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Hydrochemical variations of a tropical mountain river system in a rain shadow region of the southern Western Ghats, Kerala, India

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ABSTRACT

River water chemistry of Pambar River Basin (PRB), draining a rain shadow region of the southern Western Ghats, India, with granite gneiss and hornblende-biotite-gneiss lithology, was monitored for three sampling seasons, such as monsoon (MON), post-monsoon (POM) and pre-monsoon (PRM) to ascertain the spatio-temporal trends in hydrochemistry. In PRB, upstream and downstream areas have differing climate (i.e., tropical-wet-dry/humid upstream, while semi-arid downstream) and land use (plantations and farmland dominate the upstream, while pristine forest environment covers the downstream). The hydrochemical attributes, except pH and K^+ , exhibit distinct temporal variation mainly due to monsoon-driven climatic seasonality. Relative abundance of cations between upstream and downstream samples of PRB shows noticeable differences, in that the upstream samples follow the order of abundance: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, while the downstream samples are in the order: $Na^+ > Mg^{2+} > Ca^{2+} > K^+$. $Ca^{2+} + Mg^{2+}/Na^+ + K^+$, $Si/Na^+ + K^+$, Cl^-/Na^+ and HCO_3^-/Ca^{2+} ratios suggest multiple sources/processes controlling hydrochemistry, e.g., atmospheric supply, silicate weathering, dissolution of carbonate minerals and soil evaporites as well as anthropogenic inputs (domestic and farm/plantation residues). Even though weathering of silicate and carbonate minerals is the major hydrochemical driver in both upstream and downstream portions of PRB, Gibbs diagram and scatter plot of Mg^{2+}/Na^+ vs. Mg^{2+}/Ca^{2+} imply the importance of evaporation in the downstream hydrochemistry. Piper diagram and partial pressure of CO_2 (pCO_2) values suggest that a groundwater dominated discharge exerts a significant control on the downstream hydrochemistry, irrespective of sampling season. Although spatial variability of rainfall in PRB shows a linear downstream (decreasing) trend, the best-fit model for the dissolved load suggests that the downstream hydrochemical variability in PRB (i.e., an increasing trend) follows a power function ($f(x) = ax^k$). This study suggests that climate has a significant role in the spatio-temporal variability of hydrochemistry in PRB.

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1. Introduction

Weathering determinants such as, climate, lithology, tectonics, topography and vegetation are the dominant factors controlling hydrochemical composition of rivers (Gibbs, 1970; Stallard and Edmond, 1981, 1983, 1987; Meybeck, 1987; Drever, 1988; Gaillardet et al., 1999). However, other factors, viz., atmospheric deposition (e.g., aerosols, sea salt spray), contribution from groundwater reservoir as well as anthropogenic inputs via point- (industrial and domestic effluents and wastewater treatment facilities) and diffuse-sources (runoff from urban area and farmlands), also have considerable influences on river water chemistry

(Berner and Berner, 1987; Carpenter et al., 1998). But, the relative importance of each hydrochemical driver significantly varies in space and time. Among various hydrochemical determinants, apparent control of climate and lithology on chemical weathering processes and hydrochemistry was explained by various researchers (e.g., Stallard and Edmond, 1983, 1987; Berner and Berner, 1997; Gaillardet et al., 1999). Moreover, surface water chemistry is remarkably sensitive to climate, predominantly to changes in precipitation and temperature (White and Blum, 1995; Dalai et al., 2002; Millot et al., 2002), even in mountainous-headwater-regions (Psenner and Schmidt, 1992; Sommaruga-Wograth et al., 1997). Hence, hydrochemical investigation of river basins provides adequate information on the rate and pattern of chemical weathering processes and the dissolved elements cycled in the continent-river-ocean system (Hu et al., 1982; Stallard and Edmond, 1983, 1987).

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Likewise, spatio-temporal patterns of river water chemistry can also provide unique insights into the hydrologic functioning of catchments (Frohlich et al., 2008) because hydrochemistry of rivers is being regulated by complex interactions among various physical, chemical and biological subsystems in the catchment (Stumm and Morgan, 1996). Spatial variation of river hydrochemistry is principally controlled by tributaries (Meyer et al., 1988), land use (Townsend et al., 1983; Bucker et al., 2010), soil matrix and lithology (Schultz et al., 1993; Stutter et al., 2006; Harmon et al., 2009; Leite et al., 2010) as well as hyporheic zones and groundwater contributions (Boulton et al., 1998, 1999; Banks et al., 2011). On the other hand, temporal variability of river water chemistry is defined predominantly by discharge (Hem, 1948; Smolders et al., 2004; Crosa et al., 2006; Ovalle et al., 2013) and hydrologic pathways (Wheater et al., 1990; Ahearn et al., 2004). In semi-arid and arid rivers, temporal variation of discharge is exceptionally high (due to clearly marked dry and wet seasons) and fluctuations in discharge have enormous effects on hydrochemistry of the rivers (Davies et al., 1994; Allan, 1995).

Hydrochemical composition of the world's largest rivers received greater attention due to their global significance toward water- and sediment-discharge and hydrochemical flux (e.g., Gibbs, 1970; Milliman and Meade, 1983; Gaillardet et al., 1999). Moreover, hydrochemistry of large river systems in the tropics, such as Amazon (Stallard and Edmond, 1981, 1983, 1987; Mortatti and Probst, 2003), Congo (Probst et al., 1992), Gambia (Lesack et al., 1984) and Orinoco (Stallard et al., 1991; Edmond et al., 1996) was also well-documented during the past decades.

After Milliman and Syvitski (1992) and Vegas-Vilarrubia et al. (1994), small mountain river systems in the tropics gained significant attention toward the global dissolved load budget and motivated numerous studies focusing on hydrochemistry and biogeochemistry of these unique systems. Recently, Jennerjahn et al. (2008) recommended mountain rivers of small areal extent as the suitable candidates for biogeochemical process studies because of the shorter response time and easier identification of the effects of individual human activities on water quality and biogeochemistry. In the past decades, several studies (e.g., Lewis et al., 1987; McDowell and Asbury, 1994; Jennerjahn et al., 2004, 2008; Brodie and Mitchell, 2005; Townsend-Small et al., 2008; Harmon et al., 2009; Bucker et al., 2010; Lloret et al., 2011, 2013; Murphy and Stallard, 2012; Moyer et al., 2013) examined the sources and spatio-temporal dynamics of dissolved load, nutrients, sediments and organic matter, and their export to the ocean, which are discussed in the purview of natural processes (e.g., atmospheric input, weathering) and/or anthropogenic activities (e.g., land use changes, pollution, and hydrologic alterations). Many of these contributions also highlighted the vital role of extreme events and climatic seasonality in the elemental flux. Recently, Wohl et al. (2012) suggested the key aspects for integrated research of biogeochemical processes, such as (1) magnitudes and rates of different flow pathways, transport and cycling of carbon and other nutrients; (2) chemical inputs from precipitation, including changes during the year and during an event; (3) the role of dust inputs; and (4) anthropogenic alteration to the systems themselves.

In the Indian context, water chemistry of the Himalayan- as well as the Peninsular-rivers was thoroughly addressed by several researchers (e.g., Subramanian, 1983; Sarin et al., 1992; Galy and France-Lanord, 1999; Das and Krishnaswami, 2006; Jha et al., 2009; Gupta et al., 2011). In addition, spatio-temporal variation in the hydrochemistry /biogeochemistry of west-flowing, smaller river basins (<10,000 km²; Milliman and Syvitski, 1992) of the Western Ghats, India was also amply discussed (e.g., Prasad and Ramanathan, 2005; Maya et al., 2007; Gurmurthy et al., 2012; Pradhan et al., 2014; Thomas et al., 2014, 2015). Even though a few researchers (e.g., Markich and Brown, 1998; Lecomte et al.,

2005) demonstrated the hydrochemical variability of the rivers draining rain shadow regions in other parts of the world, hardly any published data is available on water chemistry of the rivers of the rain shadow regions of the southern Western Ghats, India. Hence, in this paper, we discussed the spatio-temporal variation as well as the processes controlling water chemistry of Pambar, draining a rain shadow region of the southern Western Ghats, Kerala, India.

2. Materials and methods

2.1. Study area

Pambar River Basin (PRB) is a sixth order sub-basin ($A = 288.53 \text{ km}^2$) of Amaravati River (a major tributary of Cauvery River) and drains between N Lat. $10^\circ 07' 59''$ and $10^\circ 21' 05''$ and E Long. $77^\circ 03' 24''$ and $77^\circ 15' 32''$ (Fig. 1). Pambar is one of the three east-flowing rivers of Kerala, India and elevation of the basin ranges from 2540 to 440 m above mean sea level (msl). The basin is developed mostly on the northern-facing scarps of the Munnar plateau (an extensive planation surface of late Paleocene age; Soman, 2002) and the plateau has a vital role in the drainage network development of PRB (Thomas et al., 2011, 2012).

Due to its NNW–SSE trend and physiography, the Western Ghats acts as a climatic barrier separating tropical humid climate of the western (and windward) slopes and semi-arid climate of the eastern (and leeward) slopes. The drainage network of PRB is developed on a rain shadow segment (of the eastern slopes) of the southern Western Ghats (in Idukki district), Kerala, India. Monsoon is the principal contributor of rainfall in PRB and is spread over two different intervals, viz., the SW monsoon (June–September) and the NE monsoon (October–November). The pre-monsoon (PRM) months (March–May) account for major thunderstorm activity and the winter months (December–February) are characterized by minimum clouding and rainfall. Weather data of PRB for a period of 1992–2008 were gathered from two meteorological stations (viz., Research and Development Division, Talaiyar Tea Ltd. in the upstream portion of PRB and Chinnar Wildlife Sanctuary in the downstream) and examined. Mean annual rainfall (P_{ma}) in the upstream portion of PRB is 1533 mm, while it is only 852 mm in the downstream region. However, several previous studies reported that some locations in the upstream portion of PRB receive 2000–5000 mm of rainfall annually (Jose et al., 1994; Chandrashekara and Sibichan, 2006). In addition, Thomas (2012) observed a linear positive relationship between P_{ma} and altitude in PRB. Contrasting mean monthly rainfall patterns between the upstream and downstream regions of PRB are shown in Fig. 2. Mean annual temperature (T_{ma}) in the upstream part of PRB varies between 20 and 25 °C, while in the downstream segment, T_{ma} is more than 30 °C. Thomas (2012) classified upstream portion of PRB under humid or tropical-wet-dry type, while downstream region as semi-arid using various climate indices and climatic classification schemes.

The drainage network of PRB is formed on the Precambrian Southern Granulite Terrain of the Peninsular India. Major rock types of PRB are hornblende-biotite-gneiss (Hbg) and granite gneiss (Ggn), while pegmatite and dolerite dykes intrude the host rocks (Fig. 3; GSI, 1992). The basement rocks are highly sheared and fractured and have well-developed joint systems. Hbg consists of quartz, plagioclase, K-feldspar as major minerals, while hornblende and biotite are accessories. Hbg shows regular, but alternating bands rich in quartzo-feldspathic and mafic minerals and individual bands vary both in thickness and mineral composition. On the other hand, Ggn is a medium grained (and pinkish coloured) rock and is foliated due to parallel planar arrangement of flakes of

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