ravichandran 2003). It serves as a major source of domestic, irrigation, and industrial water supplies. There are numerous small-scale industries and major industries like textile plants, paper mills, chemical industries, cement factories, etc., at various places in the basin for which the river is a perennial source.

Sampling and analytical methods

Twenty sites were selected along the riverside; the water samples were collected in 2-L pre-sterilized bottles from each location at four seasons, i.e. pre-monsoon (June to August), post-monsoon (January to February), monsoon (September to December), and summer (March to May) during 2008–2009. Measurements of pH, temperature ($^{\circ}\text{C}$), and electrical conductivity were made on the spot using a field kit (Thermo Orion 5-Star pH Multi-Meter). The samples were brought to the laboratory in an icebox and stored at 4°C until physicochemical analyses. For nutrient analysis the samples were immediately processed and analyzed within 24 h of sampling. All samples were filtered through $0.45\ \mu\text{m}$ fiber glass filters to remove suspended particles in the laboratory and then analyzed using standard methods (APHA 2005; Ramesh and Anbu 1996). The chemicals and reagents used were of AR-grade and the analytical data quality was ensured through careful standardization, procedural blank measurements, spiked, and duplicate samples. The statistical analysis was performed by Statistica-6 sigma software packages to run R-mode hierarchical cluster analysis (HCA) and factor analysis.

Results and discussion

Chemistry of river water

The quality of aquatic system is reliable indicator of the ongoing environmental changes. The physicochemical

processes are responsible for the mobility of the river-borne materials in the present day environment (Ittekkot and Subramanian 1999; Shin et al. 2013). The basic statistics of the 1-year data set on Tamiraparani river water quality are summarized in Table 1. The pH value of all water samples lies in the range of 6.3–8.5. It was slightly alkaline with average values of 7.5; 7.3; 7.5, and 7.2 in the respective seasons (pre-monsoon, monsoon, post-monsoon and summer season). The upstream region of the river water was acidic due to excessive amounts of humic and fulvic acids from plant leaves and decaying matter; the mid and downstream area was slightly alkaline in nature. The total dissolved solid (TDS) values of the downstream and estuarine stations (S17–S20) of all ions were high; especially the values of Na^+ and Cl^- were high during the summer season as compared with those of other seasons (Table 1). It is generally accepted that the solutes of river water are a result of a complex atmosphere–hydrosphere–lithosphere interaction (Raymahasay 1987; Ramanathan et al. 1994). The bicarbonate concentrations vary between 15 and 110 and 16–256 mg l^{-1} during the monsoon and the summer season, indicating that intense chemical weathering is taking place in the river basin, particularly during the summer season. Sulfate contributes $>36.3\%$ of the average chemical composition followed by bicarbonate (27 %); chloride (17.5 %) and H_4SiO_4 (1.7 %) in the river

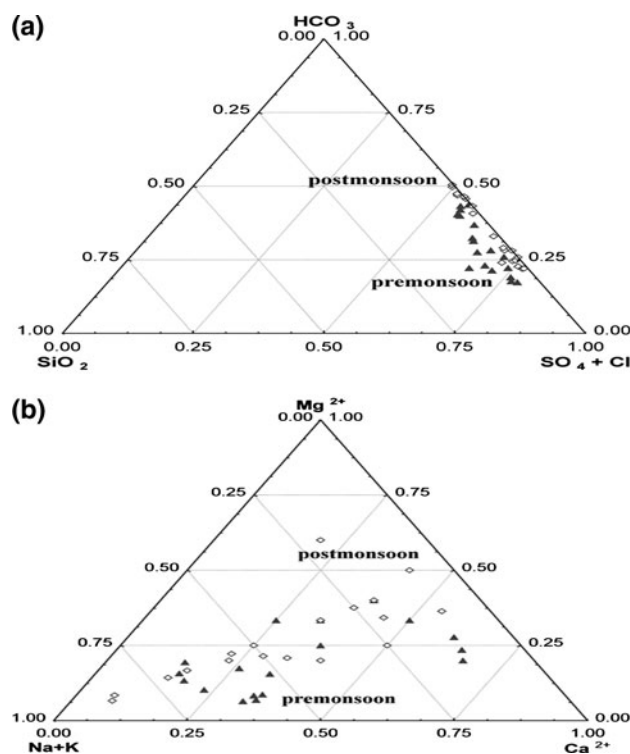


Fig. 2 Ternary plots illustrating the major ion chemistry; **a** major anion and **b** major cation during pre-monsoon and post-monsoon seasons

Table 2 Correlation coefficient matrix for water quality parameters in all four seasons ($N = 80$)

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	H ₄ SiO ₄	SO ₄ ²⁻	NO ₂ ⁻	PO ₄ ³⁻	TDS	EC	pH
Pre-monsoon													
Ca ²⁺	1.00												
Mg ²⁺	0.53	1.00											
Na ⁺	0.55	0.78	1.00										
K ⁺	0.30	0.61	0.62	1.00									
HCO ₃ ⁻	0.63	0.76	0.98	0.55	1.00								
Cl ⁻	0.64	0.75	0.97	0.55	0.99	1.00							
H ₄ SiO ₄	0.24	-0.29	-0.03	-0.15	0.00	0.02	1.00						
SO ₄ ²⁻	0.21	0.17	0.26	0.30	0.19	0.20	0.16	1.00					
NO ₂ ⁻	-0.19	-0.35	-0.66	-0.32	-0.63	-0.61	-0.25	-0.51	1.00				
PO ₄ ³⁻	0.27	0.44	0.76	0.29	0.70	0.68	0.30	0.52	-0.89	1.00			
TDS	0.66	0.77	0.98	0.62	0.98	0.98	0.05	0.36	-0.67	0.74	1.00		
EC	0.66	0.77	0.98	0.62	0.98	0.98	0.05	0.36	-0.67	0.74	1.00	1.00	
pH	0.51	0.62	0.89	0.53	0.88	0.86	0.10	0.37	-0.81	0.82	0.90	0.90	1.00
Monsoon													
Mg ²⁺	0.81	1.00											
Na ⁺	0.90	0.71	1.00										
K ⁺	0.64	0.69	0.74	1.00									
HCO ₃ ⁻	0.94	0.81	0.91	0.65	1.00								
Cl ⁻	0.80	0.72	0.85	0.67	0.91	1.00							
H ₄ SiO ₄	-0.37	-0.43	-0.35	-0.45	-0.39	-0.44	1.00						
SO ₄ ²⁻	0.31	0.05	0.38	0.08	0.43	0.60	-0.25	1.00					
NO ₂ ⁻	0.71	0.58	0.62	0.24	0.79	0.72	-0.21	0.37	1.00				
PO ₄ ³⁻	0.77	0.59	0.93	0.68	0.84	0.84	-0.37	0.44	0.63	1.00			
TDS	0.88	0.70	0.90	0.63	0.95	0.97	-0.41	0.66	0.74	0.86	1.00		
EC	0.88	0.70	0.90	0.63	0.95	0.97	-0.41	0.66	0.74	0.86	1.00	1.00	
pH	0.77	0.58	0.77	0.54	0.76	0.79	-0.54	0.57	0.45	0.69	0.82	0.82	1.00
Post-monsoon													
Mg ²⁺	0.95	1.00											
Na ⁺	0.31	0.39	1.00										
K ⁺	0.40	0.47	0.65	1.00									
HCO ₃ ⁻	0.93	0.96	0.57	0.61	1.00								
Cl ⁻	0.52	0.58	0.95	0.69	0.75	1.00							
H ₄ SiO ₄	-0.36	-0.37	-0.45	-0.41	-0.46	-0.48	1.00						
SO ₄ ²⁻	0.43	0.41	0.21	0.07	0.47	0.35	-0.32	1.00					
NO ₂ ⁻	0.83	0.81	0.16	0.15	0.77	0.37	-0.23	0.71	1.00				
PO ₄ ³⁻	0.29	0.29	0.31	0.46	0.39	0.37	-0.46	0.47	0.39	1.00			
TDS	0.71	0.76	0.87	0.71	0.89	0.96	-0.51	0.46	0.56	0.43	1.00		
EC	0.71	0.76	0.87	0.71	0.89	0.96	-0.51	0.46	0.56	0.43	1.00	1.00	
pH	0.45	0.40	0.46	0.50	0.47	0.46	-0.37	0.19	0.20	0.53	0.51	0.51	1.00
Summer													
Mg ²⁺	0.89	1.00											
Na ⁺	0.66	0.36	1.00										
K ⁺	0.49	0.19	0.95	1.00									
HCO ₃ ⁻	0.97	0.91	0.56	0.35	1.00								
Cl ⁻	0.87	0.63	0.93	0.82	0.79	1.00							
H ₄ SiO ₄	-0.35	-0.30	-0.41	-0.33	-0.36	-0.47	1.00						
SO ₄ ²⁻	0.98	0.84	0.75	0.57	0.96	0.92	-0.43	1.00					

Table 2 continued

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	H ₄ SiO ₄	SO ₄ ²⁻	NO ₂ ⁻	PO ₄ ³⁻	TDS	EC	pH
NO ₂ ⁻	0.51	0.66	-0.06	-0.15	0.54	0.17	0.11	0.41	1.00				
PO ₄ ³⁻	0.18	0.28	-0.19	-0.21	0.20	0.01	-0.09	0.13	0.18	1.00			
TDS	0.95	0.76	0.86	0.72	0.90	0.97	-0.44	0.98	0.31	0.05	1.00		
EC	0.95	0.76	0.86	0.72	0.90	0.97	-0.44	0.98	0.31	0.05	1.00	1.00	
pH	0.68	0.48	0.75	0.57	0.71	0.80	-0.63	0.79	-0.05	-0.07	0.80	0.80	1.00

Pearson’s correlation; significance level, *P* < 0.05

basin. The river basin is characterized by anions (SO₄²⁻, HCO₃⁻ and Cl⁻) and it accounts for 73.6 % of the total major ion composition. Sulfate was observed with higher concentrations, particularly at Tenkasi (S7) during post-monsoon (115 mg l⁻¹) and summer (363 mg l⁻¹), due to agricultural runoffs with fertilizer input from dual agriculture practices. Similarly, high bicarbonate concentrations observed in the same location during pre-monsoon (177 mg l⁻¹) and summer (256 mg l⁻¹) were due to an increase in the dissolution rates of soil organic matter where root respiration and oxidation of organic carbon produce higher levels of carbonic acid (Bluth and Kump 1994). Rivers with silicate weathering in their basins have the following anions present in the form of H₄SiO₄ > HCO₃⁻ + Cl⁻ + SO₄²⁻ (Zhang et al. 1990). In the present study we have a different situation. The river basin, where carbonate weathering prevails, has the characteristic feature of predominant Ca²⁺ and Mg²⁺ cations and a high (Ca + Mg):(Na + K) ratio. On a ternary anion diagram (Fig. 2a) relating SiO₂, HCO₃⁻, SO₄²⁻, and Cl⁻ most of the data clusters fall towards the alkalinity side of the field. A similar cation diagram relating to Ca²⁺, Mg²⁺, and (Na⁺ + K⁺) demonstrates that most of the data point towards the left corner of the triangle (Fig. 2b). The HCO₃⁻ concentration increases downstream during all four seasons (1.2-fold during monsoon and pre-monsoon; 1.3-fold during summer). Downstream variations of major ions have been reported for a number of other rivers (Zhang 1995; Datta and Subramanian 1998; Jonathan et al. 2012).

Chloride represents the third major anion providing about 20.2 % followed by HCO₃⁻ in the river water. Its concentration ranged from 9 to 106 mg l⁻¹ during pre-monsoon, 15–110 mg l⁻¹ during monsoon, 9–261 mg l⁻¹ during post-monsoon, and 8–152 mg l⁻¹ during the summer season. An annual average of 43 mg l⁻¹ has been observed in this study which is comparable with studies of other South Asian and world rivers. Berner and Berner (1987) estimated that 55 % of the Cl⁻ in the river was derived from weathering and the remaining 45 % was recycled through precipitation from the atmosphere. In general, a very high positive correlation of Cl⁻, TDS, and EC was observed with Ca²⁺ during all seasons (Table 2).

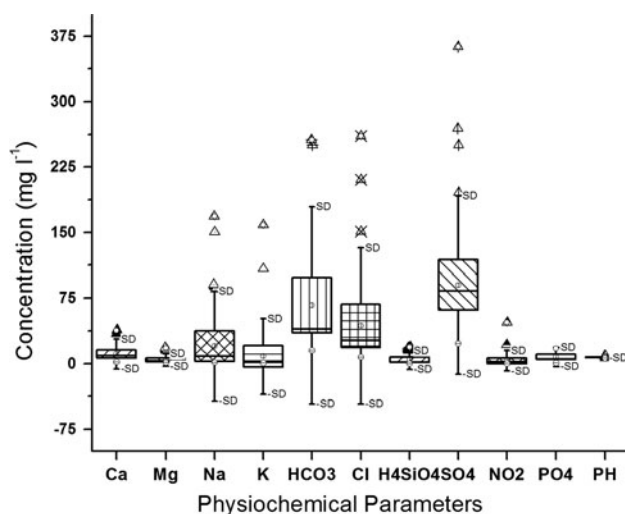
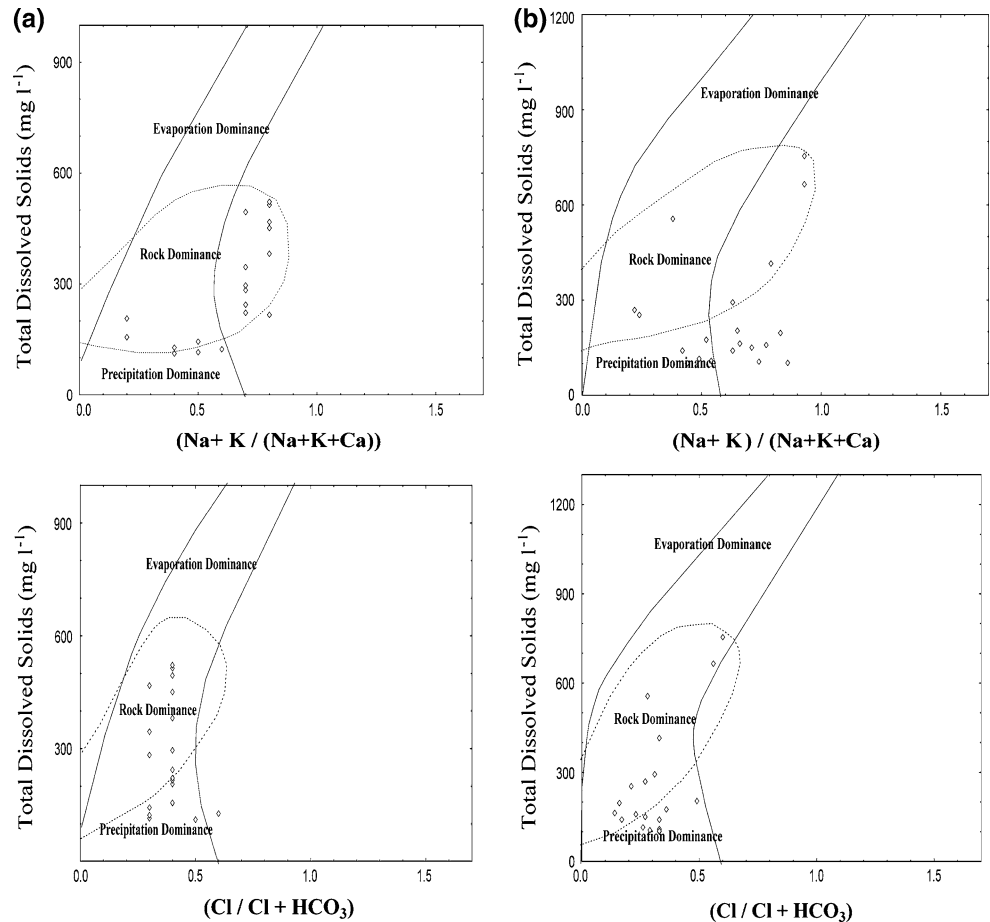


Fig. 3 Box and Whisker plot showing variations of water chemistry with average and standard deviation values

But dissolved silica show a weak negative correlation with other parameters irrespective of season presume a non-reactive element. Other nutrients like NO₂⁻ and PO₄³⁻ show moderate positive correlation with monsoon and post-monsoon seasons indicate agriculture and municipal discharge during the wet period. The box and whisker plots of the selected parameters, including four seasonal variations, are shown in Fig. 3. It indicates SO₄²⁻, Cl⁻ and HCO₃⁻ are observed as pronounced major ions. This suggests that the increase in ionic concentration is due to the drain flow in wet and evaporation process during the dry season. The total dissolved solids of the surface water was at reduced levels during the pre-monsoon and monsoon season because of heavy rains during the months of June–September, October–December in the catchment area. Heavy rainfalls during the monsoons dilute the contaminants. As for the Indian Standard (BIS 2004) on potable water, a desirable limit of hardness (300 mg l⁻¹), alkalinity (200 mg l⁻¹), chloride (250 mg l⁻¹), sulfate (200 mg l⁻¹), and total dissolved solids (1,000 mg l⁻¹) are very well fit into the Tamiraparani river water.

The concentration of dissolved silica fluctuates widely throughout the river basin. During the pre-monsoon, the

Fig. 4 Gibb's plot explaining seasonal variation with mechanism controlling water chemistry; **a** pre-monsoon and **b** post-monsoon season



concentration varies from 2.7 to 18.8 mg l⁻¹. The possible source of dissolved silica is kaolinization of silicates such as feldspar and biotite. The temperature of the river basin always exceeds 38 °C during summer, immediately followed by rainfall on southwest monsoon in the catchments areas, which enhances the weathering of the country rocks such as charnockites, granitic gneiss, calc-gneisses, calc-granulites, and quartzites resulting in high concentrations of silica (18.8 mg l⁻¹) in the pre-monsoon season. The alkaline nature of the river further enhances the solubility of amorphous silica and also the mineral–water interaction responsible for the dissolved silica concentration of the river basin (Gupta and Subramanian 1994). At earth surface temperature, quartz has a solubility of 6.5 mg l⁻¹, whereas other forms of silica have solubility up to 115 mg l⁻¹ (Garrels and Mackenzie 1971). Meybeck (1979) suggested that the dissolved silica content of river water is affected by the average temperature and geology of the basin.

An analytical study of major cations of the river has been carried out to assess the weathering processes within the basin. Calcium and potassium levels in river water are increased due to weathering processes. Calcium constitutes about 5 % of the average chemical composition and Mg²⁺

about 1.8 % of the total dissolved solids of the river basin. The Ca and Mg are probably derived from the dissolution of Kanker, limestone's, plagioclase feldspar, and other ferromagnesian minerals (Balasubramanian et al. 1985). Magnesium is derived from the hydrolysis of olivine bearing rocks in the source area. In summer, the Ca²⁺ concentration ranges from 2 to 38 mg l⁻¹ in upstream and 12 to 23.6 mg l⁻¹ in downstream. Similarly, during the pre-monsoon season the calcium concentration ranged from 4.4 to 38 mg l⁻¹ and the magnesium concentration ranged from 1.2 to 16.2 mg l⁻¹. The ratio of (Ca²⁺ + Mg²⁺):(Na⁺ + K⁺) indicated that carbonate weathering could be the primary source of the major ions in these waters. Wide seasonal and spatial variations were observed in the TDS concentration of the river basin. The ratio (>1) of (Ca²⁺ + Mg²⁺):(Na⁺ + K⁺) in the Tamiraparani river suggests that the contribution of these ions by silicate weathering was less significant. Gaillardet et al. (1997) computed Ca²⁺/Na⁺; HCO₃⁻/Na⁺ and Mg²⁺/Na⁺ ratios to differentiate between the carbonate and silicate weathering in the Amazon river basin. In the upstream region of the river basin, high values of Ca²⁺/Na⁺ (0.61–7.3) were observed by the authors when compared with the downstream region (0.07–4.48), indicating the

predominance of carbonate weathering in the catchment area.

Sodium provides a dominant cation in the river system and accounts for 9 % of the average TDS. The catchment silicate weathering and atmospheric inputs are the major sources of the Na^+ in river water. The sodium concentration is lower than chloride values from upstream to downstream for all seasons. This indicates that the atmospheric cycling and input by rain is the main source for sodium and is less influenced by physical weathering (Subramanian et al. 1987). During the pre-monsoon season, the average sodium concentration was higher (59.8 mg l^{-1}) in comparison with the monsoon season (30.2 Na^+). Potassium concentration is lower by about two times when compared with sodium during all seasons and at all stations possibly due to a lower mobility.

Gibbs diagram has three distinct fields, i.e., rock dominance, evaporation dominance, and precipitation dominance areas (Gibbs 1970). The ratio I, $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$ for anion and ratio II, $\text{Na}^+ + \text{K}^+(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ for cations in water samples were plotted separately against the respective values of total dissolved solids. Ratios I and II range from 0.14 to 0.6 and 0.22 to 0.93 during the post-monsoon, 0.31–0.55 and 0.19–0.84 during the pre-monsoon season. These patterns provide a characteristic boomerang-shaped plot, depicting the major factors operating behind the water chemistry. It can be seen that the points fall in the region of rock dominance consistently (Fig. 4a, b). This shows that the dissolution of various minerals is a prime factor affecting the water chemistry of the Tamiraparani basin. Total cations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs. $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ demonstrate that rock weathering dominates in the river basin (Fig. 5a, b). One of the unifying factors is the excellent relationship between the major parameters calcium and magnesium. All the rivers, in general, show high carbonate alkalinity independent of local lithology; rock weathering involving atmospheric CO_2 and minerals in different lithology uniformly release Ca^{2+} , Mg^{2+} and HCO_3^- to the river water (Berner and Berner 1996). The correlation between Ca^{2+} and other parameters Mg^{2+} , HCO_3^- , Cl^- , TDS, EC, pH are significantly positive, whereas Na^+ , K^+ , H_4SiO_4 , SO_4^{2-} , and PO_4^{3-} are not significant among the four seasons as shown in Table 2. In the river basin, Ca^{2+} and Mg^{2+} constitute together 36.4 % of the total cations and HCO_3^- contributes about 32.7 % to the total anionic balance. Carbonate and silicate weathering and evaporite dissolution can supply Ca^{2+} and Mg^{2+} in water, whereas the sources for Na^+ and K^+ represent atmospheric deposition, evaporite dissolution, and silicate weathering. The sodium concentration is significantly less compared with chloride and $(\text{Cl}^-/\text{Na}^+ + \text{K}^+)$ suggesting that much of the alkaline waters originated from a source other than

precipitation, probably from the weathering of silicate minerals. On an average $(\text{Na}^+ + \text{K}^+)$ contributes 63.8 % of the total cationic balance and relatively high concentrations of dissolved silica and $(\text{Na}^+ + \text{K}^+)/\text{TZ} +$ ratio (1.6) suggesting that silicate weathering could be the major source of alkalis. However, the above ratios represent an upper limit of silicate weathering, as there could be other evaporite sodium/potassium minerals and/or contributions from alkaline soil and groundwater (Subramanian 1987). The evaporite encrustations of sodium/potassium salts were developed in some part of the drainage area due to cyclic wetting and drying during high and low water levels. This commonly causes the formation of alkaline/saline soils,

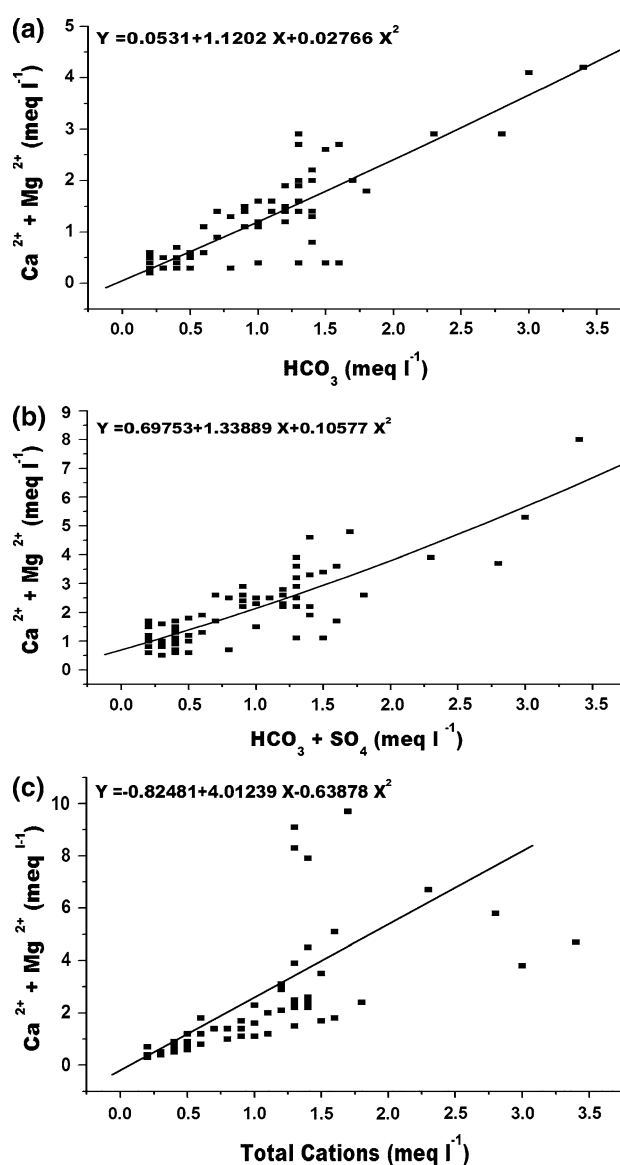


Fig. 5 Scatter plot showing analytical results with interrelationship among major ions for all four seasons

Table 3 Varimax rotated factor matrix for major ions and nutrients

Variables	Pre-monsoon				Post-monsoon			
	Communality	F-I	F-II	F-III	Communality	F-I	F-II	F-III
Ca ²⁺	0.97	0.62	0.11	-0.61	0.97	-0.85	0.37	-0.27
Mg ²⁺	0.85	0.79	0.46	0.05	0.98	0.88	0.29	-0.3
Na ⁺	0.98	0.97	0.12	-0.01	0.97	0.67	-0.62	-0.08
K ⁺	0.99	0.64	0.31	0.28	0.90	0.66	-0.54	-0.11
HCO ₃ ⁻	0.98	0.96	0.14	-0.14	0.99	0.96	0.11	-0.22
Cl ⁻	0.96	0.95	0.14	-0.16	0.99	0.82	-0.45	-0.11
H ₄ SiO ₄	0.97	0.07	-0.75	-0.55	0.99	0.58	0.29	-0.37
SO ₄ ²⁻	0.99	0.41	-0.51	0.42	0.93	0.58	-0.39	0.53
NO ₂ ⁻	0.92	-0.74	0.50	-0.25	0.96	-0.75	0.61	0.05
PO ₄ ³⁻	0.96	0.80	-0.48	0.15	0.95	-0.56	-0.12	0.66
Eigenvalue		5.54	1.67	1.06		5.55	1.75	1.11
% Total variance		55.35	16.71	10.62		55.49	17.49	11.11
Cumulative %		55.35	72.07	82.60		55.49	72.98	84.09

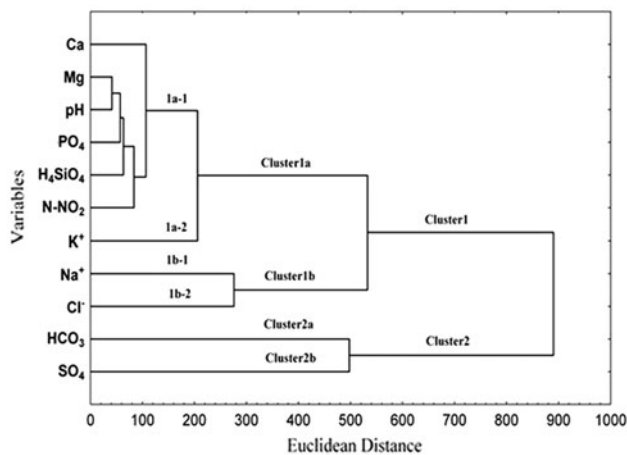


Fig. 6 Dendrogram for chemical parameters with major assemblage

which may also serve as a source of sodium and potassium (Sarin et al. 1989).

The (Ca²⁺ + Mg²⁺)/HCO₃⁻ ratio marks the upper limit of bicarbonate input from the weathering of carbonate rock (Stallard and Edmond 1983; Arunkumar et al. 2012). The variation diagram between Ca²⁺ + Mg²⁺ vs. HCO₃⁻ for reservoir water samples show that in many samples, (Ca²⁺ + Mg²⁺) contents is in excess of alkalinity which explains kanker, limestone, plagioclase feldspar, and other ferromagnesian minerals in the rock type in the catchment area, i.e., pre-monsoon (Ca²⁺ + Mg²⁺/HCO₃⁻ = 3.6) and post-monsoon (Ca²⁺ + Mg²⁺/HCO₃⁻ = 5.8). The excess of Ca²⁺ + Mg²⁺ over bicarbonate in these waters indicated some extra source of Ca²⁺ and Mg²⁺. This part of the excess positive charge has to be balanced by other anions like SO₄²⁻ and/or Cl⁻ (Fig. 5a). The excess of bicarbonate

over Ca²⁺ + Mg²⁺ requires that part of the alkalinity should be balanced by alkalis (Na⁺ + K⁺). A plot of (Ca²⁺ + Mg²⁺) versus (HCO₃⁻ + SO₄²⁻) shows a better correlation throughout the data range (Fig. 5); more than 50 % of the plotted points fall below the 1:1 equiline requiring a portion of the (HCO₃⁻ + SO₄²⁻) to be balanced by alkalis (Na⁺ + K⁺). Furthermore, the plot of (Ca²⁺ + Mg²⁺) vs total cations (TZ⁺) shows a similar trend, the departure being more pronounced at high concentrations and during lean flow periods (pre-monsoon), reflecting an increasing contribution of Na⁺ and K⁺ with increasing amounts of (Fig. 5) dissolved solids (Subramanian 1987; Yao and Xu 2013).

Factor analysis

Factor analysis is a way of classifying variables to explain the observed relationship among numerous physicochemical parameters and their sources. Principal components (PCs) are thus weighted linear combinations of the original variables (Helena et al. 2000; Wunderlin et al. 2001; Wan et al. 2013). In this study, three factors have been extracted from the principal factor matrix with 84 % variance (Table 3). The first factor accounting for 55.5 % of the total variance showed high positive loading of chloride, bicarbonate, magnesium, sodium, and potassium during the pre-monsoon and post-monsoon seasons. Thus, factor I contains natural hydro-geochemical variables which originate from sediments and influence the surface water column. The contribution of Na⁺, K⁺ and Mg²⁺ to this factor can be considered as a result of cation exchange processes at the soil water interface (Guo and Wang 2004). Balasubramanian et al. (1985) reported that dissolution of

sodium bearing minerals are found in the region as kanker, limestones, plagioclase feldspar and other ferromagnesian minerals in the rock types involved in geological weathering. The second factor accounting for 17 % of the total variance showed high negative loading of silicate and moderate positive loading of nitrite due to the fertilizer discharge from agriculture into the river basin. The third factor responsible for 11 % of variance with moderate positive loading of phosphate and sulfate can be explained by the input of house hold drain sources. Total variance of the data matrix indicated that the majority of the variables are controlled by soil/rock mediated natural processes.

Cluster analysis

Hierarchical cluster analysis is a statistical tool which gives equal weight to each variable in a multivariate analysis for data standardization and its calculated euclidean distances would be affected by the variables with greatest magnitude (Guler et al. 2002). The aim of cluster analysis is to organize the closest variables, which belong to the same cluster, whereas dissimilar objects belong to different clusters (Anderberg 1973; Everitt 1993; Karaca et al. 2000; Vieira et al. 2012). The results separate two different clusters in the river consisting of all measured values (Fig. 6). The first cluster was characterized by the high contribution of sodium and chloride, followed by other parameters such as potassium, calcium, nitrite, silicate, phosphate, magnesium, and pH. The second cluster was made by the combination of bicarbonate and sulfate, which mainly resulted from natural precipitation/weathering processes coupled with agriculture drainage which also provide a source of sulfate. Based on these cluster ordination, the Tamiraparani basin is not primarily affected by anthropogenic activities but receives its ion charge from natural weathering.

Conclusions

The dissolved major ions and inorganic nutrient concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , NO_2^- , PO_4^{3-} , and H_4SiO_4 during four seasons show that river water is less contaminated anthropogenically than by natural weathering. Statistical analysis performed here confirms that the spatial as well as temporal variation in the river water chemistry is mainly controlled by natural weathering processes. River water is shown to be suitable as a resource for drinking water and other domestic and agricultural purposes.

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