CHAPTER 5

MAJOR IONS AND RADIOGENIC STRONTIUM ISOTOPIC COMPOSITION IN THE NETHRAVATI-GURUPUR RIVER BASIN, SOUTHWESTERN INDIA
Abstract

The dissolved and particulate major ion/element, trace element and $^{87}$Sr/$^{86}$Sr isotopic compositions were measured from Nethravati-Gurupur river and its main tributary channels. The river basin lies on the metamorphic transition boundary demarking peninsular gneiss and southern granulitic province belonging to Archean and tertiary-quaternary period (Western Dharwar Craton). The basin lithology mainly composed of granite gneisses, charnockites and metasediments. The surface area of the Nethravati River is 3657 km$^2$ and the Gurupur river is 883 km$^2$. The Nethravati and Gurupur rivers discharge 388 m$^3$ s$^{-1}$ and 84 m$^3$ s$^{-1}$ of water and 14x10$^5$ and 1.0x10$^5$ tons of sediments respectively. Rivers exhibit low major cation concentrations i.e., Na, Mg, K, Ca. but high concentrations of Si, Al, Fe compared to other tropical rivers. The total dissolved concentrations (TDS) are less (46 mg L$^{-1}$) and dominated by silica. The major and minor elements in the basin are higher during base flow and lesser during peak flow and the relationship can be explained by Power Law reduction equation. The basin is characterized with lesser dissolved Sr concentration (avg. 150µmol L$^{-1}$) and radiogenic $^{87}$Sr/$^{86}$Sr isotopic ratios (avg. 0.72041 at outlet) that can be explained by the weathering of silicate basement rock in the basin. $^{87}$Sr/$^{86}$Sr isotopic ratios are higher than the world river average (avg. 0.7119) and other tropical major rivers. The Sr concentration and $^{87}$Sr/$^{86}$Sr isotopic compositions correlate with silicate derived cations (corrected for atmospheric and carbonate contribution). The $^{87}$Sr/$^{86}$Sr isotopic composition shows strong seasonal variation in the basin, i.e., highly radiogenic values during the dry period of sampling whereas less radiogenic values during peak flow season, which corresponds to variations in the silicate weathering components in the basin. The calculated Chemical Index of Alteration (CIA) suggests intense weathering in the basin and the variation in intensity of weathering in the basin is negligible. The normalized REE pattern shows depletion of light REE compared to middle and heavy REEs in both dissolved and particulate phases. There is a strong cerium anomaly (Ce/Ce*) in both dissolved and particulate phase which can be attributed to elemental redistribution due to redox reactions.

5.1. Introduction

The dissolved chemical elements in the river water is mainly contributed from the weathering of source rock (Stallard and Edmond, 1981), the only exception could be the contribution of chemical elements through atmosphere which dominates in few exceptional
cases (Berner and Berner, 1987). During this weathering process, the chemical elements in primary mineral phases are fractionated between dissolved and suspended particulate phases (secondary mineral). The secondary minerals formed are removed by physical erosion and are transported as particulate matter, either as suspended matter or bed particulate load. Thus transported chemical elements (as dissolved and as particulate) often carries the geological and geochemical information of source rock composition, geochemical processes it has witnessed and the climatological and geochemical conditions of its formation. However, the geochemical conditions prevailing in the riverine environment and associated redistribution of elements could obscure the source rock information and the conditions of its formation in the weathering site. Therefore, understanding the past and depositional history often requires studying the geochemical processes that are taking place in the riverine environment.

While addressing the source rock weathering and elemental transport in the fluvial environment, the role of organic matter, pH, temperature, redox conditions are often discussed (Millot et al., 2003, Shiller and Mao, 2000; Viers et al., 1997; Dupre et al., 1999). The organic matter oxidation in the sediments defines the oxic/anoxic conditions in water column (Emerson and Bender, 1981), organic acids enhances mineral matter dissolution (Millot et al., 2003), organic complexation (Reuter and Perdue, 1977; Mantoura et al., 1978) and elemental scavenging (Devis, 1984). Temperature and pH governs the mineral dissolution (Velbel, 1991) and solubility and surface properties of the scavengers (Johnson, 1990; Abollino et al., 2003; Eby, 2004). Similarly, the redox conditions determine the solubility, precipitation and bioavailability of trace metals (Shiller, 1997). All these geochemical processes affect the elemental mobility, distribution, abundance and transport of chemical elements in the fluvial system. However, an understanding of the redistribution of chemical elements in the riverine environment is still poorly addressed and limited to large rivers of the world and estuarine environments. In addition to large river basins, studies on geographically limited basins are of interest because they allow a more precise and detailed understanding of the processes occurring during weathering and element transport. Except few notable time series geochemical studies on large tropical rivers (Mora et al., 2009; Tosiani et al., 2004; Viers et al., 1997; Barroux et al., 2006; Tripathy et al., 2010), there is a lack of time-series data of major ions/element, REE and $^{87}$Sr/$^{86}$Sr isotopic ratios in regional scale river basins draining silicate basement rocks and lateritic environment.
An attempt has been made to address the processes of weathering and transport of weathered products in the riverine environment having a smaller catchment size. The present study reports time series of dissolved trace elements and REE along with geochemical data from the sub-continental region for the first time. Although the Indian subcontinent is a place for many large rivers in the world, there is no systematic data on the dissolved and suspended particulate chemistry of the rivers flowing in this region. The present research investigation has been taken up to meet the following set objectives: (a) To generate the first documented geochemical characteristics of the surface waters draining this basin. (b) To derive information concerning the source-rock origin and weathering intensity using the dissolved and particulate geochemical data. (c) The last and more important objective was to focus attention on the behaviour of the elements in the river environment and particularly upon the fractionation between the dissolved and suspended materials.

5.2. Results and discussion

5.2.1. Dissolved composition of river water samples

Physicochemical and major ion characteristics: The physico-chemical parameters, major ion, minor ion and organic carbon composition in the Nethravati River and Gurupur River and its tributaries are presented in Table 5.1. The pH of Nethravati River varies from 5.2 to 8.0 (avg. 7.2) in different time periods of sampling over three years (between Oct-2006 and Sept-2007 and between January 2009 and December 2010). The data shows slightly lower pH values during the monsoonal period of sampling compared to non-monsoonal months (Fig. 5.1a). The conductivity of the river water ranges from 20 to 87 µS cm⁻¹ (avg. 46 µS cm⁻¹) with lesser values during monsoon and higher values during pre-monsoon season at all stations (Fig. 5.1b). Overall, the pH and conductivity of Nethravati and its streams are typical of rivers draining granitic terrains (Oliva et al., 2003). The dissolved oxygen concentration in the Nethravati river ranges from 6.5 to 8.46 (avg. 7.2). The concentrations of dissolved oxygen are higher during the monsoonal months of sampling and lesser during the non-monsoonal months of sampling (Fig. 5.1a). The dissolved oxygen level indicates oxidising condition and self-purification ability in the river water.

The DOC concentration in the Nethravati-Gurupur river basin varies from 0.6 to 7.6 mg L⁻¹ (avg. 3.4 mg L⁻¹). The DOC concentration is higher during dry season and lesser
during monsoon season (Fig. 5.1a). The DOC are also higher at densely forested tributary stations of Nethravati whereas slightly lesser at tributary stations of Kumaradhara. Though the river drains dense forests from Western Ghats, DOC in Nethravati-Gurupur river basin is comparatively lesser than other humid tropical river basins for e.g., Mengong river (10-20 mg L\(^{-1}\); Viers et al., 2000), Congo River (10.5 mg L\(^{-1}\); Seyler et al., 1995) and comparable to the world river average (4 mg L\(^{-1}\); Meybeck et al., 1996).

The river total dissolved solids (TDS) range from 26 to 77 mg L\(^{-1}\) (avg. 48.6 mg L\(^{-1}\)). The low TDS in the river basin suggests that the river drains acidic igneous rocks. The TDS are slightly higher during the summer (pre-monsoon) and getting diluted as the monsoon proceeds. The TDS and EC are comparatively lesser at Shishilahole, a tributary of Nethravati, which predominantly drains metasediments and granite gneisses (Fig. 2.2).

Figure 5.1: Monthly variation in Physicochemical and dissolved organic carbon (DOC) concentration (average and standard deviation) in the Nethravati-Gurupur river basin.

Sodium is the dominant dissolved cation, with concentrations ranging from 75 to 260 µmol L\(^{-1}\) (avg. 152 µmol L\(^{-1}\)). It is followed by Ca (38 to 157 µmol L\(^{-1}\), avg. 76 µmol L\(^{-1}\)), Mg (26 to 183 µmol L\(^{-1}\), avg. 62 µmol L\(^{-1}\)) and K (10 to 54 µmol L\(^{-1}\), avg. 23 µmol L\(^{-1}\)). The lowest concentrations are observed in the Shishilahole tributary, located in the foothills of the Western Ghats. Overall, major cation concentrations in the Nethravati watershed decrease during monsoon (Fig. 5.2a) while spatially, it increases further downstream. The Kumaradhara tributary (station Shanthimugeru), which partly drains the Ca - Mg bearing hypersthene-rich charnockites, exhibits slightly higher Ca/Na (0.52±0.07) and Mg/Na (0.45±0.07) molar ratios than the Nethravati upper watershed, Ca/Na (0.48 ±0.06) and Mg/Na (0.36 ±0.11) (Station Mugeru) and Gurupur river Ca/Na (0.46 ±0.05) and Mg/Na (0.29 ±0.04) (Fig. 2.2).
Figure 5.2: Monthly average and standard deviation of major ions and minor ions in the Nethravati-Gurupur River basin.

An important feature of the Nethravati river basin is that the HCO$_3^-$ account for an average of 77% of the anion budget. The bicarbonate concentrations range from 170 to 710 µmol L$^{-1}$ (avg. 385 µmol L$^{-1}$), which is believed to be originated from soil or atmospheric carbon dioxide. Chloride concentrations range from 42 to 141 µmol L$^{-1}$ (avg.
85 µmol L\(^{-1}\)). Like cations, the lowest bicarbonate and chloride values were observed during the monsoon season (Fig. 5.2b). In all sampling stations, SO\(_4\) concentrations are ranging from 6 to 22 µmol L\(^{-1}\) (avg. 10 µmol L\(^{-1}\)) which is about 20 times lesser than the bicarbonates. The NO\(_3\) concentrations range from 0.5 to 20 µmol L\(^{-1}\) (avg. 3.9 µmol L\(^{-1}\)) with maximum values observed during the onset of monsoon when fertilizers are added to freshly sown agricultural crops (Fig. 5.2c). Chloride and SO\(_4\) concentrations are not correlated to NO\(_3\) variations. Silica concentrations in the river basin range from 100 to 319 µmol L\(^{-1}\) (avg. 200 µmol L\(^{-1}\)). Silica concentrations account for about 25% of the total dissolved salts in the river basin. Average SiO\(_2\) concentration is comparable to world river average (180 µmol L\(^{-1}\); Meybeck et al., 1996).

**Minor element composition of river water:** The dissolved strontium concentration varies from 96 to 457 nmol L\(^{-1}\) (avg. 229 nmol L\(^{-1}\)), dissolved Rb varies from 9 to 46 nmol L\(^{-1}\) (avg. 19 nmol L\(^{-1}\)) and Ba varies from 28 to 86 nmol L\(^{-1}\) (avg. 47 nmol L\(^{-1}\)), with higher concentrations during base flow and lesser concentrations during monsoon season (Fig. 5.2d & 5.2e). These concentration values are lesser than world average Sr (684 nmol L\(^{-1}\)) and Ba (162 nmol L\(^{-1}\)), whereas Rb is similar to world average (19 nmol L\(^{-1}\)). Lesser concentrations of Sr, Rb and Ba are observed at Shishilahole tributary, which drains primarily meta-sediments. The strontium isotopic ratio (\(^{87}\)Sr/\(^{86}\)Sr) measured in the sample varies from 0.71855 to 0.72286 (avg. 0.72041). The \(^{87}\)Sr/\(^{86}\)Sr ratio in water was observed to be more radiogenic in the Nethravati River whereas Kumaradhara River has lesser radiogenic ratios (avg. 0.71944) because it drains predominantly Charnockites and amphibolites. The station Shishilahole tributary which drains predominantly meta-sediments is having highly radiogenic Sr in the basin (avg. 0.72273).

The dissolved aluminium concentration varies from 0.03 to 50 µmol L\(^{-1}\) (avg. 4.2 µmol L\(^{-1}\)), Fe 0.049 to 11 µmol L\(^{-1}\) (avg. 2 µmol L\(^{-1}\)) and Mn 3.2 to 658 nmol L\(^{-1}\) (avg. 125 nmol L\(^{-1}\)). The concentrations of Al and Fe are higher at upper catchment and lesser at the outlet. However, the Mn concentrations are higher at Dharmasthala, a tributary of Nethravati draining meta-sediments. The concentration of Fe is slightly higher than world average (1.18 µmol L\(^{-1}\)), concentrations of Al is higher by a magnitude of four than world average (1.18 µmol L\(^{-1}\)) whereas Mn is six times lesser than the world average (618 nmol L\(^{-1}\); Gaillardet et al., 2003). Unlike other tropical rivers of Africa, the river exhibits lesser concentrations of dissolved immobile elements (Al, Fe and Mn). The
concentrations are higher during non-monsoon and lesser during monsoon (Fig. 5.2f, 5.2g & 5.2h).

The monthly measurement of major and minor ion composition of Nethravati at BC Road (Bantwala), Mugeru (Uppinangadi) and Gurupur River (at Addoor) allows us to establish the relationship between water discharge with the major and minor ions. The TDS, major cations (Na, K, Mg, Ca), major anions (HCO\textsubscript{3}, Cl) and minor ions (Ba, Sr, and Rb) shows power law reduction with discharge i.e., decreasing concentration with increasing discharge (figures not shown). This could be explained by the mixing of concentrations with discharge. The higher concentrations during low discharge could be explained by the base flow contribution coupled with evaporation of water. Lesser concentration during higher discharge could be explained by the dilution by rainwater and surface runoff. The power law relationship between major ions with discharge is common for most of the river basins of the world which shows either power law reduction or linear increase (Probst et al., 1992, Meybeck et al., 1996, Picouet et al., 2002). Silica is not showing significant relationship with discharge. Whereas, lesser mobile elements like Fe and Al are showing contrasting relationship with discharge i.e., increase in the concentration with discharge but the statistical significance is less.

**Spatial variation of major and minor ions in Nethravati-Gurupur river catchment**

The spatial variation of major and minor ionic concentrations is presented in Fig. 5.3. The major ions originating from marine aerosols or from atmosphere (Cl, F, SO\textsubscript{4}, NO\textsubscript{3}) are increasing from the upper to the lower catchment, i.e., lesser concentrations at upper catchment higher concentrations at lower catchment (Fig 5.3a-5.3d). Whereas, the major ions originating from continental weathering (geogenic) are decreasing from upper catchment to lower catchment (Fig. 5.3e-5.3h) i.e., higher concentrations at upper catchment and lesser concentrations at lower catchment, except for Mg and K which are increasing from the lower to the upper catchment. The spatial variation of Mg and K could be due to presence of Mg-rich and K-rich silicate minerals of charnockite rocks in the Kumaradharha River catchment. It is observed that the Nethravati River tributary stations Neriyahole (NH) and Shishihalehole (SH) are having lesser abundance of major cations compared to the Kumaradharha River stations such as Shanthimugeru (SMKR) and Gundyahole (GH). The reason could be due to lithological differences in the catchment i.e., metasediments and charnockite rocks respectively. The metasedimentary rocks are formed from the metamorphism of sediments that had undergone weathering and erosion.
processes. Thus, these formations should be abundant in minor refractory elements (Fe, Al, and Mn) and less abundant in major elements. This contention is also supported by the abundance of minor ions (Al, Fe and Mn) in the water from these stations (Fig. 5.3i-5.3k). These stations are also exhibiting higher radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ compared to lower catchment and other stations (Fig.5.3i).

Figure 5.3 (a-f): Spatial variations of major and minor ion concentrations in the Nethravati-Gurupur river basin (GR-Gurupur River, BCR-BC Road, Bantwala, MNR-Mugeru, Nethravati River, SMKR-Shantimugeru, Kumaradhara River, GH- Gundyahole, SH-Shishilahole, NH-Neriyahole, DRMH-Dharmasthala, MH-Mundajehole). The vertical intervals represent the concentration ranges observed over the monitored period of time. Open circle connected by a straight line shows the main river channel, and blocked circle shows the tributary water samples.
Figure 5.3 (g-l): Spatial variations of major and minor ion concentrations in the Nethravati-Gurupur river basin (GR-Gurupur River, BCR-BC Road, Bantwala, MNR-Mugeru, Nethravati River, SMKR-Shantimugeru, Kumaradhar River, GH- Gundyahole, SH-Shishilahole, NH-Neriyahole, DRMH-Dharmasthala, MH-Mundajehole). The vertical intervals represent the concentration ranges observed over the monitored period of time. Open circle connected by a straight line shows the main river channel, and blocked circle shows the tributary water samples.

**Relationship of dissolved major ion and minor ions:** Relationship between Fe and Al could be found only during the monsoonal months of sampling and there is no significant relationship between both elements during the dry period of sampling (Fig. 5.4). Dissolved iron concentration is higher compared to Al during the dry period of sampling. This suggests that Fe and Al are equally mobile during the monsoonal months. This
corresponds to inflow of fresh solution and creation of thermodynamic disequilibrium between mineral and solution interface, leading to intense weathering of source rocks and release of Al and Fe. Dissolved Fe was found to be abundant relative to Al during the dry period of sampling. The enhanced concentrations of Fe cannot be explained by complexation process by organic colloids in the river basin, because Fe lacks correlation with DOC. Another possible process which can modify the elemental concentration is by redox exchange. The remobilization of Fe under reduced condition as $\text{Fe}^{2+}$ during the dry periods of sampling could have contributed to observed higher concentrations of Fe. Iron is known to be sensitive to redox changes in the subsurface region and it is reported that under reducing conditions the $\text{Fe}^{3+}$ is reduced to $\text{Fe}^{2+}$ (Bose and Sharma, 2002). The mean dissolved oxygen (DO) concentration in the subsurface water during the month of May is 2.7 mg L$^{-1}$ (discussed in Chapter 4) supports the possibility of reduced environment in the subsurface region. Further, another immobile element Ti shows positive correlation with Al ($R^2 = 0.725$) suggesting both immobile elements are preferentially leached at the same rate during weathering and transportation. The observed correlation between Al and Fe is consistent with African tropical rivers such as Nyong and Mengong River (Viers et al., 2000). However, the authors reported correlations between these two elements throughout year. This suggests that change in the weathering regime or redox equilibrium in the Nethravati River basin have dominant control over the abundance of these elements. The minor elements, Sr, Rb and Ba are showing positive correlation with most of the major cations in the river basin pointing to the weathering source.

Figure 5.4: Relationship between dissolved Al and Fe in the Nethravati-Gurupur River basin
Normalized dissolved REE pattern: The dissolved rare earth Element concentrations are presented in Chapter 6. The upper continental crust normalized (Rudnik and Gao, 2003) REE pattern in Nethravati River water is presented in Fig. 5.5a. The normalized pattern of REE shows upward convexity centred on the middle and heavy REE which is due to depletion of light REE compared to middle and heavy REE. The pattern is consistent with the world major rivers such as Amazon, Congo, Cuyuni River. The Eu enrichment in the Nethravati River water is consistent with the observed Eu enrichment in other world tropical rivers like Congo, Zaire, Nyong and Cuyuni. However, the Nethravati River displays pronounced upward convexity at middle REE region compared to other river basins. The dissolved REE pattern for other large rivers (both during high flow and low flow) is presented in Fig. 5.5b. The fractionation of LREE and HREE in the Nethravati River (La_N/Yb_N ratio) shows significant variation at different flow rates, average at BC Road, Bantwala 0.87 to 0.57 respectively for high water stage and less water stage. The range at different sampling station is 0.46 to 1.19 for higher water stage and 0.28 to 1.20 for less water stage. This contrasts with the observed lesser variation in the Amazon River and its main tributaries (Amazon 0.41 to 0.34, Rio Negro 0.60 to 0.58, Solimoes 0.35 to 0.32, and Madeira 0.45 to 0.41 respectively for high water stage and less water stage conditions; Barroux et al., 2006). Similarly, the fractionation between MREE and LREE (Gd_N/Nd_N ratio) in the Nethravati River shows significant seasonality at different flow conditions, during high flow (1.17-2.03) and base flow (1.17 to 3.20) conditions at different sampling stations. This fractionation of MREE and LREE is higher in the Nethravati River than the Amazon and its tributaries. Most of the water samples from the Nethravati River show cerium anomaly (Ce/Ce*) (range 0.42 to 1.57) at different time periods of sampling. It could be attributed to redistribution of element Ce between dissolved and particulate phases at different redox conditions, as evident from the negative correlation between the Ce anomalies with dissolved Oxygen concentration (discussed in Chapter 6, Figure 6.9).
Figure 5.5: Upper Continental Crust (UCC) normalized dissolved REE pattern in the Nethravati-Gurupur river basin (5.5a). The comparison of normalized dissolved REE pattern with other tropical river basins of the world (5.5b). (Data Source: Amazon, RioNegro, Solimoes, Madiera river, Barroux et al., 2006; Cuyuni River, Tosiani et al., 2004; Oubangai, Zaire and Congo river, Dupre et al., 1996 and Nyong and Mengong rivers, Viers et al., 2000).
Strontium isotope systematics: The mean Sr isotopic composition in river Nethravati at the outlet is 0.72041, which is quite higher than the average of global rivers 0.7119 (Palmer and Edmond, 1992). The isotopic composition in the Nethravati River is more radiogenic than west flowing peninsular rivers viz Arjuna (0.70683), Gad (0.70984), Sukh (0.70687), Kajli (0.70614), Shastri (0.70652) and Vashishti (0.70711) (Das et al., 2006) and east flowing rivers viz Kaveri (0.71002-0.712770), Palar (0.71015 to 0.718754) and Ponnaiyar (0.716045 to 0.718446) (Pattanaik et al., 2007). The isotopic values of Nethravati River basin are more radiogenic than the felsic granulites (avg. 0.70392; Tomson et al., 2006) and mafic volcanics and granulites (avg. 0.709423; Bhaskar Rao et al., 1992, Durand et al., 2006) while the values are lesser than the granitic gneissic rocks (avg. 0.850425; Bhaskar Rao et al., 1992, Taylor et al., 1984). However, the isotopic values are not showing simple mixing of these lithologies (plot of Ca/Sr or Mg/Sr vs $^{87}$Sr/$^{86}$Sr not shown). This implies that the other minor lithologies like metasedimentary rocks are significantly impacting the Sr isotopic composition. The highly radiogenic isotopic values observed in the tributary channel, Shishilahole supports this observation. The Sr isotopic composition of the Nethravati River falls in the silicate rock mineral weathering range with highly radiogenic isotopic values. The observed correlation between the Sr and silicate derived cation concentration (Fig. 5.6a) in the river basin and their isotopic values suggest a silicate origin of Sr. Furthermore, the $^{87}$Sr/$^{86}$Sr isotopic composition closely follows silicate cation concentration (Fig. 5.6b & 5.6d). This suggests that increase in the silicate weathering rate produces radiogenic Sr isotopic composition. The isotopic composition shows two distinct trends of variation with season. During the monsoonal months, Sr concentration and isotopic composition appear to be slightly lesser than the non-monsoonal sampling which is having higher Sr concentrations and higher isotopic ratios. The only exception to this observation is Shishilahole, which drains predominantly metasediments, and is showing highly radiogenic isotopic values and lesser concentrations of Sr. A possible explanation for the observed temporal variations in the Sr isotopic composition could be the duration of interaction between the mineral and water. During monsoon, more exposure of fresh mineral surfaces to the fresh water and there could be leaching of least resistant minerals but as the time of interaction increases the more radiogenic silicate minerals leaches to the water, for eg., mica minerals (Erel et al., 2004; Tripathy et al., 2010). The plot of $^{87}$Sr/$^{86}$Sr vs 1/Sr shows three distinct groups of samples belonging to different lithological settings (Fig.5.6c). First group, Shishilahole station, shows higher Sr isotopic ratio and
lesser Sr concentration in both the monsoon and non-monsoon sampling. Abundance of Rb can be observed in this station in both the sampling seasons (not shown) which could explain the higher isotopic ratio in this tributary. The abundance of Rb over Sr suggests dominance of K-rich minerals in these rocks. Second group of samples which are having slightly higher (compared to first group) concentrations of Sr and higher radiogenic isotopic values (station Mugeru, Gundyahole, Neriyahole, Dharmasthala, Mundajehole and Gurupur river), which are draining predominantly granite and gneisses. Granite and gneisses are known to be naturally radiogenic. In contrast, the third group, stations Bantwala and Shanthimugeru shows higher concentrations of Sr and lesser radiogenic Sr isotopic composition. The fact that the station Shantimugeru is draining charnockite rock minerals, which are abundant in the lower catchment, could explain the observed lesser radiogenic isotopic values. The observed less radiogenic isotopic composition of Sr in the Bantwala could be due to mixing of two distinct water masses draining two different lithologies. The observed higher radiogenic isotopic ratio in river water is also consistent with the observed radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the silicate fraction of particulate matter (avg. 0.73; n=5).

5.2.2. Bed Sediment and Particulate composition

The major and minor element composition were measured in suspended particulate matter (monsoonal) and sediment (dry period) samples (Table 5.2). The suspended particulate concentration in the Nethravati River is increasing with the discharge i.e., higher concentrations of particulates during monsoon and lesser concentrations during the nonmonsoon. Chemical Alteration Index (CAI) is one way of assessing the influence of sediments recycle on potential soluble product that can be generated from chemical erosion. The CAI was initially proposed by Nesbitt and Young, (1982).

$$\text{CAI} = \left[\frac{(\text{Al}_2\text{O}_3)}{(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})}\right] \times 100$$

This index is based on the principle that as rocks weather, they preferentially loose soluble elements like Na, K and Ca and become enriched with immobile elements like Al. Therefore, higher CAI yield indicates intense weathering it has undergone. In general, the CAI for unaltered rocks ranges from 46 to 51 and the terrains subjected to intense weathering conditions could yield CAI of ~100. The calculated CAI in this study ranges from 87.6 to 91.6 (avg. 90.1) for SPM and 81 to 92 (avg. 87) for bed sediments of Nethravati River basin. These values are quite higher compared to the UCC composition
This observation is consistent with the previous studies made by Shankar and Manjunatha (1994) and Gurumurthy et al., (2012), who have reported intense weathering in the catchment, based on SPM and dissolved chemistry respectively. The intense weathering in the basin is not unexpected as the basin has been evidencing intense rainfall, higher surface runoff and warm temperature.

The major and minor elemental compositions of bed sediments and particulate matter are normalized to upper continental crust (compiled by Rudnik and Gao, 2003) and presented in Fig. 5.7a. The normalization to upper continental crust could be justified here by the fact that the study area is composed of granite gneisses, metasedimentary formations, and charnockites. These formations do not have visible carbonate minerals and the composition is not much different from the granite gneisses (Sharma and Rajmani, 2000). The plot shows an overall distribution and abundance of chemical element in different phases displaying different geochemical behaviour.

The elements, Ca, Mg, Na, K, Sr, Ba and Rb show a considerable depletion in the suspended and bed load relative to the UCC. The upper continental crust normalized ratio in these samples range from Na$_2$O 0.1 to 0.3, K$_2$O 0.3 to 0.6, CaO 0.1 to 0.3, MgO 0.2 to 0.8, Sr 0.2 to 0.3, Ba 0.5 to 0.7, Rb 0.4 to 1.0, B 0.3 to 1.1, Zr 0.4 to 1.4 and Cs 0.2 to 1.1. All these elements are known to be more mobile during the weathering and transport. The Neriyahole tributary is showing slightly higher values compared to main channel and other tributaries. For Zr and Cs, the bed sediments are showing slightly higher values compared to their respective SPM. The depletion of these elements in the particulate and bed sediment have been reported for the other tropical river basins studies conducted by Dupre et al., (1996), Canfield (1994), Gaillardet et al., (1995, 1997), Viers et al., (1997, 2009). The trace elements, minor elements and REEs in SPM and bed Sediment are enriched with respect to UCC composition in the Nethravati basin. The only exception to this is depleted values of REE and certain trace elements in bed sediments of Gurupur River and Mundajehole.
Figure 5.6: Dissolved Sr and its relationship with silicate derived dissolved major cations (a). Correlations between dissolved strontium and rainwater corrected major cation concentrations (b). Mixing diagram of strontium isotopic composition and dissolved strontium in Nethravati-Gurupur river basin (c), temporal variation of $^{87}\text{Sr}/^{86}\text{Sr}$ and silicate derived cations in the river Nethravati (d). The grey colour area plot in the background shows the discharge variation during the sampling.
The river REE compositions in the SPM and Bed sediments are enriched relative to the UCC composition except in two bed sediment samples of Mundajehole and Gurupur River. In spite of variation in the concentration values in different tributaries of the Nethravati River, the REE pattern is quite similar throughout the basin. The REE pattern shows LREE depletion compared to MREE and HREE with a normalized La/Yb <1 and Gd/Nd >1 for most of the samples. The MREE concentrations in the Nethravati basin are relatively enriched. There is a significant positive anomaly in Ce and Eu in the SPM and Bed load (Fig. 5.7b and 5.7c). The SPM REE pattern in Nethravati is quite similar to Cuyuni River, which drains granite gneiss and green schist rock types, but with highly enriched values. The La concentration in Nethravati river basin is slightly higher (range between 32 mg kg\(^{-1}\) and 90 mg kg\(^{-1}\)) when compared to average upper continental crust composition whereas, the concentrations are lesser than volcanic island river basins. The higher concentrations of La (avg. 47 mg kg\(^{-1}\)) suggest lesser mobility of REE in the River Nethravati compared to global rivers and other tropical rivers.

Comparison of REE pattern with other tropical rivers: The World Rivers are characterized by contrasted SPM REE patterns. For instance, Himalayan rivers (Yamuna, Ganges, Brahmaputra), and Cuyuni River are depleted in REE compared to UCC whereas, tropical rivers draining shield terrains are enriched in REE compared to UCC (Fig. 5.8). The comparison of SPM REE geochemistry with other tropical river basins shows that the Nethravati River REE pattern is unique. The Nethravati River SPM shows enrichment of MREE compared to LREE and HREE. Furthermore, none of the previously published REE patterns from tropical rivers exhibit positive Ce anomaly (\(\text{Ce/ Ce}^* = 3\text{Ce} / (2\text{La+Nd})\)) that ranges from 1.12 to 1.77 (avg. 1.34) in the SPM and bed sediment. The interpretation of Ce/Ce\(^*\) in natural systems is not straightforward as the calculation of the Ce anomaly depends on the neighbouring elements La and Nd. However, it should be noted that the observed positive anomaly is about twice the expected concentration. Therefore, the possibility of occurrence of a Ce anomaly due to variation of neighbouring REE concentration is insignificant. The calculated cerium anomaly in the dissolved and particulate phase are showing relationship with the dissolved oxygen concentrations in the river water (discussed in Chapter-6, Figure 6.7). This suggests that the redox-sensitive Ce is increasingly fractionated into particulate matter because of preferential scavenging of dissolved Ce on to the surface of oxyhydroxides associated with changing redox conditions in the riverine environment.
Figure 5.7: Upper Continental Crust (UCC) normalized major element pattern (5.7a) in bed sediments and SPM, normalized REE pattern in SPM (5.7b) and bed sediment samples (5.7c).
Figure 5.8: Comparison of normalized SPM REE pattern with world major tropical river basins. Data Source: World Average, Viers et al., 2009; Ganges, Yamuna and Brahmaputra, Ramesh et al., 2000; Cuyuni river, Tosiani et al., 2004; Congo and Zaire, Dupre et al., 1996, Mackenzie, Niger, St. Lawrence and Rio Negro, Gaillardet et al., 1995)
5.3. Summary

The dissolved and particulate major ion/element, trace element and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions were measured from Nethravati-Gurupur river and its main tributary channels. These rivers exhibit low major cation concentrations i.e., Na, Mg, K, Ca but high concentrations of Si, Al, Fe. The total dissolved solids (TDS) are less (46 mg L$^{-1}$) and dominated by silica concentration. The major and minor elements in the basin are higher during base flow and lesser during peak flow season and the relationship can be explained by Power Law reduction equation. The basin is characterized with lesser dissolved Sr concentration (avg. 150 µmol L$^{-1}$) and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios (avg. 0.72041 at outlet) that can be explained by the weathering of silicate basement rock in the basin. These values are higher than the world river average (avg. 0.7119) and other tropical major rivers. The Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions are strongly correlating with silicate derived cations (corrected for atmospheric and carbonate contribution). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition shows strong seasonal variation in the basin, i.e., highly radiogenic values during the dry period of sampling whereas less radiogenic values during peak flow season, which corresponds to variations in the silicate weathering components in the basin. The observed seasonality suggests, the seasonality of strontium isotopic composition has to be taken care while using the Sr isotopic composition paleoclimate studies. The calculated Chemical Index of Alteration (CIA) suggests intense weathering in the basin and the variation in intensity of weathering in the basin is negligible. The normalized REE pattern shows depletion of Light REE compared to middle and heavy REEs. There is a strong cerium anomaly (Ce/Ce*) in both dissolved and particulate phase which can be attributed to elemental redistribution due to redox reactions.
References


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