Hydrogeochemical Drivers and Processes Controlling Solute Chemistry of Two Mountain River Basins of Contrasting Climates in the Southern Western Ghats, India

Jobin Thomas, Sabu Joseph and K.P. Thrivikramji

Abstract Water samples were collected from two mountain rivers of contrasting climates, viz., humid, Muthirapuzha River Basin (MRB) and semi-arid, Pambar River Basin (PRB) during monsoon (MON), post-monsoon (POM) and pre-monsoon (PRM) seasons, and were analyzed to understand the spatio-temporal variability as well as the sources and processes controlling hydrogeochemistry. In MRB and PRB, Ca^{2+} and Mg^{2+} dominate the cations, while Cl^{-} dominates the anions in MRB and HCO_3^{-} dominates the anions in PRB. PRB shows an elevated level of ionic abundance and higher degree of mineralization, due to multiple factors such as semi-aridity, discharge dominated by groundwater, lithological variations and the influences of carbonates and soil evaporites. However, K^{+}, Cl^{-} and H_4SiO_4 are relatively higher in MRB, implying significance of both anthropogenic activities and intense silicate weathering. The $Ca^{2+} + Mg^{2+}/HCO_3^{-}$ ratios in MRB are also relatively larger than PRB, suggesting high intensity of anthropogenic influences in MRB. Downstream variation of hydrogeochemistry implies a general decreasing trend in MRB, which is attributed to dilution due to high discharge, whereas hydrogeochemistry of PRB shows an increasing downstream trend, by which, the significance of semi-arid climate of the downstream tracts of the basin is implied. Both MRB and PRB show temporal variability in hydrogeochemical attributes implying the role of monsoon rainfall determining stream water composition. The Na^{+}-normalized Ca^{2+} versus

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J. Thomas
Inter University Centre for Geospatial Information Science & Technology,
University of Kerala, Thiruvananthapuram 695 581, Kerala, India

J. Thomas (✉) · S. Joseph
Department of Environmental Sciences, University of Kerala,
Thiruvananthapuram 695 581, Kerala, India
e-mail: jobinenv@gmail.com

K.P. Thrivikramji
Department of Geology, University of Kerala, Thiruvananthapuram 695 581,
Kerala, India

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Na^+-normalized HCO_3^- plots suggest the control exercised by mixing between silicate and carbonate end members in both the basins. However, in PRB, dissolution of soil evaporites during MON and POM is evident by relatively lower Ca^{2+}/Na^+ ratios. The $Ca^{2+} + Mg^{2+}/Na^+ + K^+$ ratios in MRB and PRB during MON (mean = 1.96 and 2.23 in MRB and PRB respectively), POM (mean = 3.29 and 2.41) and PRM (mean = 5.74 and 4.40) also suggest sources other than silicate weathering. Relative enrichment of Cl^- (with respect to Na^+) indicates multiple sources for Cl^- (i.e., anthropogenic as well as atmospheric). Even though there are significant differences in water types between MRB and PRB, most of the waters of both the basins are considered to be "transitional". Relatively higher pCO_2 in stream waters (compared to atmosphere) is observed and the phenomenon is attributed to the influent nature of the stream discharge (i.e., contributed by groundwater which is significantly enriched in CO_2) and the slower rate of re-equilibration (i.e., solubility vs. release of CO_2) with atmosphere. Hence, evidently the hydrogeochemical composition of MRB and PRB is jointly controlled by weathering of silicate and carbonate minerals as well as anthropogenic activities and is influenced by climatic seasonality. The spatio-temporal variability of hydrogeochemical attributes of MRB and PRB is mainly due to the variations in climate, lithology, hydrologic pathways and degree of various anthropogenic activities.

Keywords Hydrogeochemistry · Tropical-mountain-rivers · Weathering · Muthirapuzha · Pambar · Western Ghats

1 Introduction

Rivers, one of the major components of the global water cycle, play a significant role in the geochemical cycling of elements (Garrels et al. 1975) by transporting continental weathered products (as solids and solutes) to the world oceans to regulate global seawater composition. The drainage basins of the world deliver roughly 37.4 × 10^{12} m^3 of water (Gaillardet et al. 1999) and about 20.0 × 10^9 tons of suspended sediment annually (Milliman and Syvitski 1992). On catchment-scale, various natural factors such as lithology, climate, tectonics, topography and vegetation influence weathering and thereby chemical composition of river water (Gibbs 1970; Stallard and Edmond 1981, 1983, 1987; Meybeck 1987; Drever 1988; Bricker and Jones 1995; White and Blum 1995; Hutchins et al. 1999; Jacobson et al. 2003). Among these factors, the significant role of lithology and climate was demonstrated by several researchers (e.g., Stallard and Edmond 1983, 1987; Bluth and Kump 1994; Johnson et al. 1994; Berner and Berner 1997). In uplifted orogenic belts, climate and tectonics regulate denudation and geomorphic development (Koons 1995; Whipple et al. 1999), and influence the patterns of river water chemistry and long-term geochemical cycles (e.g., Stallard and Edmond 1983; Jacobson et al. 2003). In addition, the role of anthropogenic activities (via point and non-point sources) on modification of chemical composition of river water has also been discussed by several workers (e.g., Carpenter et al. 1998; Zhang et al. 1999; Bennett et al. 2001).

Weathering of silicate and carbonate minerals (by various processes such as hydrolysis, dissociation, dissolution, oxidation and reduction) is an important determinant of river hydrogeochemistry (Bricker and Garrels 1967; Hem 1985; Edmond and Huh 1997; Gupta and Subramanian 1998; Gaillardet et al. 1999; White 2002). Silicate weathering has a crucial role in determining the chemical composition of river waters of the world, especially in the humid tropics (e.g., Harmon et al. 2009; Gurumurthy et al. 2012; Thomas et al. 2014) as the active orogenic belts and island arcs promote intensive chemical weathering in the humid tropics (Stallard 1988). It is evident from the fact that though the tropical ecosystems cover only 25 % of the Earth's land surface, they are responsible for 38 % of the dissolved ions and 65 % of the dissolved silica (Meybeck 1987).

Hydrogeochemical composition of rivers shows strong spatial- and temporal-variations. Spatial variation of hydrogeochemical attributes is generally influenced by lower-order tributaries (Meyer et al. 1988), land use (Townsend et al. 1983; Bucker et al. 2010), soil and/or geology (Meybeck 1987; Schultz et al. 1993; Stutter et al. 2006; Harmon et al. 2009; Leite et al. 2010) as well as groundwater contributions (Boulton et al. 1998, 1999; Banks et al. 2011). Even though temporal variability in river water chemistry is primarily controlled by discharge (Hem 1948; Smolders et al. 2004; Crosa et al. 2006; Ovalle et al. 2013), hydrologic pathways are also significant (Harriman et al. 1990; Wheater et al. 1990; Creed and Band 1998). According to Church (1997), the relative abundance of each of the four basic flow paths operating in streams (i.e., direct interception of precipitation, surface flow, subsurface flow and groundwater flow) also strongly depends on topography, geology, soil makeup and vegetation. In the semi-arid and arid rivers, temporal variation of discharge is remarkably high (due to clearly marked dry and wet seasons) and fluctuations of discharge may have enormous effects on the hydrogeochemistry (Allen 1995; Davies et al. 1996).

Since river water chemistry exhibits significant spatio-temporal variability, depending on the geologic environment, physical system and biotic responses, data collected from different sites of a river basin during different seasons can be used to model the possible relationships between chemical composition of the surface water and their controlling factors (e.g., Ahearn et al. 2004; Lindell et al. 2010). The studies on spatio-temporal patterns in river water chemistry are also important for sustainable management of river basins (Meyer et al. 1988; Petts and Calow 1996; Xie et al. 2013). The estimations of sources of dissolved load enable quantification of CO_2 utilization by the acid decomposition of continental rocks, which has critical implications in the context of climate change (e.g., Mortatti and Probst 2003; Jha et al. 2009; Moquet et al. 2011; Zhu et al. 2013).

Mean chemical composition of river and lake waters of the world has been the subject of discussion from the very early decades of 20th century (e.g., Clarke 1924; Conway 1942; Rodhe 1949; Livingstone 1963). However, after Garrels and Mackenzie (1971a), several river geochemistry studies have been carried out in two main and complimentary approaches, viz., small-scale studies of rivers draining uniform lithology under a given climate and studies on the world's largest rivers for a more global picture (Gaillardet et al. 1999). In addition, they also opined that the large-scale studies demonstrate the significance of lithology only and obscure the contributions from other parameters such as climate, topography etc. It is also very noteworthy that the world's largest rivers (e.g., Amazon, Congo-Zaire, Mississippi, Nile, Parana, Changjiang, Mackenzie, Ganges-Brahmaputra, Orinoco) have received greater attention due to their global significance towards water and sediment discharge (e.g., Gibbs 1967, 1970; Milliman and Meade 1983; Gaillardet et al. 1999; Mortatti and Probst 2003; Cai et al. 2008). In fact, the significance of small-mountain-rivers on global hydrological cycle remained underestimated until Milliman and Syvitski (1992), whose observations revealed that mountain rivers draining southern Asia and Oceania have much greater yields (two to three times) than rivers draining other mountainous areas of the world (and an order of magnitude greater than the rivers draining the high-Arctic and the non-alpine European mountains).

Documentation of hydrogeochemistry of rivers of India has also followed the global trends (e.g., Subramanian 1983; Abbas and Subramanian 1984; Biksham and Subramanian 1988; Bartarya 1993; Gupta and Subramanian 1994, 1998; Pandey et al. 1999; Das et al. 2005; Krishnaswami and Singh 2005; Jha et al. 2009; Gupta et al. 2011; Mehto and Chakrapani 2013). In addition, spatio-temporal patterns of hydrogeochemistry of several small rivers of the southern Western Ghats were reported by many researchers (e.g., Thrivikramaji 1989; Bajpayee and Verma 2001; Thrivikramaji and Joseph 2001; Prasad and Ramanathan 2005; Maya et al. 2007; Kannan 2009; Raj and Azeez 2009; Padmalal et al. 2012; Gurumurthy et al. 2012; Thomas et al. 2014). However, the rivers draining the rain shadow regions of the southern Western Ghats (in Kerala) have gone into oblivion as hardly any studies have been carried out in the east flowing rivers of Kerala. The smaller mountain river basins of varying climates of the southern Western Ghats amply qualify as candidates of study in the perspective of chemical weathering as tropical climates promote accelerated rock weathering and landscape denudation (Thomas 1994). Further, such information will be useful for a comparative understanding of tropical mountain watersheds of small to intermediate size and their contribution to global chemical weathering (White et al. 1998; Turner et al. 2003; Harmon et al. 2009). Hence, this paper examines the spatio-temporal patterns of chemical composition of surface water and processes controlling solute chemistry of two mountain river basins of contrasting climates (i.e., humid, Muthirapuzha River Basin, MRB and semi-arid, Pambar River Basin, PRB).

2 Study Area

Two contiguous and nearly equal-sized mountain river basins in the Anaimalai-Cardamom Hills of the southern Western Ghats, viz., MRB and PRB (N Lat. 10° 01′ 55″ and 10° 21′ 05″ and E Long. 76° 59′ 45″ and 77° 15′ 32″) were selected for

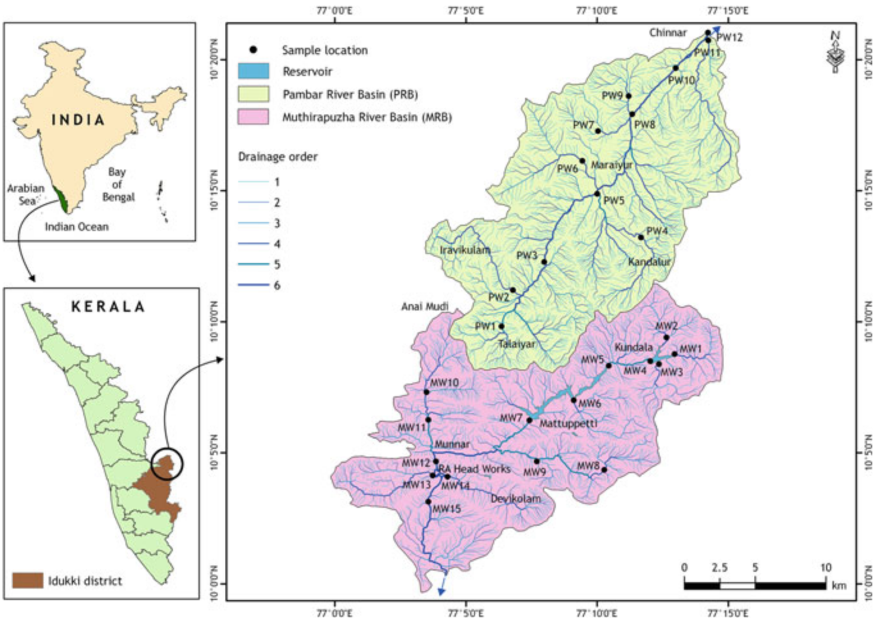

Fig. 1 Location map: stream network (from survey of India topographic maps of scale 1: 50,000) and river water sample locations of MRB and PRB

the present investigation (Fig. 1). MRB (basin order = 6; A = 271.75 km^2) is a major sub-basin of the west-flowing Periyar (the longest river of Kerala—244 km), whereas PRB (basin order = 6; A = 288.53 km^2) is a sub-basin of the east-flowing Amaravati River (a tributary of the Cauvery River). MRB is a modified hydrologic system of 14 fourth order sub-basins and three dams and reservoirs (Kundala or Setuparvatipuram, Mattuppetti and RA Head Works), whereas PRB with 18 fourth order sub-basins is devoid of dams and reservoirs with the exception of a few flow diversion structures (e.g., east of PW4 at Gokhanathapuram and immediate downstream of PW5 at Kovilkadavu). The basin elevation of MRB ranges between 2,690 and 760 m above mean sea level and that of PRB varies from 2,540 to 440 m above mean sea level. The drainage network of both MRB and PRB is influenced by the Munnar plateau, an extensive planation surface of Paleocene age (Soman 2002), which has several local planation surfaces and terrain with concordant summits at varying elevations (Thomas et al. 2012).

Due to the characteristic NNW-SSE alignment and topographic configuration (Gunnell and Radhakrishna 2001), the Western Ghats acts as a climatic barrier (Nair 2006), separating tropical humid climate of the western slopes of the Western Ghats (e.g., MRB) and semi-arid climate on the leeward side (e.g., PRB). The analysis of climatic data of this region by Thomas (2012) revealed that the mean annual rainfall (P_{ma}) of MRB was 3,700 mm (period = 1989–2009), whereas that of PRB was 1,100 mm (period = 1992–2008). Many previous studies (e.g., CESS

1984; Jose et al. 1994; Chandrashekara and Sibichan 2006) also imply that P_{ma} of the basins shows strong spatial and temporal variability. In both basins, monsoon in two different spells, i.e., southwest monsoon (June–September) and northeast monsoon (October–November), contributes major share of the annual rainfall budget. Even though southwest monsoon contributes nearly 85 % of the annual rainfall of MRB and upstream of PRB, roughly 50 % of the annual rainfall in the downstream tracts of PRB is obtained during northeast monsoon (Thomas 2012). MRB has relatively high rainfall in July (949 mm) and low rainfall in January (14 mm). In PRB, maximum rainfall occurs in July (178 mm), while minimum rainfall during February (38 mm). The mean annual temperature of MRB is 17 °C, whereas that of PRB is 26 °C. Various climate classification schemes (e.g., Koppen 1936; Trevartha 1954; Chorley et al. 1984) suggest that MRB has monsoon dominated tropical humid climate, whereas dry tropical savannah (i.e., semi-arid) climate prevails in PRB.

The basins are developed in the Madurai Granulite Block of the Precambrian Southern Granulite Terrain (in southern India). Major rock types in MRB are hornblende-biotite gneiss, granitoids (granite and granite gneiss) and calc-granulite, whereas hornblende-biotite gneiss and granite gneiss dominate PRB (Fig. 2; GSI 1992). Granite gneiss is a medium-grained, pink-colored rock and is foliated due to parallel planar arrangement of flakes of biotite, prisms of hornblende and lenticular and flattened quartz veins. Hornblende-biotite gneiss (consisting of hornblende, plagioclase, K-feldspar, quartz, clinopyroxene and biotite as major minerals and

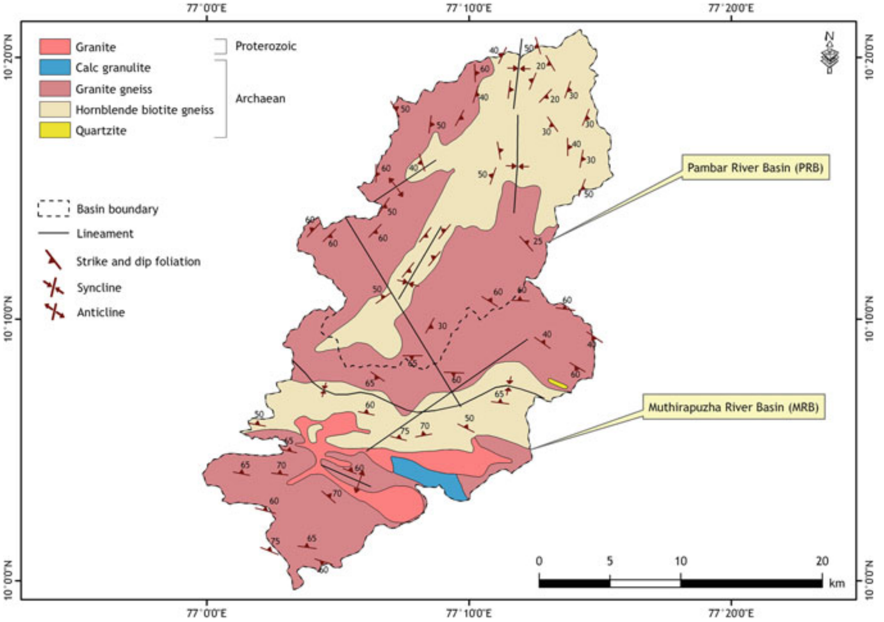

Fig. 2 Geology of MRB and PRB (after GSI 1992)

sphene, apatite, secondary calcite and opaques as the minor and accessory minerals) shows regular but alternating bands rich in quartzo-feldspathic (0.5–3.0 cm thick) and mafic (0.2–0.5 cm thick) minerals. Granite is mainly composed of K-feldspar (mostly microcline), plagioclase (albite-oligoclase) and quartz. Biotite, sphene, apatite and zircon are the accessory minerals, while magnetite is the dominant opaque (Soman 2002). Calc-granulite is a medium-grained rock, exhibiting faint layering due to the segregation of calc-silicate minerals as well as incipient development of metamorphic foliation defined by biotite and pyroxene (Thampi 1987). Pegmatite, aplite and quartzite patches as well as basic intrusives traverse the older host rocks. Nair et al. (1983) reported crystalline limestone patches and syenite-carbonatite veins in MRB. Laterite layers of varying thickness (<15 cm to $\sim$1.0 m) are also exposed at many places in MRB, while laterite layers occur only in the upstream segments, that too sparsely in PRB.

Major soil series in MRB are the Anai Mudi, Pambadumpara, and Venmani series, whereas the Anai Mudi and Chinnar series cover PRB. The soil characteristics of each soil series in MRB and PRB are given in Table 1 (after SSO 2007). MRB is covered by several natural vegetation types such as southern montane wet temperate grassland, southern montane wet temperate forest (also known as *shola* forest), southern subtropical hill forest and southern west coast evergreen forest. On the contrary, natural vegetation of PRB covers an entire spectrum ranging from southern montane wet temperate forest to dry scrubs (characteristic of the arid plains of Tamil Nadu; Nair 1991). Dominant vegetation types in PRB are southern tropical thorn forest, southern dry mixed deciduous forest, southern moist mixed deciduous forest, tropical riparian “fringing” forest, southern montane wet temperate grassland, southern montane wet temperate forest and southern subtropical hill forest (Sankar et al. 2000). The study area is renowned for the presence of sandalwood (*Santalum album*) and *Strobilanthes* sp., especially *Strobilanthes kunthianus* (which blooms en masse once in a blue moon, i.e., roughly at an interval of 12 years).

Tea (*Camellia sinensis*) and Eucalyptus (*Eucalyptus grandis*; *E. globulus*) plantations have pervaded both basins (60 % of MRB and 10 % of PRB). Besides the plantations, intensive and ubiquitous vegetable farming is practiced in the sediment fills of the interfluves in MRB and upstream of PRB. Further, cardamom plantations are predominantly distributed in the downstream of MRB. Vast areas of farmlands ($\sim$12 % of the basin area) in the central region of PRB are under sugarcane and paddy cultivation. The regional landscape has enormous tourism potential and tourist inflow is high during non-monsoon period, i.e., December–May (Department of Tourism 2008). The river basins support a human population of $\sim$0.1 million. Munnar and Devikolam (in MRB) and Maraiyur and Kandalur (in PRB) are the major towns, whereas settlement clusters (of smaller extent) are common and are associated with tea plantations in MRB and upstream of PRB.

Table 1 Soil characteristics of MRB and PRB (after SSO 2007)

Soil series	Anai Mudi	Pambadumpara	Venmani	Chinnar
	Both in MRB and PRB	MRB	MRB	PRB
Order	Ultisols	Ultisols	Inceptisols	Mollisols
Sub-order	Humults	Humults	Ustepts	Ustolls
Great group	Kandihumults	Kandihumults	Dystrustepts	Haplustolls
Sub-group	Typic Kandihumults	Ustic Kandihumults	Oxic Dystrustepts	Typic Haplustolls
Family	Clayey, mixed, isothermic	Clayey, mixed, isohyperthermic	Fine, mixed, isohyperthermic	Loamy skeletal, mixed, thermic
Extent	9° 15′–10° 29′N; 76° 56′–77° 25′E	9° 30′–10° 26′N; 76° 44′–77° 25′E	9° 27′–10° 22′N; 76° 48′–77° 11′E	10° 19′–10° 29′N; 77° 10′–77° 16′E
Pedogenesis	Gneissic parent; on steep to very steep slopes; above 1,200 m amsl	Gneissic parent; on steep to very steep slopes and hill tops; between 600–1,200 m amsl	Gneissic parent; on moderate to steep slopes; between 600–900 m amsl.	Gneissic parent; on gentle slopes of rain shadow region; between 400–900 m amsl
Colour	Dark reddish brown to dark brown (A horizon); dark reddish brown to reddish yellow (B horizon)	Dark reddish brown to dark brown (A horizon); yellowish red to red (B horizon)	Reddish brown to dark reddish brown (A horizon); reddish brown to red (B horizon)	Brown to dark greyish brown (A horizon); brown to very dark greyish brown (B horizon)
Texture	Silt loam to clay loam (A horizon); silty clay loam to clay (B horizon)	Silty clay to clay (A horizon); clay (B horizon)	Loam to clay (A horizon); gravelly sandy clay to gravelly clay (B horizon)	Sandy loam to sandy clay loam (A horizon); gravelly loamy sand to gravelly sandy loam (C horizon); presence of $CaCO_3$ nodules and mica flakes in the subsurface soil
Soil thickness	>150 cm	>180 cm	>150 cm	75–100 cm
Drainage	Well-drained	Moderately well-drained	Well-drained	Moderately well-drained
Permeability	Moderately rapid	Moderate	Moderately rapid	Moderately rapid
Productivity	High	Medium	Medium	Medium to high
Erodibility	Severe	Severe	Severe	Moderate
pH	Extremely to very strongly acidic	Extremely to very strongly acidic	Very strongly acidic	Neutral to mildly alkaline

3 Materials and Methods

River water samples from the main stream as well as major tributaries of MRB (n = 15; MW1–MW15) and PRB (n = 12; PW1–PW12) were collected in three different seasons, viz., monsoon (MON; July 2007), post-monsoon (POM; December 2007) and pre-monsoon (PRM; April 2008). The findings of this study are based on the analytical results of 45 water samples from MRB (n = 15 × 3) and 36 samples from PRB (n = 12 × 3). Water samples were collected at each sampling points, 20–30 cm below the water surface in prewashed (with dil. HCl) and labeled HDPE bottles (1.0 L). The sample bottles were pre-rinsed with water from the sampling sites before acquisition of the final sample. The samples for cation analysis were preserved by acidification with 2M HNO_3. Whatman No. 42 filter was used for the determination of total suspended solids (TSS) and the filtrate was analyzed following the standard procedures of APHA (Eaton et al. 2005).

Each sample was screened for various physico-chemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+), major anions (Cl^-, SO_4^{2-} and HCO_3^-) and dissolved silica (H_4SiO_4). The data were analyzed for spatio-temporal variations, relationships with lithology, climate, land use, etc., hydrogeochemistry of other river systems, processes that controlled the observed variability, and relative contribution of natural and anthropogenic sources.

4 Results and Discussion

4.1 Spatio-temporal Variation of Hydrogeochemistry

Charge balance error (CBE) is a good measure of quality of the hydrogeochemical data of MRB and PRB, which is estimated as Eq. (1):

$$\mathrm{CBE} = \frac{\mathrm{TZ}^+ - \mathrm{TZ}^-}{\mathrm{TZ}^+ + \mathrm{TZ}^-} \times 100 \tag{1}$$

where TZ^+ is the sum of cations and TZ^- is the sum of anions and all cations and anions are expressed in milliequivalents per liter.

According to CBE, the total dissolved cations and total dissolved anions of all the samples are well-balanced in that all the samples have normalized inorganic charge balance less than 10 %. Tables 2 and 3 provide a descriptive summary of the hydrogeochemical attributes (during the sampling seasons) of MRB and PRB. Both MRB and PRB waters are slightly acidic to slightly alkaline during all the seasons (i.e., MON: 6.99–7.52 in MRB, 6.75–7.55 in PRB; POM: 6.54–7.35 in MRB, 6.54–7.70 in PRB; PRM: 6.92–7.97 in MRB, 6.45–7.63 in PRB). Generally, river water in areas unaffected by pollution has a pH in the range between 6.50 and 8.50

Table 2 Spatio-temporal variation of hydrochemistry in MRB

Attribute	Unit	MON		POM		PRM	
		Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
pH		7.25 ± 0.17	6.99–7.52	6.93 ± 0.25	6.54–7.35	7.36 ± 0.33	6.92–7.97
EC	$\mu S\ cm^{-1}$	132.04 ± 30.03	87.62–215.62	259.33 ± 73.80	145.48–412.81	226.52 ± 50.48	151.63–359.89
TDS	$mg\ L^{-1}$	83.68 ± 18.97	59.11–135.88	165.71 ± 47.24	93.86–264.73	143.75 ± 32.22	95.90–228.96
TSS	$mg\ L^{-1}$	12.21 ± 2.41	9.20–18.43	13.08 ± 2.50	9.84–20.86	12.12 ± 3.75	8.55–24.69
TH	$mg\ L^{-1}$	29.60 ± 12.45	16.00–64.00	54.93 ± 14.30	36.00–80.00	55.47 ± 12.91	40.00–80.00
TA	$mg\ L^{-1}$	26.67 ± 9.03	12.00–48.00	56.00 ± 23.52	24.00–112.00	43.47 ± 15.99	24.00–92.00
Ca^{2+}	$\mu eq\ L^{-1}$	352.56 ± 174.30	167.66–839.32	570.76 ± 196.05	252.00–923.15	604.36 ± 177.28	335.83–1007.48
Mg^{2+}	$\mu eq\ L^{-1}$	240.03 ± 174.48	51.82–630.11	529.37 ± 155.84	369.35–847.28	506.23 ± 134.75	292.85–770.78
Na^{+}	$\mu eq\ L^{-1}$	261.15 ± 127.88	134.42–576.38	310.01 ± 120.89	194.88–608.13	160.98 ± 62.56	65.69–317.99
K^{+}	$\mu eq\ L^{-1}$	57.40 ± 18.37	31.71–92.56	54.21 ± 25.18	25.83–99.47	59.68 ± 20.41	29.15–92.56
Cl^{-}	$\mu eq\ L^{-1}$	549.55 ± 120.51	400.30–880.43	1339.54 ± 341.68	728.66–1840.42	1178.91 ± 242.78	800.32–1600.35
SO_4^{2-}	$\mu eq\ L^{-1}$	61.46 ± 49.38	3.33–173.64	80.16 ± 50.51	19.99–213.82	92.65 ± 48.15	33.31–213.82
HCO_3^{-}	$\mu eq\ L^{-1}$	533.22 ± 180.54	239.95–959.80	1119.76 ± 470.28	479.90–2239.53	869.15 ± 319.74	479.90–1839.61
H_4SiO_4	$\mu eq\ L^{-1}$	140.01 ± 50.10	77.00–239.73	210.40 ± 66.49	114.04–324.22	187.18 ± 55.57	116.95–302.99

MON monsoon, *POM* post-monsoon, *PRM* pre-monsoon, *SD* standard deviation, *EC* electrical conductivity, *TDS* total dissolved solids, *TSS* total suspended solids, *TH* total hardness, *TA* total alkalinity

Table 3 Spatio-temporal variation of hydrochemistry in PRB

Attribute	Unit	MON		POM		PRM	
		Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
pH		7.20 ± 0.23	6.75–7.55	7.11 ± 0.34	6.54–7.70	7.15 ± 0.31	6.45–7.63
EC	$\mu S\ cm^{-1}$	146.97 ± 66.38	70.09–322.48	275.28 ± 133.10	165.89–620.98	290.08 ± 192.20	136.94–855.12
TDS	$mg\ L^{-1}$	92.89 ± 42.01	46.51–204.18	175.34 ± 83.89	104.45–394.18	185.53 ± 120.98	88.35–540.07
TSS	$mg\ L^{-1}$	12.65 ± 3.11	8.04–18.48	16.25 ± 5.40	10.81–28.43	15.04 ± 5.34	9.49–26.52
TH	$mg\ L^{-1}$	36.00 ± 19.60	16.00–76.00	54.00 ± 20.07	32.00–104.00	65.67 ± 24.63	40.00–136.00
TA	$mg\ L^{-1}$	37.00 ± 19.23	16.00–88.00	68.67 ± 36.42	40.00–160.00	70.00 ± 55.75	28.00–232.00
Ca^{2+}	$\mu eq\ L^{-1}$	300.81 ± 115.70	167.66–503.49	524.53 ± 196.46	335.83–1091.31	622.46 ± 200.79	335.83–1091.31
Mg^{2+}	$\mu eq\ L^{-1}$	420.49 ± 362.41	60.05–1272.56	556.97 ± 255.52	292.85–991.23	692.77 ± 316.93	457.37–1633.68
Na^{+}	$\mu eq\ L^{-1}$	349.49 ± 325.72	54.38–1131.44	584.86 ± 571.15	90.92–2210.24	440.69 ± 533.90	62.64–2002.74
K^{+}	$\mu eq\ L^{-1}$	44.75 ± 11.09	30.94–69.55	51.10 ± 15.60	27.62–76.45	48.41 ± 21.77	15.09–100.75
Cl^{-}	$\mu eq\ L^{-1}$	373.52 ± 92.40	240.07–560.25	1073.63 ± 347.04	640.08–1840.42	1147.28 ± 494.68	720.20–2564.57
SO_4^{2-}	$\mu eq\ L^{-1}$	71.01 ± 49.32	3.33–143.66	88.52 ± 49.27	13.32–160.31	135.89 ± 63.02	40.18–237.14
HCO_3^{-}	$\mu eq\ L^{-1}$	739.84 ± 384.53	319.93–1759.63	1373.04 ± 728.15	799.83–3199.33	1399.71 ± 1114.82	559.88–4639.03
H_4SiO_4	$\mu eq\ L^{-1}$	121.43 ± 43.31	56.19–193.53	144.66 ± 65.23	64.51–282.18	149.90 ± 57.15	64.51–254.71

MON monsoon, *POM* post-monsoon, *PRM* pre-monsoon, *SD* standard deviation, *EC* electrical conductivity, *TDS* total dissolved solids, *TSS* total suspended solids, *TH* total hardness, *TA* total alkalinity

(Hem 1985) and these mountain rivers are no exception. In both basins, EC, an effective measure of dissolved ionic strength, shows relatively larger values during POM (mean = 259.33 ± 73.80 μS cm^{-1} in MRB; 275.28 ± 133.10 μS cm^{-1} in PRB) and PRM (mean = 226.52 ± 50.48 μS cm^{-1} in MRB and 290.08 ± 192.20 μS cm^{-1} in PRB), compared to MON (mean = 132.04 ± 30.03 and 146.97 ± 66.38 μS cm^{-1} respectively in MRB and PRB). Similarly, MON samples register lower values for the total dissolved ions in both MRB and PRB, whereas POM and PRM record comparatively higher values (Tables 2 and 3). Mean TDS of MRB during MON, POM and PRM is 83.68 ± 18.97 mg L^{-1} (range = 59.11–135.88 mg L^{-1}), 165.71 ± 47.24 mg L^{-1} (range = 93.86–264.73 mg L^{-1}) and 143.75 ± 32.22 mg L^{-1} (range = 95.90–228.96 mg L^{-1}) respectively. In PRB, mean TDS is 92.89 ± 42.01 mg L^{-1} (range = 46.51–204.18 mg L^{-1}) during MON, 175.34 ± 83.89 mg L^{-1} (range = 104.45–394.18 mg L^{-1}) during POM and 185.53 ± 120.98 mg L^{-1} (range = 88.35–540.07 mg L^{-1}) during PRM. According to Gaillardet et al. (1999), most of the rivers of the world have TDS less than 500 mg L^{-1}, while the exceptions are representatives of either pollution or semi-arid and arid climate. Stallard and Edmond (1983, 1987) stated that relatively high concentrations of TDS in river water imply weathering of evaporites, while waters with low TDS characterize weathering of silicates. In comparison with other rivers draining the Western Ghats (e.g., Achankovil, 54.0 mg L^{-1}, Prasad and Ramanathan 2005; Netravati, 38.0 mg L^{-1}, Gurumurthy et al. 2012; upstream of Krishna, 112.0 mg L^{-1}; west-flowing rivers of the Deccan Traps, 82.0 mg L^{-1}, Das et al. 2005), mean TDS values of MRB and PRB are relatively higher, which might be due to the differences in basin size, climate, discharge, lithology and the intensity of anthropogenic interferences.

When compared to MRB, PRB shows an elevated level of ionic abundance (Fig. 3) and hence a higher degree of mineralization, which might be due to semi-arid climate and the contribution of carbonates and evaporites occurring in the soil and shallow regolith (see Table 1). Even though lithology of MRB and PRB is similar, the mainstream of PRB (i.e., Pambar) prefers the terrain underlain by weaker hornblende biotite gneiss, sandwiched between granite gneiss to the NW and SE (Fig. 2). In addition, the areal extent of hornblende biotite gneiss is also relatively larger in PRB, compared to MRB. Hence, the higher dissolved flux of PRB might also be a result of the differences in lithology between the basins. For example, basins underlain by mafic rocks have relatively high ion flux rates compared to basins underlain by felsic rocks (Meybeck 1987). However, in contrast to the general trend, ions such as K^+, Cl^- and H_4SiO_4 show relatively higher concentrations in MRB during all the sampling seasons, implying significance of agriculture- and tourism-related activities (i.e., K^+, Cl^-) as well as intense chemical weathering of silicate minerals (i.e., H_4SiO_4) in the tropical humid climate. Unlike major cations and anions derived from multiple sources (i.e., lithologic, atmospheric, biologic and anthropogenic), H_4SiO_4 is predominantly derived from the dissolution of primary silicate minerals (Eq. 2).

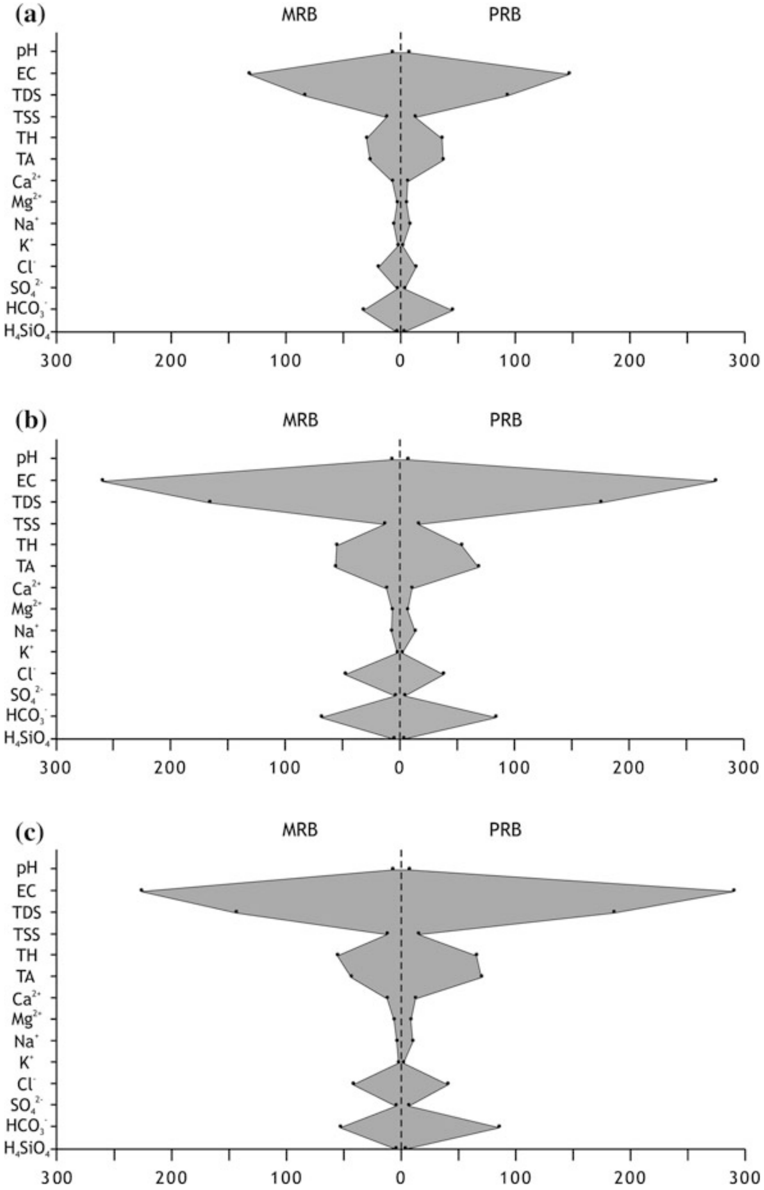

Fig. 3 Comparison of hydrogeochemistry between MRB and PRB during **a** MON, **b** POM and **c** PRM. All units in mg L^{-1} except EC (μS cm^{-1}) and pH

$$\mathrm{(Na, K, Ca, Mg)Silicate} + H_2CO_3 \rightarrow H_4SiO_4 + HCO_3^- + Na^+ + K^+ + Ca^{2+} + Mg^{2+} + \mathrm{Solids} \quad (2)$$

Further, the riverine silica is mainly controlled by the natural processes which contribute approximately 80 % of annual silica load into the ocean (Treguer et al. 1995), whereas anthropogenic and atmospheric sources have only negligible contributions (Berner and Berner 1996; Nixon 2003). Hence, the spatial variability of H_4SiO_4 in PRB is mainly attributed to the difference in climate between upstream and downstream tracts, while in MRB local factors (e.g., soil moisture, reservoirs) might have decisive roles.

An inter-basin comparison of the downstream variation of hydrogeochemical attributes implies a general decrease in the attributes of water samples in MRB (Fig. 4), whereas the opposite is true in PRB, i.e., an increasing downstream trend for attributes (Fig. 5). In addition, hydrogeochemical attributes generally vary consistently within the specific zones of mainstream (i.e., upstream, midstream and downstream) of MRB and PRB. The commonly observed downstream trends are (a) a pronounced rise or fall of dissolved load towards downstream, (b) a consistent concentration gradient through the upstream zone that is considerably different and

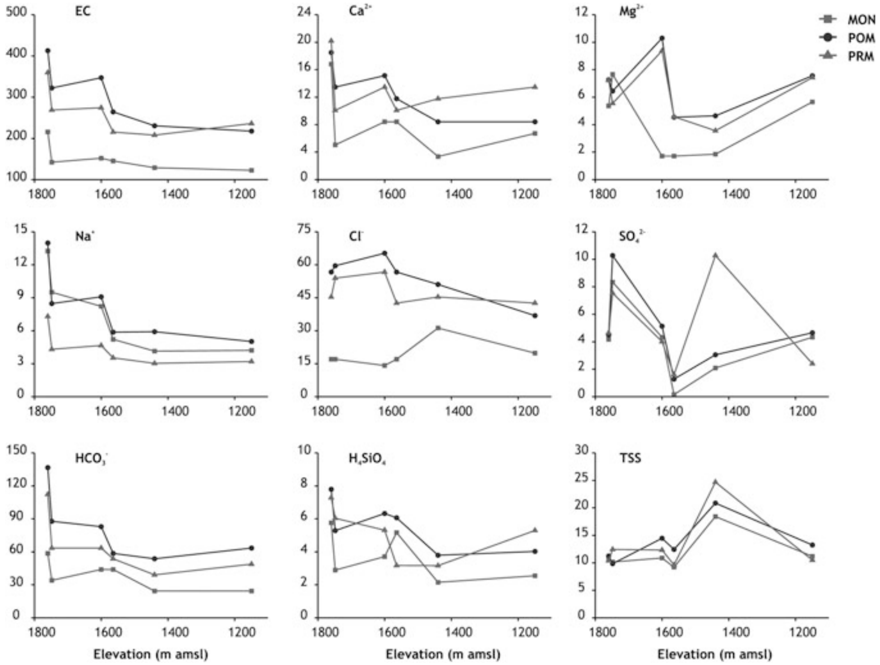

Fig. 4 Downstream variation of hydrogeochemistry, MRB. All units in mg L^{-1} except EC (μS cm^{-1}) and pH

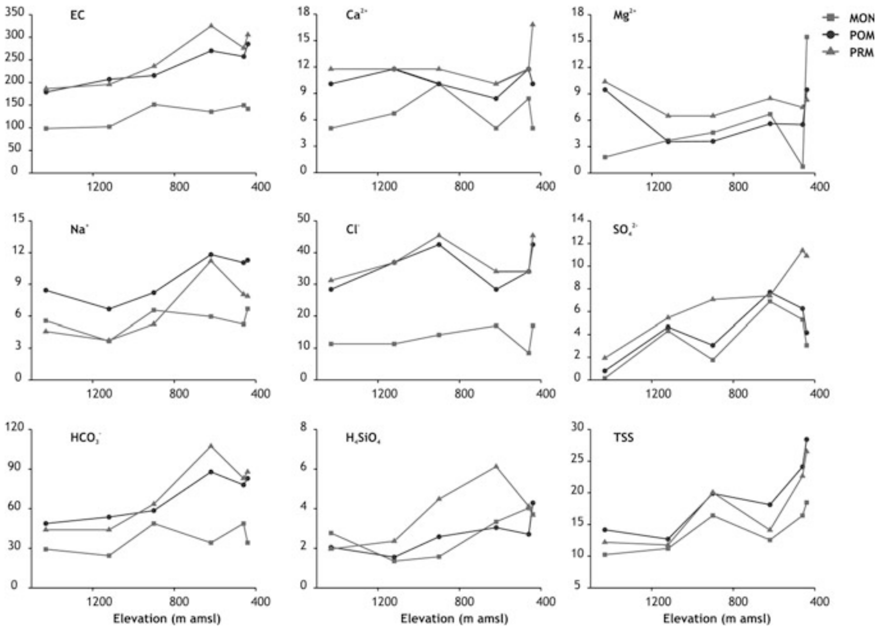

Fig. 5 Downstream variation of hydrogeochemistry, PRB. All units in mg L^{-1} except EC (μS cm^{-1}) and pH

sometimes opposite to that of downstream and (c) a trend reversal during some sampling periods, suggesting highly complex spatio-temporal relationships between hydrogeochemical attributes and their determinant factors.

In MRB, the decreasing downstream trend of hydrogeochemistry is mainly attributed to dilution due to rise in discharge. Such dilution is reported by Mortatti (1995). He had studied the relationships between the concentrations of the major dissolved ions and the river discharge in the lower Amazon and reported the decreasing patterns, similar to the theoretical dilution curves defined by Probst (1992). However, TSS shows a reversal of trend in MRB (i.e., increases toward downstream; Fig. 4) with sudden drops at MW7 (elevation = 1,564 m amsl) and MW15 (elevation = 1,149 m amsl). The increasing trend of TSS is possibly a result of logging and related activities in plantations as well as erosion from hillslopes, which add to the TSS load in the streams. However, the stations (MW7 and MW15) are located at the immediate downstream of Mattuppetti dam (i.e., MW7) and RA Head Works (i.e., MW15) respectively and the sudden drop of TSS in these stations can be a result of damming whereby the reservoirs effectively subtracted a bulk of TSS. Milliman and Mead (1983) pointed out that suspended sediment loads normally transported to the oceans by Colorado River were reduced to nearly nothing and in Mississippi River by one third due to the construction of dams.

From Fig. 4, it is also evident that only EC, Na^+ and HCO_3^- show a more or less discernible downstream decrease in MRB. But other attributes exhibit interim variations in their downstream trend (e.g., Mg^{2+}, H_4SiO_4), which might be a reflection of the contributions by the tributaries. Contrastingly, in PRB, an overall increasing trend of dissolved constituents is obvious (Fig. 5), which is chiefly due to the differing rainfall conditions between the upstream and downstream segments. In other words, the influx of highly "mineralized" water (i.e., with higher dissolved constituents) from the semi-arid downstream segment of PRB plays a significant role in enriching the dissolved load.

In PRB, samples from PW9 and PW11 in two downstream tributaries of Pambar (viz., Alampatti *odai* and Atti *odai*) do exhibit relatively higher solute levels, compared to rest of the sampling stations and in all the sampling periods. These streams drain the dry deciduous forests of Chinnar Wildlife Sanctuary, which is practically devoid of any anthropogenic activities with the exception of a few tribal settlements. Hence, these tributaries (PW9 and PW11) are considered as "hot spots" (Parkin 1987; Hill et al. 2000), which by definition is a specific form of spatial heterogeneity due to higher biogeochemical reaction rates. McClain et al. (2003) also described biogeochemical hot spots as areas (or patches) that show disproportionately high reaction rates relative to the surrounding area (or matrix).

Generally, discharge in the rivers draining the southern Western Ghats during monsoon is predominantly contributed by rainfall as well as surface runoff and recharges the groundwater reservoir (i.e., effluent rivers). But, the flow in these rivers during non-monsoon season is mainly contributed by the groundwater system (i.e., influent rivers). Hence, the relatively lower levels of various hydrogeochemical attributes measured on MON samples (Tables 2 and 3) can be directly related to dilution due to heavy monsoon rainfall (i.e., 1,146 mm during July, 2007), leading to higher water discharge, during the sampling period. However, the higher ionic content during the dry summer season is a reflection of combined contribution from aquifers and anthropogenic activities (e.g., agricultural and tourism-related). Hence, the temporal variability of hydrogeochemistry in MRB and PRB can also be attributed to the changes in hydrologic pathways between the sampling seasons. Christophersen et al. (1990), Wheater et al. (1990) and Neal et al. (1992) suggested that the rapid changes in water chemistry in upland regions are predominantly a result of changing flow paths during hydrologic events. Hence stream water may be considered to be consisting of two or more end members of differing chemistries, the proportions of which change with discharge. Mortatti and Probst (2003) documented that the seasonality in stream water chemistry is a signature of silicate weathering processes, which are highly dependent on the fluctuations in runoff. Rice and Bricker (1995) also demonstrated that there are strong seasonal cycles in the water chemistry resulting from seasonal hydrologic processes superimposed on geologically controlled groundwater compositions. Hence, the temporal variability of hydrogeochemistry can be attributed to the variation in rainfall (and thereby discharge), changes in hydrologic pathways as well as intensity of various anthropogenic activities.

Broadly, cation abundance in MRB has the following order during the sampling seasons, i.e., $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ (MON), $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ (POM and PRM). In PRB, the order of abundance of cations is $Mg^{2+} > Na^{+} > Ca^{2+} > K^{+}$,

$Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ in MON, POM and PRM respectively. In PRB, the dominance of Mg^{2+} over Ca^{2+} might be a reflection of chemical weathering of ferromagnesian minerals of the basement rocks. Relatively lower levels of K^+, compared to Na^+, suggest conservative behavior of K^+ in river systems (Garrels and Mackenzie 1971b). Moreover, in MRB, the K^+ content is only about one-fifth of the Na^+, whereas in PRB, it is roughly one-tenth of Na^+. Such behavior of Na^+ in natural systems may be explained by its tendency to remain in solution compared to K^+, which shows strong affinity for reincorporation in the (solid) weathering products (Hem 1985). The anion abundance in MRB is $Cl^- > HCO_3^- > SO_4^{2-}$ in all the three seasons, but in PRB it is $HCO_3^- > Cl^- > SO_4^{2-}$. In MRB and PRB, the temporal variation of major cations and anions closely reflects the pattern of EC.

4.2 Hydrogeochemical Drivers

The bivariate plot of weight ratio of $Na^+/(Na^+ + Ca^{2+})$ versus TDS suggesting major natural mechanisms controlling surface water chemistry (after Gibbs 1970), provides significant information on the relative importance of climate and lithology in three different perspectives, i.e., (a) climate via atmospheric precipitation, (b) rock weathering and (c) climate via evaporation and fractional crystallization. The hydrogeochemical data of MRB and PRB on Gibbs (1970) plot (Fig. 6) clearly demonstrate the significance of rock weathering and mineral dissolution controlling chemical composition of the river waters. In comparison with other rivers of India, hydrogeochemistry of MRB is similar to the headwaters of Krishna River as well as the small west-flowing rivers draining the Deccan Traps (Das et al. 2005), whereas the PRB data show better similarity with Godavari (Jha et al. 2009), one of the east-flowing rivers of Peninsular India.

While the MRB data (during all the seasons) are clustered in the zone of rock dominance (Fig. 6), the PRB data fall along a line trending from the rock dominance zone (i.e., upstream samples) towards the zone of evaporation-crystallization dominance (i.e., downstream samples). This can be a result of the semi-arid climate prevailing in the downstream of PRB, where evaporation is significant in raising the TDS. In PRB, TDS of the downstream samples reaches up to 550 mg L^{-1} and such elevated TDS values emphasize the importance of weathering of silicates as well as dissolution of carbonates and soil evaporites. Gupta et al. (2011), in their hydrogeochemical study of Narmada River in western India, reported relatively high TDS values and inferred weathering of carbonate/saline–alkaline minerals as the reason for such a phenomenon.

The Na^+-normalized Ca^{2+} versus Na^+-normalized HCO_3^- plot (Fig. 7; after Gaillardet et al. 1999) of MRB and PRB shows that most of the samples occur outside the domain of silicate weathering, yet the sample poles align parallel to the trend line between silicate and carbonate weathering domains, which can be inferred as possible mixing between silicate and carbonate end members. Even

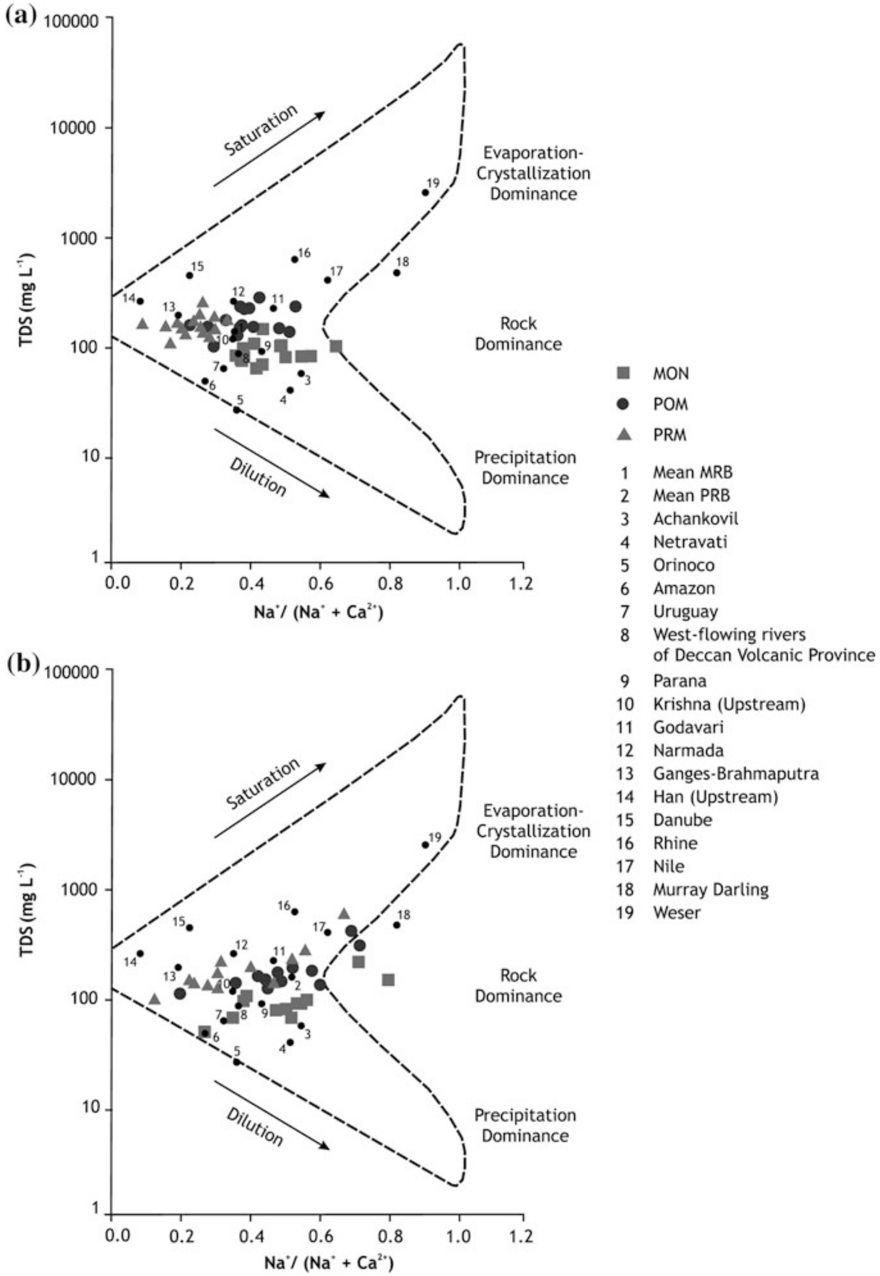

Fig. 6 Gibbs (1970) plot of **a** MRB and **b** PRB. Comparison of hydrogeochemistry data from Galy and France-Lanord (1999), Gaillardet et al. (1999), Mortatti and Probst (2003), Das et al. (2005), Prasad and Ramanathan (2005), Li and Zhang (2008), Jha et al. (2009), Gupta et al. (2011) and Gurumurthy et al. (2012)

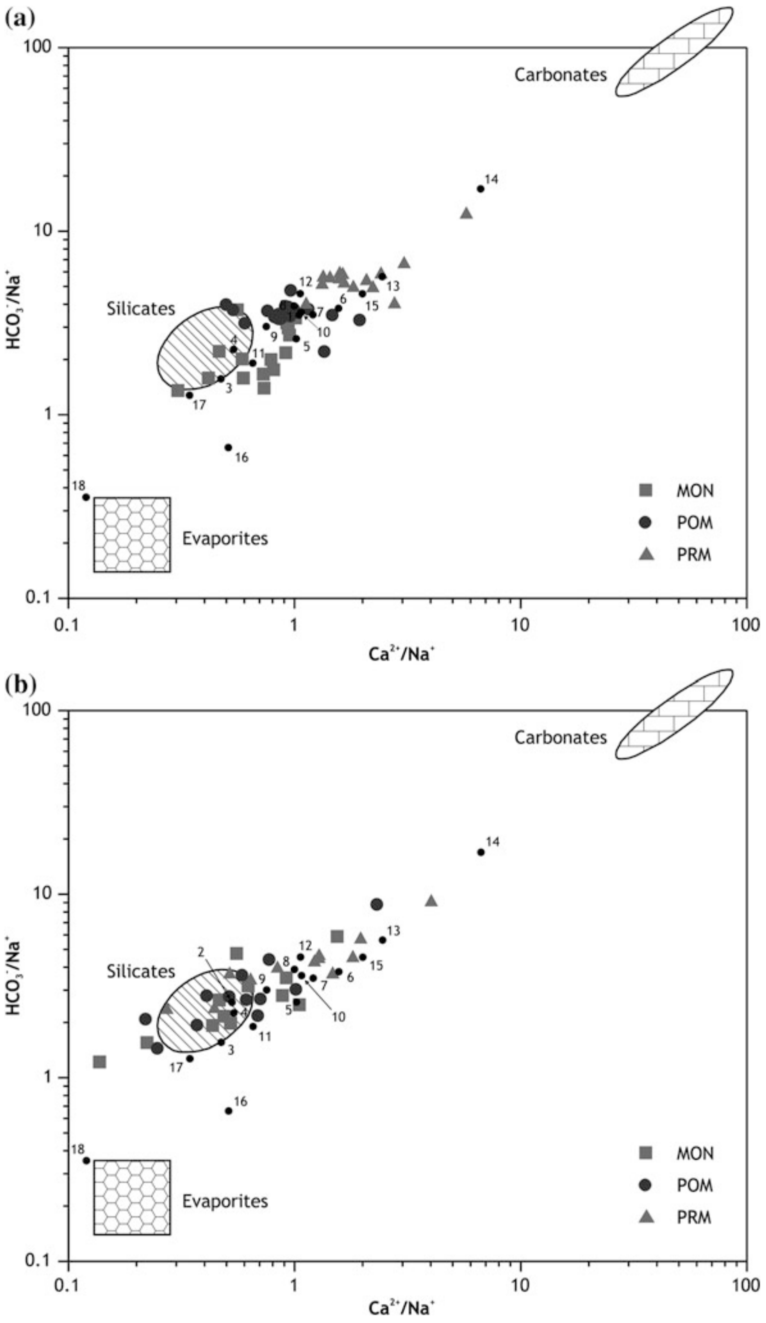

Fig. 7 Mixing diagrams (after Gaillardet et al. 1999) using Na^+-normalized Ca^{2+} versus Na^+-normalized HCO_3^- of **a** MRB and **b** PRB. The numeric river codes are same as Fig. 6

though silicate rocks dominate MRB and PRB, carbonate sources (e.g., crystalline limestone, carbonatite, kankar nodules) also co-exist in the basins (see Sect. 2). In spite of relatively minor occurrences, the carbonate minerals weather in orders of magnitude faster than Ca-Mg silicate minerals (Gaillardet et al. 1999). In addition, preferential weathering of Ca- and Mg-rich silicate minerals as well as contribution from secondary calcite can also have significance in such mixing pattern in MRB and PRB. Dessert et al. (2003) and Gupta et al. (2011) observed similar trends for the rivers draining the basaltic terrains in India. Gupta et al. (2011) opined that weathering of calcite disseminated in silicates would be limited by the degree of their exposure; nonetheless, high rate of sediment erosion coupled with monsoon climate is bound to enhance the calcite dissolution (Gupta and Chakrapani 2005). In addition, an overall linearity is observed between molar ratios of Na^+-normalized Ca^{2+} versus Na^+-normalized HCO_3^- for PRB during all the seasons (Fig. 7). However, in MRB, the sample poles are more scattered. In comparison with other rivers of India, mean of MRB plots beside upstream of Krishna River and west-flowing rivers of the Deccan Traps, while mean of PRB plots with Netravati and Godavari rivers.

In MRB and PRB, $Ca^{2+} + Mg^{2+}/Na^+ + K^+$ ratios for MON (mean = 1.96 and 2.23 in MRB and PRB respectively; Table 4), POM (mean = 3.29 and 2.41) and PRM (mean = 5.74 and 4.40), also suggest sources other than silicate weathering, e.g., carbonate dissolution, anthropogenic (domestic and farm/plantation residues) inputs etc. In both the basins, relatively lower ratios of $Ca^{2+} + Mg^{2+}/Na^+ + K^+$ in MON (in comparison with POM and PRM) can be attributed to the higher overland flow and resultant addition of Na^+ and K^+ from the terrestrial anthropogenic sources. The $H_4SiO_4/(Na^+ + K^+)$ ratio is also a proxy related to the intensity of silicate weathering (Edmond et al. 1995) and the mean ratios during MON, POM and PRM for MRB and PRB are 0.48 and 0.42, 0.59 and 0.30 and 0.92 and 0.46 respectively (Table 4), suggesting additional sources of Na^+ and K^+ other than silicate weathering. This observation affirms the inference of additional anthropogenic sources of Na^+ and K^+. In comparison with MRB, PRB has relatively smaller ratios during all the seasons, which might be due to relatively lower rate of silicate weathering (and hence lower H_4SiO_4) in semi-arid climate. In PRB, due to semi-aridity, the contribution of Na^+ and K^+ by soil evaporites can also be a factor for relatively lower $H_4SiO_4/(Na^+ + K^+)$ ratios. Further, contribution by dissolution of soil evaporites in PRB (during MON and POM) is also evidenced by relatively lower Ca^{2+}/Na^+ ratios (Fig. 6; e.g., semi-arid, downstream samples, PW9, PW11).

Relatively higher Mg^{2+}/Ca^{2+} ratios (i.e., >0.50; Table 4) in MRB and PRB suggest the contribution of Mg^{2+} from weathering of ferromagnesian minerals such as hornblende and biotite in the basement rocks (Fig. 2). When compared to MRB (i.e., 0.82, 1.02 and 0.89 in MON, POM and PRM respectively; Table 4), the PRB has relatively larger ratios during all the sampling seasons (i.e., 1.50, 1.09 and 1.12 in MON, POM and PRM respectively), which can be attributed to the relatively larger areal extent of hornblende-biotite-gneiss in PRB. Meybeck (1987) suggested that ion flux rates from basins underlain by amphibolites (mafic) are approximately five times greater than watersheds underlain by granitic (felsic) rocks and the same

Table 4 Various ionic ratios used in the present study of MRB and PRB

Ionic ratio	MRB						PRB					
	MON		POM		PRM		MON		POM		PRM	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
[a]$Ca^{2+} + Mg^{2+}/Na^{+} + K^{+}$	1.96	1.10–3.43	3.29	1.60–6.74	5.74	2.66–15.20	2.23	1.07–4.64	2.41	0.91–6.76	4.40	1.32–12.36
[a]$H_4SiO_4/Na^{+} + K^{+}$	0.48	0.24–0.82	0.59	0.45–0.85	0.92	0.63–2.34	0.42	0.14–0.81	0.30	0.12–0.60	0.46	0.10–0.83
[a]Mg^{2+}/Ca^{2+}	0.82	0.09–2.50	1.02	0.53–1.86	0.89	0.50–1.63	1.50	0.14–5.05	1.09	0.50–1.87	1.12	0.81–1.50
[b]Ca^{2+}/Mg^{2+}	2.67	0.40–11.33	1.13	0.54–1.90	1.25	0.61–2.01	1.43	0.20–6.99	1.06	0.54–2.01	0.94	0.67–1.23
[a]$Ca^{2+} + Mg^{2+}/HCO_3^{-}$	1.19	0.57–2.34	1.12	0.48–2.50	1.37	0.87–2.50	1.07	0.44–2.72	0.86	0.60–1.60	1.16	0.59–2.00
[a]Ca^{2+}/SO_4^{2-}	26.60	1.45–125.98	9.64	3.14–22.04	8.30	2.75–15.44	15.20	1.75–75.65	10.33	2.58–31.49	5.59	2.48–14.62
[a]$HCO_3^{-}/HCO_3^{-} + SO_4^{2-}$	0.90	0.73–1.00	0.93	0.85–0.98	0.90	0.75–0.96	0.91	0.80–0.99	0.94	0.87–0.98	0.90	0.85–0.96

MON monsoon, *POM* post-monsoon, *PRM* pre-monsoon

[a] Ratios derived from μeq values

[b] Ratios derived from μmolar concentrations

may hold true for the dominance of Mg^{2+} in PRB. In addition, Stallard and Edmond (1983), Meybeck (1987) and Bluth and Kump (1994) also underscored the well-established dependency of bedrock weathering rates on basin lithology. The mean Ca^{2+}/Mg^{2+} molar concentrations for the andesites/greenstones, diorites, gabbros and granites are 1.20, 1.18, 1.32 and 3.44 respectively (Harmon et al. 2009). Both in MRB (except during MON) and PRB, mean values of Ca^{2+}/Mg^{2+} molar ratios range from 0.94 to 1.43 (Table 4), which are far below the global average, i.e., 2.40, (Harmon et al. 2009). Even though, both MRB and PRB have granitoids, existences of relatively lower ratios might be the result of weathering of Mg-rich minerals. This is further supported by the relatively higher molar ratios of Ca^{2+}/Mg^{2+} in MRB (compared to PRB), where granitoids (granite and granite gneiss) are the main lithologic types. In addition, Ca^{2+}/Mg^{2+} ratios nearing unity (~ 1.0) may also reflect near congruent dissolution of Mg- and Ca-rich minerals (Harmon et al. 2009). The molar ratios of MRB and PRB are also comparable with several rivers draining the Western Ghats (Prasad and Ramanathan 2005; Das et al. 2005; Gurumurthy et al. 2012), e.g., Achankovil (1.37), Netravati (1.40), Bhima (1.26), upstream of Krishna (1.57), and west-flowing rivers in the Deccan traps (1.30).

The major contributions of SO_4^{2-} in surface water are from dissolution of gypsum, oxidation of pyrite, pollution, volcanism, rainout of natural biogenic emissions and cyclic salts (Berner and Berner 1996). However, in MRB and PRB, most of the SO_4^{2-} in the water samples might be derived from the fertilizers (e.g., ammonium sulphate) applied in the farmlands. $Ca^{2+} + Mg^{2+}/HCO_3^-$ ratio provides significant information on the importance of pyrite oxidation and gypsum dissolution relative to weathering reactions involving carbonic acid (Moon et al. 2007). In MRB and PRB, $Ca^{2+} + Mg^{2+}/HCO_3^-$ ratios (except POM in PRB) are greater than 1.0 (Table 4), indicating that a small proportion of the divalent cations is balanced by anions other than HCO_3^- (i.e., predominantly Cl^-). Such an enrichment of Ca^{2+} and Mg^{2+} in MRB and PRB results when weathering and anthropogenic contributions (e.g., fertilizers) co-occur. A comparison of PRB with MRB suggests that $Ca^{2+} + Mg^{2+}/HCO_3^-$ ratios of all the sampling seasons in PRB are relatively smaller (Table 4), suggesting lesser intensity of anthropogenic activities in the catchment. According to Moon et al. (2007), weathering of carbonates or Ca-Mg-silicates by sulfuric acid also results in an excess of Ca^{2+} and Mg^{2+} over HCO_3. Even though gypsum dissolution and acid hydrolysis coupled with sulphide oxidation may also increase $Ca^{2+} + Mg^{2+}/HCO_3^-$ ratio (Fairchild et al. 1994; Hodson et al. 2002; Moon et al. 2007), their contributions are comparably lesser in these basins. This is further confirmed by the higher Ca^{2+}/SO_4^{2-} ratios (Table 4) in all the three sampling seasons, indicating the supply of protons to enable chemical weathering predominantly by H_2CO_3 (Stallard and Edmond 1987). The ratio of HCO_3^- to $HCO_3^- + SO_4^{2-}$ is also used to characterize the relative importance of two major proton-producing reactions: carbonization and oxidation of sulfides (Prasad and Ramanathan 2005). The ratios of HCO_3^- to $HCO_3^- + SO_4^{2-}$ in MRB and PRB (Table 4) are also closer to unity, suggesting carbonization reaction involving dissolution and acid hydrolysis, which draws protons from atmospheric sources.

Anthropogenic signatures in hydrogeochemistry of MRB and PRB are evident in the bivariate plot of Na^+ versus Cl^- (Fig. 8), in which the data poles plot above 1:1 equiline implying an enrichment of Cl^-. Higher molar ratios between Cl^- and Na^+ (>1.0) indicate multiple sources for these ions such that Cl^- is predominantly from anthropogenic activities, while Na^+ is from weathering. However, supply of these ions from atmospheric deposition (e.g., rainfall, aerosols) as well as dissolution of soil salts might also have significance. Peters and Ratcliffe (1998) suggested supply of Cl^- from rainwater and then concentration by evaporation within the shallow soil horizon. Trace level of Cl^- (for OH^-) in amphibole minerals in the rocks is also a minor natural source (Buell and Peters 1988). Gaillardet et al. (1999) explained such Cl^- enrichment and Na^+ depletion (in Indian rivers) either as a result of pollution or presence of alkali soils (in semi-arid and arid zones) where minerals such as $NaHCO_3$, Na_2CO_3 and $CaCO_3$ precipitate. This might be true for the semi-arid zones of PRB as Chinnar soil series in semi-arid segment is slightly alkaline (Table 1), but enrichment of Cl^- in humid MRB could be from anthropogenic sources. Further, it is also evident that MRB has relatively higher ratios during all the seasons compared to PRB (Fig. 8), implying relatively larger contribution of Cl^- as a result of intense anthropogenic activities. Even though anthropogenic interferences are common to both basins, the intensity is relatively higher in MRB, compared to PRB. This is further supported by Jenkins et al. (1995), who reported comparatively higher concentrations of acid anions (e.g., Cl^- and SO_4^{2-}) in stream water draining agricultural catchments of Himalayas as a result of mineral fertilizer inputs as well as from greater water use for irrigation and, therefore, potentially increased evapotranspiration losses that would increase the concentration of Cl^-, which is considered as conservative.

4.3 Characterization of Water Types

The use of major ions as natural tracers (Back 1961) is a common method to delineate generic water types (or hydrogeochemical facies). The evolution of hydrogeochemical composition of samples of MRB and PRB can be explained by plotting the major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (HCO_3^-, SO_4^{2-} and Cl^-) in the Piper (1944) diagram (Fig. 9). In the diagram, grouping of water types is based on the hydrogeochemical similarities and the hydrogeochemical relationships are presented in more precise terms (Walton 1970; Todd 2001), which is useful for exploring trends that provide insights into various processes (Hem 1985). Harvey et al. (2002) suggested that Piper diagrams show the effects of various factors, including major ion composition of possible source waters as well as the proportions of mixing between the source waters in samples.

In both MRB and PRB, during all sampling seasons, dominant cation facies are principally mixed type or ‘no dominant type’. But, dominant anion facies of MRB is Cl^- type, while that of PRB is HCO_3^- type. In Fig. 9, sample poles of PRB are scattered on either sides of the HCO_3-Cl line, while MRB samples fall above the

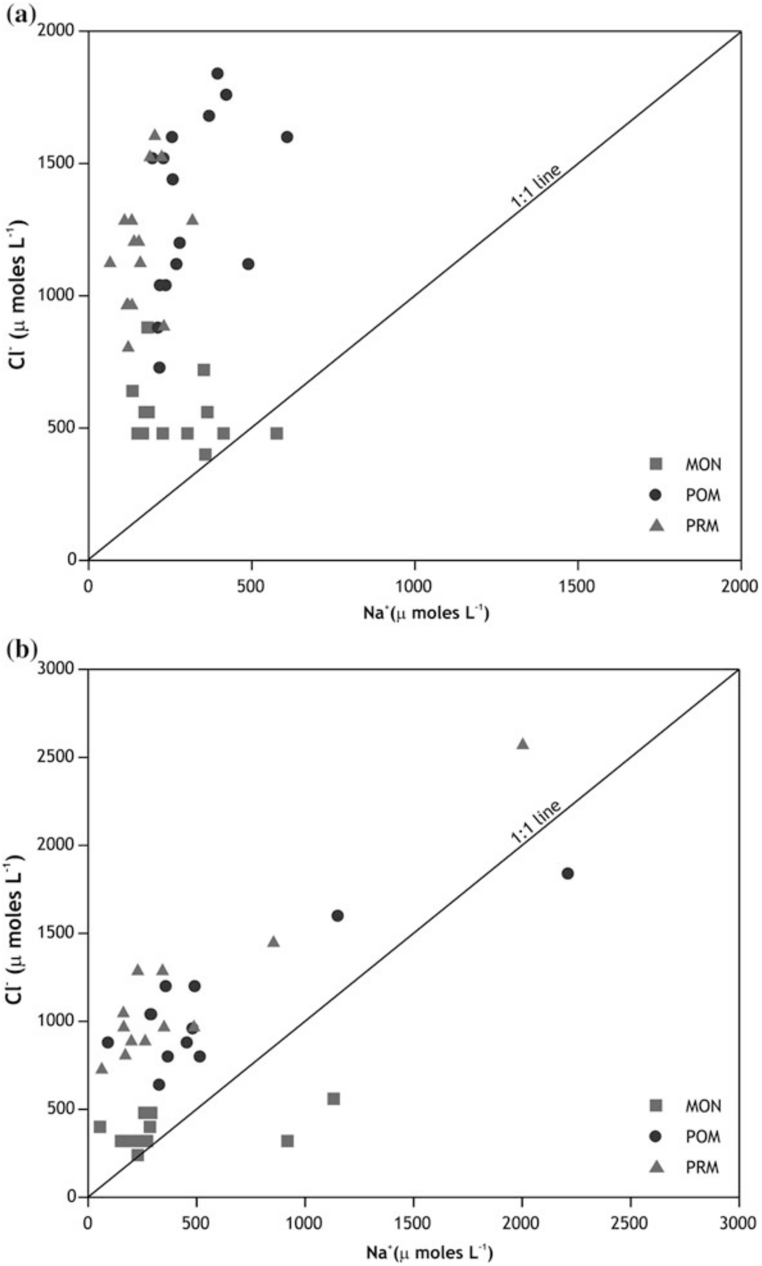

Fig. 8 Bivariate plot of Na^+ versus Cl^- of **a** MRB and **b** PRB

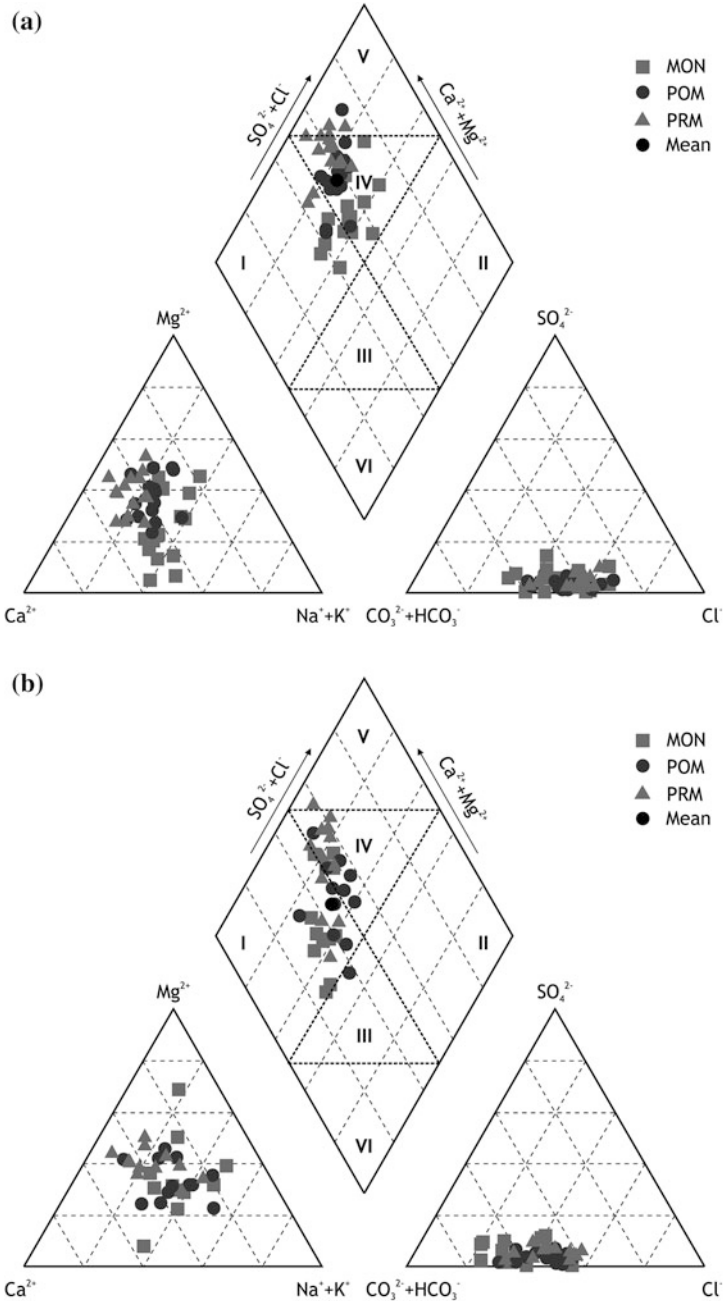

Fig. 9 Piper (1944) diagram of **a** MRB and **b** PRB

line, suggesting the dominance of Cl^- ions. Water types in PRB (semi-arid), generally dominated by HCO_3^-, indicate active groundwater flushing, whereas the waters of MRB (humid) were subjected to anthropogenic modifications.

The diagram has been classified into six subdivisions (Fig. 9), viz., I (Ca-Mg-HCO_3 type), II (Na-Cl type), III (mixed Ca-Na-HCO_3 type), IV (mixed Ca-Mg-Cl type), V (Ca-Cl type) and VI (Na-HCO_3 type), wherein III and IV are characterized by their mixed ionic content in that no cation-anion pair exceeds 50 %. In MRB, Ca-Mg-Cl type dominates all the three seasons followed by Ca-Mg-HCO_3 type. On the contrary, in PRB, Ca-Mg-HCO_3 and Ca-Mg-Cl types are roughly in equal proportions. In general, MRB waters (i.e., mean hydrogeochemical concentration) belong to Ca-Mg-Cl type, implying modification of water chemistry by anthropogenic inputs, whereas PRB waters fall in Ca-Mg-HCO_3 type (suggesting groundwater-dominating discharge).

Frazee (1982) developed a specialized interpretive water classification and later Upchurch (1992) suggested a descriptive classification of natural waters based on Piper diagram. Both schemes were used in this study to interpret the hydrogeochemical composition of samples, which enabled identification of 11 water types in MRB and PRB, viz., mixed cation-HCO_3, Ca-Na-HCO_3-Cl, Mg-Na-HCO_3-Cl, mixed cation-HCO_3-Cl, mixed cation-Cl, Ca-Na-Cl, Ca-Mg-Cl, Ca-Mg-HCO_3-Cl, Mg-Na-HCO_3, Ca-Na-HCO_3 and Mg-HCO_3-Cl (Table 5). Interestingly, these water types do show significant spatio-temporal variations (Table 5). MON samples of MRB are dominantly mixed cation-HCO_3-Cl (6 of 15 samples) followed by Ca-Na-HCO_3-Cl type (4 of 15 samples), while dominant water types of PRB are mixed cation-HCO_3 (5 of 12 samples) and mixed cation-HCO_3-Cl type (4 of 12 samples). During POM, mixed cation-HCO_3-Cl dominates in MRB (9 of 15 samples) as well as in PRB (8 of 12 samples). Similarly, PRM samples in MRB (12 of 15 samples)

Table 5 Classification of water types in MRB and PRB based on Piper (1944) diagram

	MRB			PRB		
Water type	MON	POM	PRM	MON	POM	PRM
Ca-Mg-Cl		2				
Ca-Mg-HCO_3-Cl		2	12		1	7
Mg-HCO_3-Cl				1		
Mg-Na-HCO_3				1		
Mg-Na-HCO_3-Cl	1				1	
Ca-Na-HCO_3				1		
Ca-Na-Cl	1					
Ca-Na-HCO_3-Cl	4					
Mixed cation-HCO_3	1			5	2	2
Mixed cation-Cl	2	2	1			
Mixed cation-HCO_3-Cl	6	9	2	4	8	3
Total	15	15	15	12	12	12

MON monsoon, *POM* post-monsoon, *PRM* pre-monsoon and PRB (7 of 12 samples) are dominantly Ca-Mg-HCO_3-Cl type. In summary, the temporal variability of dominant water types in MRB is as follows: mixed cation-HCO_3-Cl and Ca-Na-HCO_3-Cl (MON) → mixed cation-HCO_3-Cl (POM) → Ca-Mg-HCO_3-Cl (PRM). Similarly, the pattern in PRB is as: mixed cation-HCO_3 and mixed cation-HCO_3-Cl (MON) → mixed cation-HCO_3-Cl (POM) → Ca-Mg-HCO_3-Cl (PRM). Such spatio-temporal variations might be reflective of variability in climate, hydrologic pathways as well as degree of anthropogenic actions (e.g., farming, tourism etc.).

The interpretations of various water types as detailed herein are based on Frazee (1982), Upchurch (1992) and Harvey et al. (2002). Ca-Na-HCO_3 water types are generally "fresh recharge waters" derived from rainfall and its interaction with soil and bedrock. Further these water types have relatively higher ionic strength (compared to Ca-HCO_3 type) and have a significant role for Na due to the occurrence of Na-rich minerals in the basement rocks and greater reaction times (due to more prolonged contact time or exposure). Mixed cation-HCO_3-Cl and Ca-Na-HCO_3-Cl types are considered "transitional", where these water types refer to waters that are evolving by geochemical reactions with bedrock and soil-matrix or waters that changed their geochemical character by mixing with other geochemically distinct waters (Frazee 1982). These waters can also be a product of mixing among two or more end members, e.g., Ca-Na-HCO_3-Cl waters might have been derived from mixing between "fresh recharge waters" and waters with anthropogenic signatures. In addition, leaching of soil evaporites (in semi-arid areas) by "fresh recharge waters" can also yield Ca-Na-HCO_3-Cl water types. However, the occurrence of Ca-Na-HCO_3-Cl waters uniquely in MRB suggests mixing of "fresh recharge waters" and waters with anthropogenic signatures. Similarly, mixed cation-HCO_3-Cl type is also comparable with Ca-Na-HCO_3-Cl type, but the former type has additional inputs of Mg, which can be derived from geogenic (i.e., ferromagnesian minerals) as well as anthropogenic sources (e.g., fertilizers). The significance of Mg^{2+} is clearly evident in the water types of MRB and PRB in that 8 of the 11 water types have Mg^{2+} either with dominant or equal controls on the hydrogeochemical composition (Table 5).

In addition, Ca-Mg-Cl and mixed cation-Cl types in MRB strongly imply the significance of anthropogenically-derived ions. Similar to the mixed cation-HCO_3-Cl type, the Ca-Mg-HCO_3-Cl type is also "transitional" water, but hardly any significance for Na. This type of water is common to both MRB and PRB, but in both basins it is prominent only during PRM. Mixed cation-HCO_3 waters, showing dominance in PRB (compared to MRB) might be derived from the interaction of "fresh recharge waters" with Mg-rich minerals in the basin lithology. In PRB, mixed cation-HCO_3 water samples were collected from locations viz., PW4, PW5, PW6, PW7 and PW11, which is a hornblende-biotite gneiss terrain (Fig. 2).

4.4 Partial Pressure of CO_2 (pCO_2)

Partial pressure of CO_2 (pCO_2) of surface waters reflects both productivity and the dynamic state of the rivers (Stallard and Edmond 1987; Zhu et al. 2013). pCO_2 levels of the water samples of MON, POM and PRM were estimated from pH and HCO_3^- content. The results show that pCO_2 during MON, POM and PRM is significantly higher than the atmospheric value of $10^{-3.5}$ atm (Table 6). Similar observations were made by Anshumali and Ramanathan (2007) for lentic and Prasad and Ramanathan (2005) for lotic systems. Earlier, Garrels and Mackenzie (1971a) and Raymahashay (1986) reported that the global trend of slightly higher pCO_2 indicates the existence of disequilibrium in natural waterbodies vis-à-vis the atmosphere. Kempe (1982) also reported such supersaturation in most of the World Rivers with respect to the atmosphere.

In MRB, mean pCO_2 of MON water samples is six times that of atmospheric pCO_2, while during POM it is more than 25 times and in PRM it is nearly ten times the atmospheric pCO_2 (Table 6). In PRB, mean pCO_2 of water samples during MON, POM and PRM is roughly 10, 22 and 23 times the atmospheric pCO_2. Relatively higher pCO_2 in stream waters is mainly due to influent (groundwater-dominating) stream discharge, which is significantly enriched in CO_2 and the slower rate of re-equilibration (i.e., solubility vs. release of CO_2) with the atmosphere (Stumm and Morgan 1970; Holland 1978). This inference is further confirmed by the relatively higher pCO_2 during POM and PRM (compared to MON) since stream discharge of the rivers draining the Western Ghats during POM and PRM is chiefly derived from aquifers. Various studies (e.g., Huh et al. 1998; Wu et al. 2005) also showed that most rivers are nearly 10 times supersaturated, while the tributaries of the Amazon are roughly 40 times supersaturated due to respiration by roots and decomposition of organic matter (Stallard and Edmond 1987; Richey et al. 2002). An inter-basin comparison of pCO_2 in water samples demonstrates that PRB (with the exception of POM) has relatively higher pCO_2, which is attributable to semi-arid climate of the basin. In both MRB and PRB, relatively lower pCO_2 during MON might be the result of dilution during monsoon. Nevertheless, lower pCO_2 can also result from relatively high photosynthetic activity of the riverine (biotic) system (Moon et al. 2007). Albeit monsoon is common to both MRB and PRB, the quantum of rainfall is significantly different, i.e., >3,000 mm in MRB versus <1,000 mm in PRB (see Sect. 2), which could be the reason for relatively higher pCO_2 of PRB during MON.

The excess CO_2 in the water samples may also have originated from the labile organic matter released during monsoon by soil erosion (Gao and Kempe 1987). In spite of higher rate of soil erosion during MON, the lower pCO_2 (in both the basins) suggests that the dilution effect due to monsoon rainfall is not compensated by the increased rate of soil erosion. Further, the plots of TSS versus log pCO_2 of MRB and PRB (Fig. 10) also do not illustrate any causal relationships between pCO_2 and soil erosion during the sampling seasons (with the exception of MON in PRB).

Table 6 Log $m\mathrm{HCO}_3^-$ and log $p\mathrm{CO}_2$ of water samples of MRB and PRB

MRB							PRB						
Sample-ID	MON		POM		PRM		Sample-ID	MON		POM		PRM	
	Log $m\mathrm{HCO}_3^-$	Log $p\mathrm{CO}_2$	Log $m\mathrm{HCO}_3^-$	Log $p\mathrm{CO}_2$	Log $m\mathrm{HCO}_3^-$	Log $p\mathrm{CO}_2$		Log $m\mathrm{HCO}_3^-$	Log $p\mathrm{CO}_2$	Log $m\mathrm{HCO}_3^-$	Log $p\mathrm{CO}_2$	Log $m\mathrm{HCO}_3^-$	Log $p\mathrm{CO}_2$
MW1	−3.02	−2.54	−2.65	−2.08	−2.74	−1.89	PW1	−3.32	−2.42	−3.10	−1.96	−3.14	−1.80
MW2	−3.25	−2.50	−2.77	−1.88	−3.06	−2.18	PW2	−3.49	−3.12	−3.10	−2.20	−3.25	−2.89
MW3	−3.19	−2.87	−2.77	−2.26	−2.95	−2.26	PW3	−3.40	−2.70	−3.06	−2.40	−3.14	−2.61
MW4	−3.25	−2.89	−2.84	−2.01	−2.98	−2.71	PW4	−3.19	−2.52	−2.84	−2.21	−3.02	−2.43
MW5	−3.14	−2.64	−2.87	−2.21	−2.98	−2.54	PW5	−3.10	−2.60	−3.02	−2.00	−2.98	−2.46
MW6	−3.32	−2.57	−3.06	−2.47	−3.19	−2.66	PW6	−3.14	−2.80	−2.98	−2.33	−3.14	−2.53
MW7	−3.14	−2.60	−3.02	−1.76	−3.06	−2.29	PW7	−3.14	−2.68	−3.06	−1.80	−3.06	−2.36
MW8	−3.62	−2.82	−3.19	−2.07	−3.10	−3.22	PW8	−3.25	−2.61	−2.84	−2.15	−2.75	−1.67
MW9	−3.25	−2.59	−3.10	−2.16	−3.14	−3.32	PW9	−2.95	−2.28	−2.62	−2.23	−2.70	−1.95
MW10	−3.49	−2.93	−3.32	−2.26	−3.32	−2.79	PW10	−3.10	−2.05	−2.89	−2.34	−2.87	−2.22
MW11	−3.25	−2.56	−3.10	−2.01	−3.19	−2.90	PW11	−2.75	−2.51	−2.49	−2.40	−2.33	−1.89
MW12	−3.40	−3.12	−3.06	−1.94	−3.19	−2.80	PW12	−3.25	−2.61	−2.87	−2.58	−2.84	−2.68
MW13	−3.40	−3.00	−3.06	−2.09	−3.14	−2.63							
MW14	−3.32	−2.90	−2.98	−2.11	−3.10	−2.45							
MW15	−3.40	−2.73	−2.98	−2.54	−3.10	−3.13							

MON monsoon, *POM* post-monsoon, *PRM* pre-monsoon

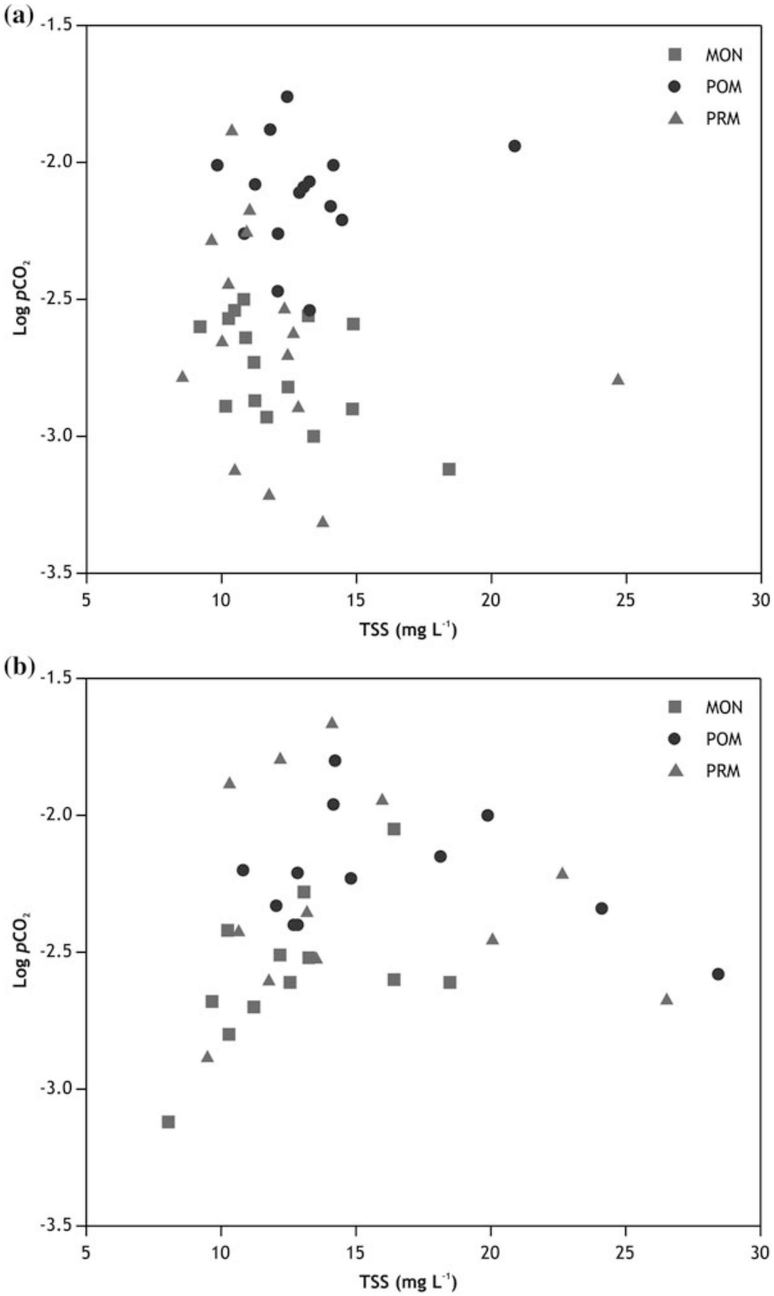

Fig. 10 Bivariate plot of TSS versus log pCO$_2$ of **a** MRB and **b** PRB

4.5 *Suitability for Domestic and Irrigation Purposes*

The chemical composition of water samples of MRB and PRB determines its suitability for domestic and irrigation purposes, which can be assessed by evaluating certain parameters such as corrosion coefficient (Cc), sodium adsorption ratio (SAR) and percent sodium (Na%). The results are summarized in the Table 7.

4.5.1 Corrosion Coefficient (Cc)

Larson and Scold (1958) proposed Cc, an important parameter in water quality evaluation, which is estimated as Eq. (3):

$$Cc = \frac{Cl^{-} + SO_4{}^{2-}}{HCO_3{}^{-}} \tag{3}$$

In MRB, mean Cc is 1.31 ± 0.59 (range = 0.59–2.71), 1.39 ± 0.47 (range = 0.74–2.56) and 1.56 ± 0.32 (range = 0.87–2.33) during MON, POM and PRM respectively (Table 7), whereas for PRB, mean Cc is 0.71 ± 0.31 (range = 0.35–1.26), 0.94 ± 0.27 (range = 0.47–1.31) and 1.09 ± 0.34 (range = 0.59–1.60) in MON, POM and PRM respectively. Balasubramanian (1986) suggested a ratio >1.0 for Cc as a safe limit for delivery of water through metal pipes. Relatively higher Cc values in MRB reflect non-corrosive nature of waters, in contrast to lower values in PRB suggesting higher probability for corrosion.

4.5.2 Sodium Adsorption Ratio (SAR)

SAR, an important parameter determining the suitability of waters for irrigation, is a measure of alkali/sodium hazard to crops. Richards (1954) defined SAR (Eq. 4) as a measure of cation exchange of irrigation water with the soil.

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \tag{4}$$

where concentrations are in meq L^{-1}.

In MRB, mean SAR is 0.47 ± 0.16 (range = 0.28–0.73) in MON, 0.42 ± 0.14 (range = 0.21–0.70) in POM and 0.22 ± 0.08 (range = 0.08–0.36) in PRM. SAR in PRB is 0.55 ± 0.39 (range = 0.13–1.41), 0.74 ± 0.54 (range = 0.14–2.17) and 0.49 ± 0.45 (range = 0.09–1.71) in MON, POM and PRM respectively (Table 7). Richards (1954) suggested that low to medium SAR of river water makes it suitable for irrigating most of the agricultural crops. In addition, based on the Bouwer's (1978) classification, the water samples belong to 'no problem category' of irrigation water quality (i.e., SAR < 6.0).

Table 7 Estimated parameters of suitability for domestic and irrigation purposes in MRB and PRB

Parameter	MON		POM		PRM	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
MRB						
Cc	1.31 ± 0.59	0.59–2.71	1.39 ± 0.47	0.74–2.56	1.56 ± 0.32	0.87–2.33
SAR	0.47 ± 0.16	0.28–0.73	0.42 ± 0.14	0.21–0.70	0.22 ± 0.08	0.08–0.36
Na%	34.98 ± 6.68	22.12-47.25	24.87 ± 6.05	12.50–38.46	16.67 ± 5.32	6.45–27.27
PRB						
Cc	0.71 ± 0.31	0.35–1.26	0.94 ± 0.27	0.47–1.31	1.09 ± 0.34	0.59–1.60
SAR	0.55 ± 0.39	0.13–1.41	0.74 ± 0.54	0.14–2.17	0.49 ± 0.45	0.09–1.71
Na%	33.65 ± 9.75	17.84–48.51	33.29 ± 10.55	13.04–52.40	23.02 ± 10.53	7.69–43.10

MON monsoon, *POM* post-monsoon, *PRM* pre-monsoon, *SD* standard deviation, *Cc* corrosion coefficient, *SAR* sodium adsorption ratio

4.5.3 Percent Sodium (Na%)

When concentration of Na^+ is high, the ions tend to be absorbed by clay particles displacing Mg^{2+} and Ca^{2+}. Exchange of Na^+ in water with Mg^{2+} and Ca^{2+} in soil reduces permeability, eventually resulting in poor internal drainage (Collins and Jenkins 1996; Saleh et al. 1999). Excess Na^+ combining with $CO_3{}^{2-}$ will lead to the formation of alkaline soils, while with Cl^- saline soils are formed and both these soils are unsuitable substrates for crops (Wilcox 1948). Hence, Na% (Eq. 5), a parameter of suitability for irrigation, is calculated as:

$$\mathrm{Na\%} = \frac{\mathrm{Na}^+ + \mathrm{K}^+}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^+ + \mathrm{K}^+} \times 100 \tag{5}$$

where all the concentrations are in meq L^{-1}.

Na% values of MRB range from 22.12 to 47.25 (mean = 34.98 ± 6.68) in MON, 12.50 to 38.46 (mean = 24.87 ± 6.05) in POM and 6.45 to 27.27 (mean = 16.67 ± 5.32) in PRM. In PRB, it spans between 17.84 and 48.51 (mean = 33.65 ± 9.75) in MON, 13.04 and 52.40 (mean = 33.29 ± 10.55) in POM and 7.69 and 43.10 (mean = 23.02 ± 10.53) in PRM (Table 7). The lower Na% suggests that the water samples of MRB and PRB during all the seasons are "excellent to good" for irrigation (after Wilcox 1955).

5 Conclusions

- In comparison with MRB, PRB has elevated levels of ionic abundance and higher degree of mineralization, possibly a result of multiple factors such as semi-arid climate, discharge dominated by groundwater, lithological variations and influence of carbonates and evaporites in the soil and shallow regolith.
- Higher K^+, Cl^- and H_4SiO_4 in MRB waters during all the seasons, implying significant contributions from farms, plantations and tourism sectors (i.e., K^+, Cl^-) as well as intense chemical weathering of silicate minerals (i.e., H_4SiO_4) in tropical humid climate.
- Downstream variation of hydrogeochemistry exhibits a general decreasing trend in MRB, which is attributed to dilution due to higher discharge, whereas hydrogeochemistry in PRB shows an increasing downstream trend, implying the significance of gradually changing rainfall (and climate), i.e., humid upstream versus semi-arid downstream.
- In MRB and PRB, hydrogeochemistry shows considerable temporal variability, which is a result of the variation in rainfall, changing hydrologic pathways controlling the stream discharge as well as intensity of various anthropogenic activities.
- MRB data (during all the seasons) on Gibbs plot are more or less clustered in the zone of rock dominance, whereas PRB data fall along a line trending from the

rock dominance zone (upstream samples) towards the zone of evaporation-crystallization dominance (downstream samples). Such a trend implies the influence of semi-arid climate prevailing in the downstream of PRB, where evaporation tends to increase the TDS.

- The Na^+-normalized Ca^{2+} versus Na^+-normalized HCO_3^- plots show that most of the sample poles occur outside the silicate weathering domain, instead fall parallel to the trend line between silicate and carbonate end members, which can be inferred as due to possible mixing between the end members.
- The Ca^{2+}+Mg^{2+}/Na^++K^+ ratios in MRB and PRB during MON (mean = 1.96 and 2.23 in MRB and PRB respectively), POM (mean = 3.29 and 2.41) and PRM (mean = 5.74 and 4.40) also reflect sources other than silicate weathering (e.g., weathering of carbonate minerals, anthropogenic inputs). Mean H_4SiO_4/(Na^++K^+) ratios during MON, POM and PRM in MRB and PRB are 0.48 and 0.42, 0.59 and 0.30 and 0.92 and 0.46 respectively, which also suggest additional sources of Na^+ and K^+ other than silicate weathering.
- According to classification schemes of Frazee (1982) and Upchurch (1992), 11 types waters have been delineated in MRB and PRB, viz., mixed cation-HCO_3, Ca-Na-HCO_3-Cl, Mg-Na-HCO_3-Cl, mixed cation-HCO_3-Cl, mixed cation-Cl, Ca-Na-Cl, Ca-Mg-Cl, Ca-Mg-HCO_3-Cl, Mg-Na-HCO_3, Ca-Na-HCO_3 and Mg-HCO_3-Cl. These water types show significant variability between the basins (MRB vs. PRB) as well as between the seasons (predominantly MON and POM vs. PRM). Most of the waters are considered "transitional", where these water types refer to waters that are evolving by geochemical reactions with bedrock as well as soil-matrix or waters that changed their geochemical character by mixing with other geochemically distinct waters.
- In both MRB and PRB, $p\mathrm{CO_2}$ during MON, POM and PRM is significantly higher than the atmospheric value of $10^{-3.5}$ atm. In MRB, mean $p\mathrm{CO_2}$ of stream water is 6 times the atmospheric $p\mathrm{CO_2}$, while during POM it is roughly 25 times and during PRM, it is nearly 10 times that of the atmospheric $p\mathrm{CO_2}$. In PRB, mean $p\mathrm{CO_2}$ of water during MON, POM and PRM is roughly 10, 22 and 23 times of the atmospheric $p\mathrm{CO_2}$. An inter-basin comparison of $p\mathrm{CO_2}$ in stream waters demonstrates that PRB (except during POM) has relatively higher $p\mathrm{CO_2}$, which might also be a result of the semi-arid climate of the basin.

In summary, the chemical composition of water samples of MRB and PRB is jointly controlled by weathering of silicate and carbonate minerals as well as anthropogenic activities and is influenced by climatic seasonality. However, the spatio-temporal variability of hydrogeochemical attributes is mainly due to the variations in climate, lithology, hydrologic pathways and degree of various anthropogenic activities.

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