Chemical Erosion rates of Peninsular Indian Rivers: An inversion approach

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Aswin Pradeep T

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Supervisor: Dr.Gyana Ranjan Tripathy

Department of Earth and Climate Science
Indian Institute of Science Education and Research Pune
Dr Homi Bhabha Road
Pashan, Pune 411008, India

Certificate

This is to certify that this dissertation entitled "Chemical erosion rate of Peninsular Indian Rivers: an Inversion Approach" towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Aswin Pradeep T at IISER Pune under the supervision of Dr. Gyana Ranjan Tripathy, Assistant Professor, Earth and Climate Science Department during the academic year 2016-17.

Tripathy

Dr. Gyana Ranjan Tripathy

Committee

Dr. Gyana Ranjan Tripathy

Dr. Rajani Panchang

Declaration

I hereby declare that the research work presented in the report entitled “Chemical Erosion rates of Peninsular Indian Rivers: An inversion approach” has been carried out by me at the Department of Earth and Climate Sciences, IISER Pune, under the supervision of Dr. Gyana Ranjan Tripathy and the same has not been submitted elsewhere for any other degree.

Aswin

Aswin Pradeep T

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Abstract

Chemical weathering of silicate minerals act as a major sink for atmospheric CO_2 in a geological timescale. These continental weathering processes are higher in tropical regions, mainly due to conducive climate (higher temperature and intense rainfall). The rivers in the peninsular India predominantly drain silicate terrains and hence, weathering in from this region is likely to play an important role in global carbon budget. Recognizing this, appreciable amount of geochemical studies of these Individual rivers have been carried out at basin-wide scale; however, a comprehensive study considering all the Peninsular Indian rivers is still pending. The present study aims to study these rivers, by using the available major element geochemical information from literature, to quantify the chemical weathering in the region, associated CO_2 consumption and understand the factors regulating the phenomenon.

The river water chemistry of the Peninsular Indian rivers are mainly dominated by Ca and HCO_3, hinting at dominant role of carbonate weathering influencing the hydrochemistry. Although the rivers predominantly flow through silicate terrains, the faster dissolution kinetics of carbonates supply significant amount of solutes to these basins. The chemical compositions of these rivers also show strong seasonal variations, mainly due to relative changes in silicate-to-carbonate weathering. The silicate weathering rates (SWR) and hence, the CO_2 consumption potential of these rivers are by and large found to be higher when compared to the corresponding rates for the global average for rivers. Two Archean flowing rivers, the Damodar and Subranrekha, are found to have high SWR compared to other Archean drain streams (Mahanadi and Nethravati). The observed higher SWR for Damodar and Subranrekha is mainly due to sulphuric acid-mediated weathering in these basins. Relatively higher SO_4/HCO_3 ratios observed for these two rivers also support the H_2SO_4-mediated weathering. The H_2SO_4, a relatively stronger acid, may form through oxidation of sulphidies and/or anthropogenic supplies from mines present in these basins. Unlike the CO_2-mediated weathering, the H_2SO_4-mediated weathering from these basins can act as an important source of CO_2.

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Chapter 1

1.1 Introduction

Rivers are important pathways in transporting dissolved and particulate materials from continents to the ocean and hence, play a crucial role in landscape evolution and geochemical cycling of elements (Berner, 2004; Krishnaswami and Tripathy, 2012). Further, riverine processes involving chemical weathering of silicate minerals act as a major sink for atmospheric CO_2 over a geological timescales. The CO_2 content in the atmosphere, on large timescales, is balanced by fluxes coming out from weathering of silicate rocks, the burial and weathering of sedimentary organic matter and volcanic degassing (Ebelmen, 1845; Walker et al., 1981; Berner et al., 1983; Berner, 2004), and in short time scales the atmospheric CO_2 is moderated by its interaction with soil, vegetation and ocean (Houghton, 2007). It has also been proposed that the carbon dioxide emitted into the atmosphere from volcanic degassing results in increase in temperature which leads to enhanced weathering rates (Berner et al., 1983; Kump et al., 2000). The weathering process in turn utilizes CO_2 and leads to reduction in the temperature. In addition to this weathering-climate linkage, Raymo and Ruddiman (1992) have also invoked important role of tectonics (*via* mountain building) in promoting chemical weathering intensity, which in turn consumptions atmospheric carbon dioxide. The chemical weathering, therefore, is a complex geological process driven by tectonic, climatic, biological and geomorphological factors.

The chemical weathering affects the carbon cycle through the process of removal of carbon from the atmosphere and storing it in the products of weathering (Fig. 1). Photosynthesis by plants initiates the fixation of carbon to the soil as organic acids and CO_2. The acids which contain the carbon react with the carbonate and the silicate minerals leading to formation of bicarbonate. These chemical reactions can be depicted as follows:

For Carbonates :- $CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$ (1)

For Silicates :- $2CO_2 + 3H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4$ (2)

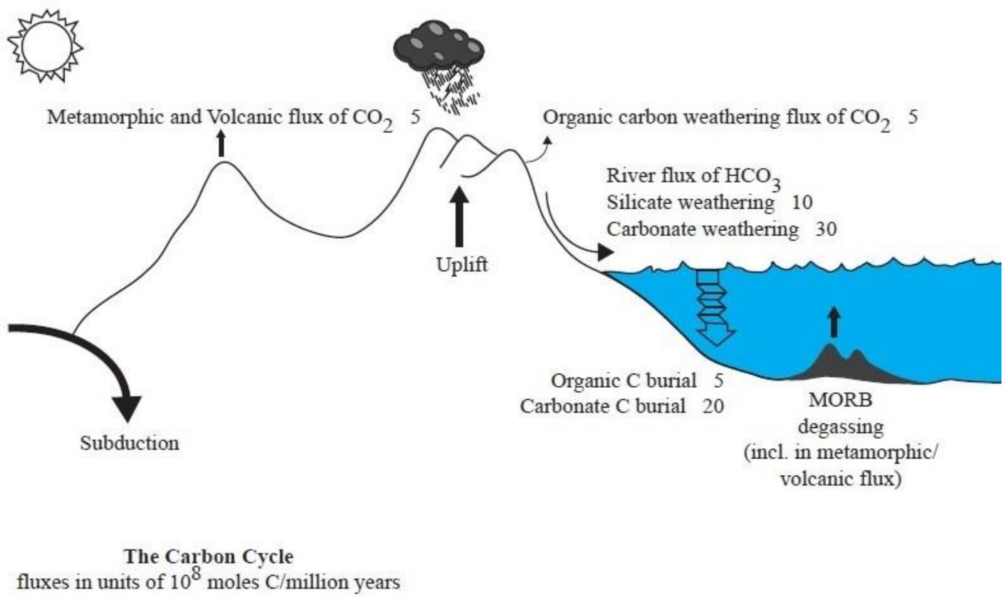

Figure 1: *Sources and sinks of carbon from various reservoirs in a long-term carbon cycle (Figure modified after Ruddiman (1997))*

The Ca^{2+} and HCO_3^- formed during the continental weathering process are transported to the oceans and are removed to the sediments as $CaCO_3$ by releasing one mole of CO_2 to the atmosphere. This chemical reaction is as follows:

In oceans - $Ca^{2+} + 2HCO_3^- \rightarrow CO_2\uparrow + H_2O + CaCO_3$ (3)

Hence it can be clearly seen that weathering of silicates (reactions 2 and 3) acts as a sink for the atmospheric CO_2, whereas during weathering of carbonates, there is no net drawdown of carbon dioxide from the atmosphere.

In addition to carbonic acids, various other natural acids can also provide the proton required for chemical weathering. These natural acids are sulphuric acids, hydrochloric acids, organic acids, etc (Lerman et al., 2007). Formation of sulphuric acid is often linked with oxidation of sulphide minerals, e.g. pyrite. The related reaction can be described by the following chemical reaction:

$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \rightarrow 2H_2SO_4 + Fe(OH)_3$ (4)

Unlike carbonic acid, the chemical weathering mediated by sulphuric acid do not consume atmospheric CO_2. In fact, the weathering of carbonate minerals involving the H_2SO_4 acid can serve as a natural source for CO_2.

$$2CaCO_3 + H_2SO_4 \rightarrow 2Ca^{+2} + 2HCO_3^{-} + SO_4^{2-} \rightarrow CaCO_3 + CO_2 + Ca^{2+} + SO_4^{2-} \quad (5)$$

Few inorganic acids, such as HNO_3 and HCl, may also produce through volcanic eruptions, biogeochemical reactions on the land or ocean surfaces. Decomposition of organic matter may also produce organic acids (RCOOH) on the land surface. All these naturally-produced acids can promote chemical weathering.

The chemical weathering of rocks can be either congruent and/or incongruent in nature; and along with dissolved solutes, may or may not residual products. The type and abundances of major ions observed in river waters is mostly driven by chemical weathering of rocks, atmospheric inputs, and/or anthropogenic supplies. The major dissolved cations observed in rivers are Na^{+1}, K^{+1}, Ca^{+2}, Mg^{+2} and SiO_2, whereas those of anions are HCO_3^{-1}, Cl^{-1}, and SO_4^{-2}. Typical sources for these major ions are listed in Table 1.

Table 1: Possible sources for dissolved major ions in rivers (Krishnaswami and Singh, 2005)

Major ions	Sources
Na	Atmospheric deposition, Silicate weathering, Evaporites, Anthropogenic inputs
K	Atmospheric deposition, Silicate weathering, Biogological activities, Anthropogenic inputs
Ca	Silicate and carbonate weathering, Evaporites, Anthropogenic Supplies
Mg	Silicates and carbonates
HCO_3	Atmospheric and soil CO_2, Weathering of silicate and carbonates
Cl	Rain, Evaporites, Anthropogenic supplies
SO_4	Rain , Evaporites, Pyrites, Anthropogenic supplies

1.2 Factors regulating Chemical weathering in Peninsular Indian river basins

Recognizing important role of silicate weathering on atmospheric CO_2, large number of geochemical studies were carried out worldwide to estimate the weathering rates and the associated CO_2 consumption rates (Krishnaswami et al., 1999; Gaillardet et al., 1999; Das et al., 2005; Singh et al., 2005; Moon et al., 2007; Tripathy and Singh, 2010). These studies showed that the weathering rates are, in general, are higher for Tropical Rivers (Lerman et al., 2007) and play dominant role in global carbon budget. Some of these major tropical rivers flow in the Indian sub-continent and these rivers have also been studied for their geochemical composition in detail (Sarin et al., 1989; Galy and France-lanord, 1999; Dessert et al., 2001; Dalai et al., 2002; Das et al., 2005; Singh et al., 2005; Jha et al., 2009; Rai et al., 2011; Gupta et al., 2011). Researches on the Himalayan Rivers have identified that intense weathering in these basins promoted the global cooling during the Cenozoic era (Krishanswami et al., 1992; Tripathy et al., 2012). Rivers draining the Peninsular India mainly flow through Deccan basalts and/or Archean granites, and hence, are likely to have high silicate weathering rates. The available results from the studies in peninsular Indian rivers show that the chemical weathering rates and the associated CO_2 consumption in these rivers vary widely and depend on many factors like heterogeneity in the lithology, the elevation and the climatic variations, intensity of monsoon, soil and the vegetation coverage in the region. The observed controlling factors driving the chemical weathering in the peninsular India has been described below.

<u>Narmada and Tapti</u>

Runoff and temperature variations within the Narmada basin has been reported as key factors controlling the chemical weathering rate in this river (Gupta et al., 2011). A strong correlation between the runoff and the chemical weathering rates has been reported for this basin. Saline and alkaline soils cover significant area of the Narmada basin. The contribution of dissolved solutes from these soils to the Narmada river water shows a fair coupling with temperature, owing to the formation of saline/alkaline soild under hotter climate. Higher concentrations of sodium, calcium and dissolved silica in Tapti River indicates presence of Na-rich silicate rocks in the basin, reflecting the role of lithology in regulating the chemical weathering intensity (Sharma and Subramanian, 2008).

Mahanadi

Previous studies on River Mahanadi suggest that the lithology plays a dominant role in controlling the chemical weathering in the basin (Chakrapani and Subramanian, 1990; Panigrahy and Raymahashay, 2005). The upper part of the basin comprises of limestones (dolomitic and stromatolitic), shales and traces of sandstones. Hence, the carbonate weathering in these sub-basins are higher than the silicate weathering (Chakrapani and Subramanian, 1990; Panigrahy and Raymahashay, 2005). The average partial pressure of the Mahanadi river and its tributaries ($P_{CO2}=10^{-2.464}$) is found to be greater than the atmospheric partial pressure ($10^{-3.5}$) (Panigrahy and Raymahashay, 2005). The disequilibrium produced thereby is possibly due to (1) contribution of CO_2 from ground water source and (2) higher rate of solubility of CO_2 than the rate of release of CO_2 into the atmosphere (Panigrahy and Raymahashay, 2005). The acidity caused by such dissolved CO_2 in the river also increases its weathering capability.

Godavari

Based on the erodibility the rock type in the Godavari basin has been classified into (1) Granites and the hard rocks, (2) Deccan traps, (3) Sedimentary rocks (Biksham and Subramanian, 1987). The Deccan traps cover nearly half of the drainage area of Godavari basin and its contribution to the solute load is also proportional. Study on the seasonal and monthly variations indicates that the maximum discharge of water and sediments occur during monsoon (93-96% of water and 96% of sediments; Biksham and Subramanian (1987)). It has also been observed that the partial pressure of CO_2 for selected seasons is higher compared to the atmospheric partial pressure of CO_2 (Jha et al., 2009), ultimately leading to increase in the concentration of CO_2 in the basin, which in turn can make the water mildly acidic, thereby accelerating the chemical weathering.

Krishna and west flowing rivers of Western Ghats

Correlation between runoff and chemical weathering rates have been reported in case of the river Krishna and certain west flowing rivers in the Western Ghats (Das et al., 2005).

The higher chemical weathering rates was observed for the west flowing rivers when compared to the Krishna river, attributable to the runoff variation between the two regions (Das et al., 2005). The CIA (Chemical Index of Alteration) values of the sediments in the basin are high (42-90) in the regions experiencing higher rainfall and runoff. At the same time the semi-arid climate in the region helps in the precipitation of $CaCO_3$, resulting in lower CIA values in sediments and hence reducing the erosion (Das and Krishnaswami, 2007).

Kaveri, Palar and Ponnaiyar

Climatic conditions and the lithology of the basin are the determining factors of chemical weathering in the Kaveri, Palar and Ponnaiyar Rivers. Both the SW and the NE monsoons influence the water flux of these rivers, which drain Archean granatoid gneisses in the upper reaches and granulites in the middle reaches respectively (Pattanaik et al., 2013). Silicate rocks are found to contribute most (90%) of the dissolved ions to the river. Compared to certain other tropical rivers (like Amazon, Orinoco, Parana), the Kaveri basin is observed to have higher rate of CO_2 consumption; intense weathering of mafic and felsic granulites in this region aided by SW and NW monsoon explains this observation (Pattanaik et al., 2013).

1.3. Objectives of this study

The Peninsular Indian rivers predominantly drain through silicate terrains and the estimated chemical weathering rates in these rivers were often reported to be higher than other large rivers in the world (e.g. Amazon and Zaire). The solute load contributed by these rivers has a crucial contribution to the global ocean budget. Although large number of geochemical studies has been carried out, a coordinated and systematic investigation of weathering pattern of all these Peninsular Indian rivers has not yet been carried out. For this, the major objectives of this study are identified as to

- Reanalyze available geochemical dataset for the peninsular Indian rivers to estimate the silicate and carbonate weathering rates.
- Develop and employ an inverse model for proper estimation of the source contribution from different sources and the weathering rates.

- Compare results from the inverse and forward models to infer type of chemical weathering in the Peninsular Indian river basins.

Chapter 2

Study Area and Data source

Large number of geochemical studies has already been reported for of the Peninsular Indian river waters (Das et al., 2005; Jha et al., 2009; Dessert et al., 2001; Gupta et al., 2011; Vaithiyanathan et al., 1992; Pattanaik et al., 2007; Chakrapni and Subramanian, 1990; Panigrahy and Raymahashay, 2005; Gurumurthy et al., 2012; Singh and Hasnain, 1998; Singh et al., 2005). In this study, these available data for the major cations and anions for the Rivers from the peninsular India were compiled and reanalyzed. The Rivers namely Narmada, Tapti, Godavari, Mahanadi, Nethravathi Krishna, Kaveri, Palar, Ponnaiyar, Subernarekha, Damodar, Subernarekha, Sabarmati and Mahi have been focused.

Table 2: Hydrological parameters of Peninsular Indian Rivers (Milliman and Fransworth, 2013)

River	Water discharge, Q (km^3/yr)	Drainage Area, A (10^3 km^2)	Climate
Narmada	38	99	Tr-SA-S
Tapti	9	65	Tr-SA-S
Godavari	120	310	Tr-H-S
Krishna	62	260	Tr-A-S
Kaveri	21	88	Tr-H-S
Palar	2	18	Tr-SA-S
Pennar	6.3	55	Tr-A-S
Ponnaiyar	1.6	16	Tr-A-S
Mahanadi	54	140	Tr-H-S
Nethravathi	4.6	4.2	Tr-W-S
Subernarekha	10	19	Tr-H-S
Damodar	9.4	22	Tr-H-S
Sabarmathi	1.4	21	Tr-H-S
Mahi	12	35	Tr-H-S

Tr-Tropical, H- Humid, SA-Sub Arid

2.1. Geohydrology of the river basins

Table 2 lists the annual water discharge and the drainage area for the Peninsular Indian Rivers. The water discharges of these rivers vary by two orders of magnitude, providing a good opportunity to assess the chemical weathering changes due to runoff. About ~80% of these water fluxes are observed during the monsoon period (Fig. 2). In addition to the south-west monsoon, some of these rivers are also influenced by the north-west monsoon. The geology of the peninsular India (Fig. 3) together with the climate of the region play important role in controlling the hydrogeochemistry of the rivers. Located in the western central part of India is the Deccan trap and with an average elevation of 750m (Dessert et al., 2001). The region has an average annual temperature of 25˚C. The period between June to September experiences the major part of the rainfall.

The Deccan provinces are one of the largest basaltic regions with a volume of 10^6 km^3 and an area of approximately 5 x 10^5 km^2 (Courtillot et al., 1986). The Deccan basalts have mainly a tholeiitic composition containing phenocrysts of plagioclase, clinopyroxene, altered olivine, opaque minerals and altered glass (Dessert et al., 2001). The rivers, Narmada and Tapti, predominantly flow through the Deccan, whereas 26% of River Krishna and 48% of River Godavari flows through the Deccan traps (Das et al., 2005; Biksham and Subramanian, 1998). Alluvial soils, black soils, red soil and lateritic soils are seen the Narmada basin (Gupta et al., 2011). These soils are observed to contain chlorides, bicarbonates and carbonates of Sodium (Das et al., 2005). The soils in the basins of this region are mostly dominated by Black colored vertisols and laterites (Das et al., 2005). Calcium carbonate forms another minor lithology in these basins. The vegetation in the western ghat region of the Deccan traps show variations according to the change in the climate. The tropical evergreen forests are located in the regions of high altitude as these regions receive more rainfall and the regions which have a semiarid climate are show dry deciduous vegetation (Das et al., 2005).

River Godavari and its tributaries, in its lower reaches mostly drain the Archean rocks, composed of phyllites, schists and amphibolites; Precambrian and the Gondwana sedimentary rocks, charnokite rocks, khondalite rocks (eastern part) and the recent alluvials, apart from the Deccan traps in the upper reaches (Jha et al., 2009). Semi-arid

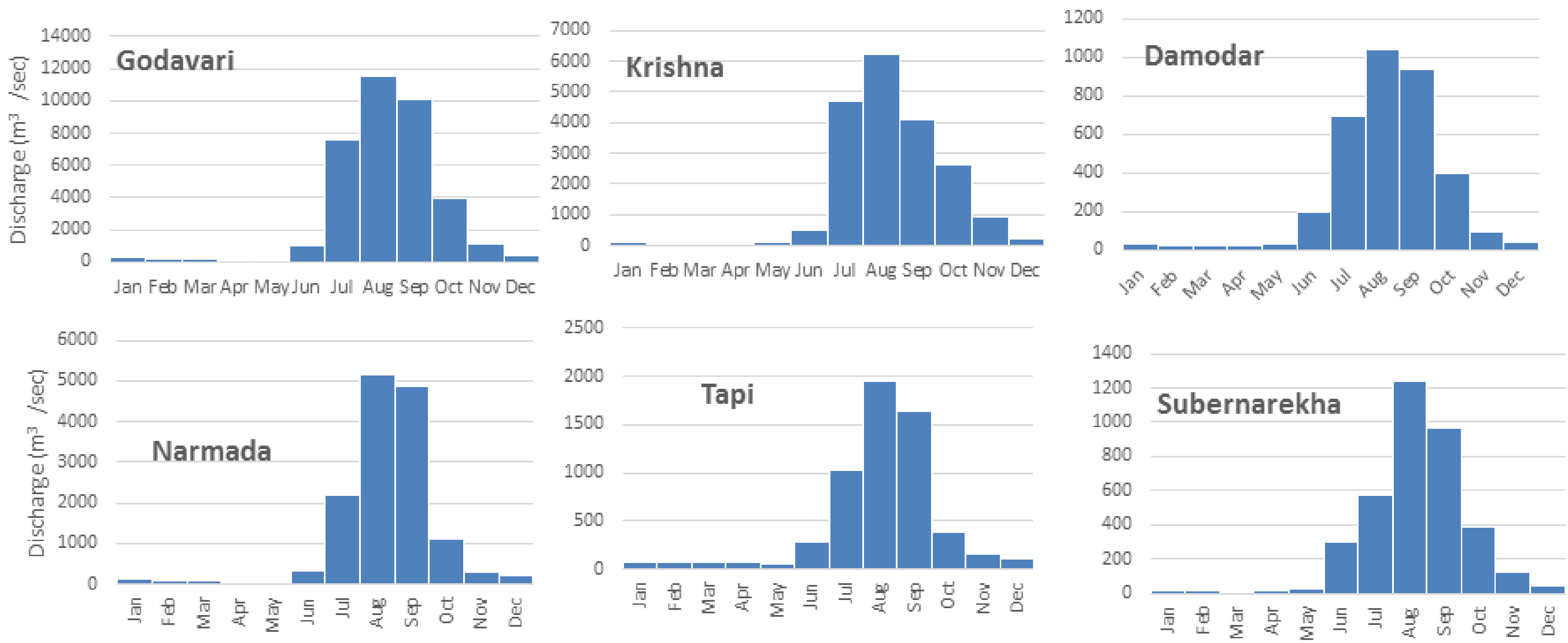

Figure 2: *Average Monthly data of water discharge for selected Peninsular Indian rivers (http://www.grdc.sr.unh.edu/index.html)*

to monsoonal climatic variations are observed in Godavari basin and the annual water discharge depends mostly on the monsoon.

Nearly 74% of the Krishna River flows through the Archean and the younger crystalline rocks and the upper region of the river flows through the Deccan traps (Fig. 3). Bhima, the largest tributary of Krishna River flows mostly (~ 80%) through the Deccan traps, whereas the tributary Thungabhadra drains 70% Archean rocks and the remaining through the Precambrian crystalline rock terrains (Sharma and Subramanian, 1988). Except a region of arid zone in the centre, the basin mainly has a semi-arid climate (Sharma and Subramanian, 1998). The southwest monsoon is the main contributor of rainfall in the basin.

The upper reaches of River Kaveri flows through Archean greenstone granite, minor granulite and dykes of Paleoproterozoic age of Dharwar craton (Pattanaik et al., 2013). In the middle reaches the river is drains through granulites and migmatitic gneisses. The granulites of the Nilgiri Hill are drained by River Bhavani, a major tributary of Kaveri and the granulites are composed of granitiferous enderbites and basic granulites (Pattanaik et al., 2013). Amaravati, another tributary of Kaveri, completely flows through the granulite, anorthosite and migmatised gneisses. Originating from the eastern Dhawar craton, the Palar and the Ponnaiyar Rivers, in the upper reaches flow through the granitoid gneisses, granitoid intrusives and supracrustal rocks (Pattanaik et al., 2007). Presences of granulites are also seen in the middle regions of the Palar River. The Archean rocks in the eastern Dharwar craton, granulites and Recent alluvium are found in the regions of flow of the Ponnaiyar River (Pattanaik et al., 2007). The rocks of Precambrian age experience most of the physical and the chemical weathering in this region. The Basin receives rainfall during South-West monsoon (June-September) and North-East monsoon (October-December), and it has been observed that the SW monsoon contributes to the maximum water flow and sediment load in the upper reaches whereas in the middle and the lower reaches the NE monsoon causes maximum water flow and sediment load.

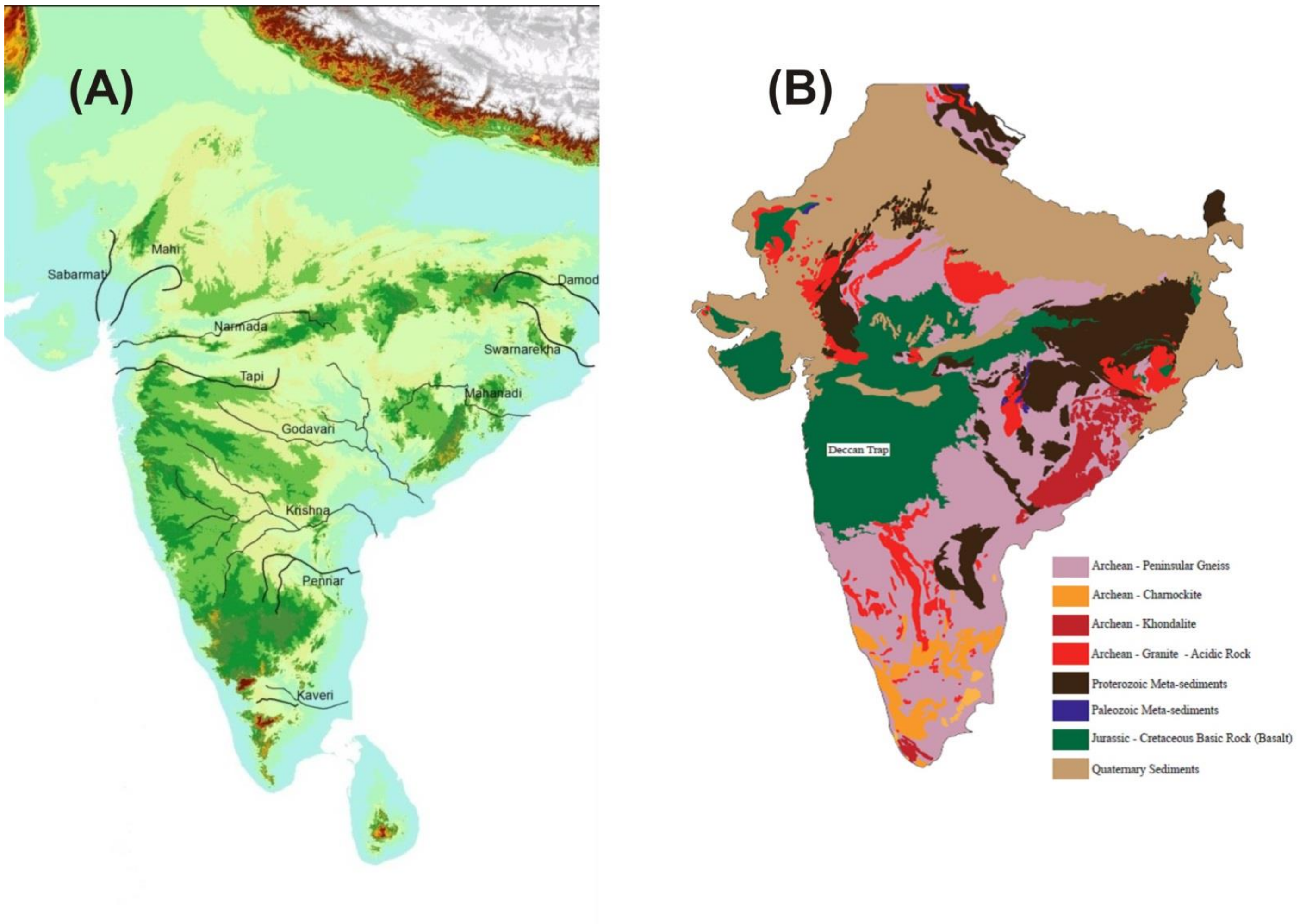

Figure 3: *(A) Digital elevation map showing the peninsular Indian rivers; (B) Geological map of the study area (Modified after the GSI, 1988-89).*

The Mahanadi, is second major river in the peninsular India with respect to its water potential (Panigrahy and Raymahashay, 2005). The upper regions of the Mahanadi basin are formed by the Chhattisgarh basin, sedimentary formations of which are underplayed by the Archean rocks (Panigrahy and Raymahashay, 2005). The dolomitic and stromatolitic limestone and shales with pockets of sandstones are found to dominate the basin area. A very high rate of evaporation (152 cm in east – 174 cm in west) has been reported for the basin by the IMD. The climate in the region varies from tropical to subtropical with 144 cm of average rainfall.

One of the largest rivers in the eastern India, River Damodar, shows a variable topography and geology. The river basin is composed of rocks of Archean age (granite and granitic-gneisses) and sandstones and shales of the gondwana and Recent alluvials (Singh et al., 2005). The granitic rocks show various textures ranging from fine to coarse grained and porphyritic. Dominance of quartzites, biotite gneisse, granetiferrous gneiss and schist and acid granulite along with hornblende and amphibolites of Archean age is seen in the basin (Singh et al., 2005). Though known to be an extremely rich reservoir of Indian coal, Damodar basin is poor in metallic minerals.

Figure.3 depicts the large variation observed in the elevation and lithology in the Peninsular Indian river basins. Figure 3A is an elevation map showing the peninsular Indian rivers. The elevations in the peninsular India are seen to vary from 106m to 1900m. Regions of very high elevation are seen in the south along the Western Ghats. These geological features of the basin play key role in driving the weathering pattern of the rivers. The lithology of peninsular India is shown in Figure (3B). The region can be broadly classified into the Deccan and Archean region. The peninsular gneiss, which are metamorphic rocks are found all over the peninsular India and are considered to be the oldest rocks in the region. Charnokite rocks are found in the margins of Dharwar craton and also southern regions of Karnataka. Khondalite rocks are found in the Eastern Ghats between Vijayawada and Cuttack. The Deccan traps are one of the largest basaltic regions and have a theolitic composition containing phenocrysts of plagioclase, clinopyroxene, altered olivine, opaque minerals and altered glasses.

2.2. Data Source and its quality

Geochemical datasets from various earlier publications have been used in this study for their reanalysis. For the river Narmada, researches by Gupta et al. (2011), Dessert et al. (2001) and Lambs et al. (2005) are used. River chemistry data from Dessert et al. (2001) and Lambs et al. (2005) are used for the river Tapi. Data for Damodar comes from Singh and Hasnain (1999) and Singh et al. (2007), whereas those for Subranrekha are reported by Negrel et al. (2007). Chemical compositions of the river Mahandi are reported by Chakrapani and Subramanian (1992), Panigrahy and Raymahashay (2005) and Lambs et al. (2005). We complied the data reported by Jha et al. (2009), Dessert et al. (2001), Das et al., (2005) and Lambs et al. (2005) for the river Godavari and Krishna river. Geochemical studies by Gurumurthy et al. (2012) and Lambs et al. (2005) have been used for the River Nethravathi. For the Rivers Kaveri, Palar and Ponaiyyar, data are compiled from Pattanaik et al. (2007, 2013) and Lambs et al. (2005). For other peninsular Indian rivers like Sabarmathi and Mahi, river chemistry data from Rahaman et al. (2012) have been used.

The cationic charge (TZ^+) and the anionic charge (TZ^-) do not seem to be in balance for some of the compiled data set. The anomaly observed can be due to either from (i) contribution of organic acids comprising of acetates, oxalates or, (ii) poor data quality. NICB (Normalized Inorganic Charge Balance) is a parameter used to identify the extent of inorganic charge balance in the river. In the present study a cut off of NICB $\leq$ 10% has been fixed as a criteria for the data quality. Samples with NICB greater than 10% are not included for the weathering rate estimation in this study.

CHAPTER 3

Results and Discussion

The river chemistry is mainly regulated by relative supply of dissolved solutes from various sources, which includes atmospheric deposition, weathering of bed rocks (silicate and carbonates) and saline-alkaline soils. Apportioning these sources is required to estimate supply of cations from silicate weathering, which is a long-term sink for atmospheric CO_2. Different models have been proposed in order to deduce the fractional contribution of various ions from their respective sources. In these models Na normalized elemental ratios have been used because of its conservative behavior in the river system and sources being better constrained. In certain basins which are dominated by alkaline and saline salts Mg and Si have been used as an index of silicate weathering and not Na (Das et al;2005).

Table 3: Typical major ion compositions in Peninsular Indian Rivers at their outflow.

	Na(μM)	K(μM)	Ca(μM)	Mg(μM)	Cl(μM)	SO_4(μM)	HCO3(μM)	NICB	Reference
Narmada	310.7	42	489	235	108	28	1739	0.92	Lambs et al., 2005
Tapti	423.1	37.6	471.9	257.6	246.8	50.4	1619.7	0.94	Lambs et al., 2005
Godavari	243.1	43.5	361.8	146.1	68.5	23.8	1240.1	0.94	Lambs et al., 2005
Krishna	2600	104.9	777.8	513.9	1205.1	529.4	2801.5	1.04	Lambs et al., 2005
Kaveri	1009	51	881	532	761	238	2624	0.96	Pattanaik et al.,2013
Nethravati	96	13	50	38	72	10	210	0.92	Gurumurthy et al.,2012
Sabarmati	11128	314	683	673	9310	1026	2792	1	Rahman et al., 2012
Mahi	2640	94	321	881	1446	188	3316	1	Rahman et al., 2012
Ponnaiyar	1624	101	940	562	1333	283	3059	0.95	Pattanaik et al.,2007
Palar	568	47	323	204	345	110	1243	0.92	Pattanaik et al.,2007
Mahanadi	274.9	48.1	319.2	140.3	72.8	16	1183.7	0.94	Lambs et al., 2005
Damodar	769	125.6	270	300	248.2	145.8	1385.2	1.06	Singh and Hasnain,1999
Suberbareka	705	72	688	379	299	164	2344	0.98	Negral et al., 2007

3.1. Hydrochemistry of the Peninsular Indian rivers

The typical water chemistry of the Peninsular Indian rivers at their outflow are listed in Table 3. These compositions are mainly dominated by Ca and HCO3, indicating dominant role of carbonate weathering in regulating the river compositions. The composition of these rivers also show strong seasonal variations. Fig. 4 depicts the Ca-Mg-(Na*+K) ternary plots for peninsular Indian rivers from the monsoon (Fig. 4A) and non-monsoon (Fig. 4B) seasons. We used this elements to qualitatively infer the source contributions from the atmospheric input, and weathering of silicate and carbonates. The samples falling near the Na+K apex indicates contribution from the silicates and the points falling towards the Ca and Mg apex are representations of carbonate weathering. We have used all reported geochemical datasets here in this ternary plot and have not employed the data quality assesment for this plot (Fig. 4). During the monsoon season, most of the samples from Tapi, Krishna, Kaveri, Godavari fall near the Na+K apex and these represent relatively higher contribution from silicates in these river basins. It is also observed that few samples from river Damodar and Mahanadi showing more contribution from the silicate rocks during the monsoon season compared to the non-monsoon. Most of the sample points of river Narmada are observed in the Ca apex which indicate carbonate weathering in this river is more compared to silicate weathering in the monsoon season. Majority of the points in Fig. 4 are seent o group in the cente of the plot indicating that during the monsoon period silicate as well as carbonate rocks are seen to contribute to the solute load in these rivers. During the non monsoon duration, which includes the post monsoon and the pre monsoon periods, it is observed that most of the samples from the Tapi river fall near the Na+K line, with exception of certain samples from River Narmada and few samples from River subernarekha which show relatively higher contribution from carbonate rocks. These results show that the weathering pattern and the relative supply of solutes from rocktypes vary depending on the season. In addition to climate, other factors like lithology, soil distribution, elevation of the basin and temperature can also contribute to the process of chemical weathering in peninsular India.

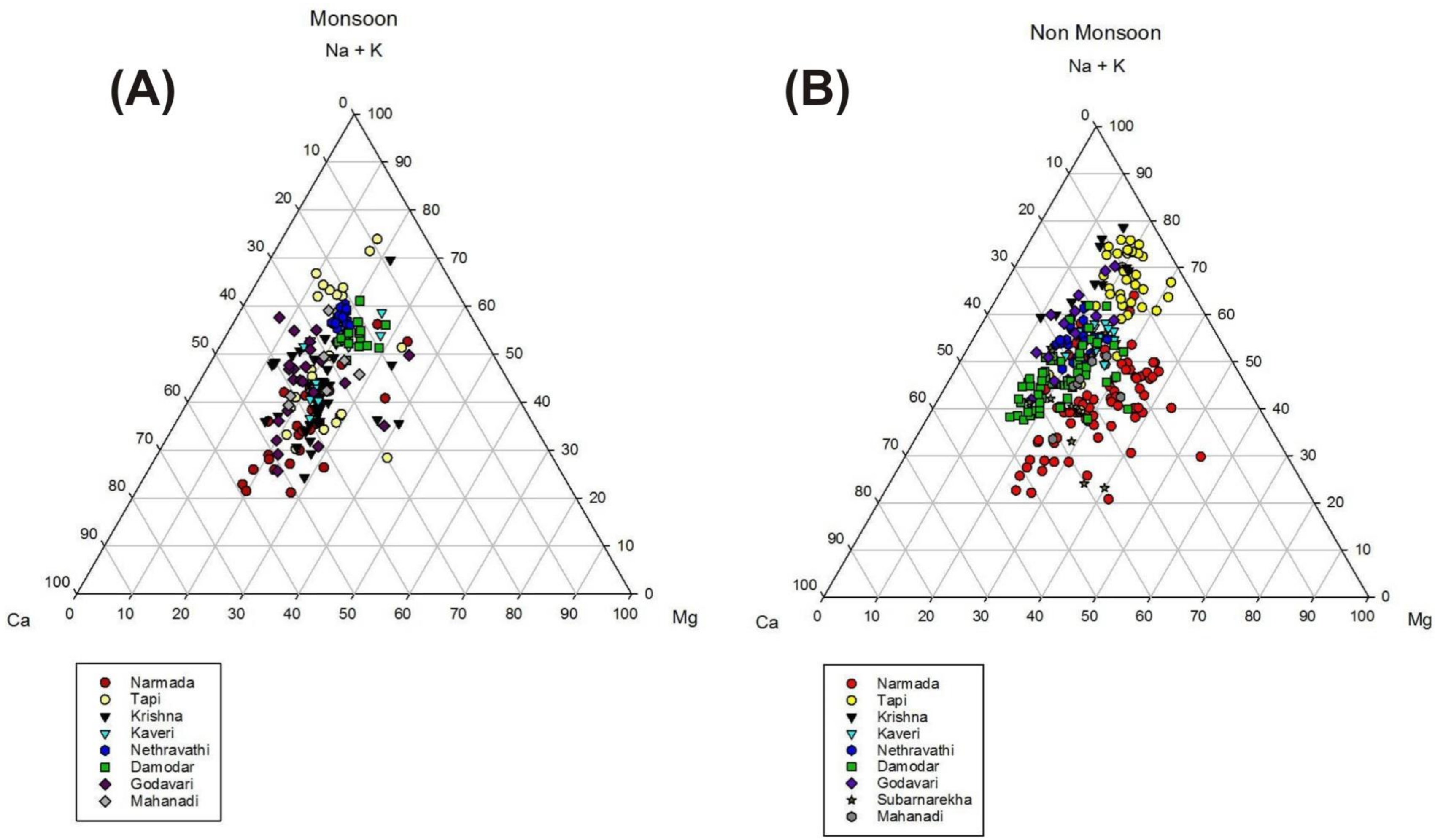

Figure 4: *Ternary diagram showing the chemical composition of Peninsular Indian rivers during (A) monsoon and (B) non-monsson seasons. See text for data source.*

3.2. Forward modelling

The forward modelling approach is based on the assumption that the Na ions are contributed only by atmosphere, halite and silicate weathering. This model also assumes that contribution of Na ions is equal to the Cl ion contribution (Krishnaswami et al; 1999). Cations derived from the silicates can be estimated as given below.

$$Na_s = Na_r - Cl_r \qquad (6)$$

$$K_s = K_r \qquad (7)$$

$$Ca_s = Na_s \times (Ca/Na)_{sol} \qquad (8)$$

$$Mg_s = Na_s \times (Mg/Na)_{sol} \qquad (9)$$

In the above equations, $(X/Na)_{sol}$ represents the elemental ratio of release of an element X to a river from the silicates. Forward modelling has been used to quantify contributions from other reservoirs too (Galy and France-Lanord, 1999; Moon et al., 2007).

In this study, a similar approach has been used to estimate the silicate weathering rate and the associated CO_2 used consumption for the peninsular Indian rivers and results from this approach is given in the Table 4. The $(Ca/Na)_{sol}$ and $(Mg/Na)_{sol}$ for the rivers draining the Deccan and the Archean regions has been attributed separately. For rivers draining the Deccan traps (Narmada and Tapi), $(Ca/Na)_{sol}$ and $(Mg/Na)_{sol}$ values used are 2.34 and 1.96 respectively (Das et al., 2005). For rivers draining the Archean terrain the $(Ca/Na)_{sol}$ and $(Mg/Na)_{sol}$ of 0.5 and 0.44 (Pattanaik et al., 2013) have been used for the analysis. Further, for rivers draining both Deccan and Archean terrains (Godavari and Krishna) area weighted value of $(Ca/Na)_{sol}$ and $(Mg/Na)_{sol}$ have been used for the analysis. The results of the forward model have been summarized in the Table 4.

The silicate weathering and the associated CO_2 consumption in the peninsular Indian rivers (Table 4) are observed to be higher when compared to the global average estimates. The CO_2 consumption values vary from 0.97×10^5 – 11.49×10^5 moles/Km^2/yr and the SWR vary between 1.9-20.9 tones/Km^2/yr. The CO_2 consumption in Narmada and Tapi are almost the same since they drain these mainly Deccan traps. Similar observations can also be seen for rivers Nethravati and Mahanadi, as both these rivers drain mainly the Archean terrains. It is interesting to note very high silicate erosion rate among rivers Damodar (15.8 t/km^2/yr) and Subarnarekha (14.1 t/km^2/yr). There are lots of industries and mining areas near these areas and as a result anthropogenic inputs do influence the chemical weathering in these rivers. Acid mine drainage, which refers to the outflow of acidic water from the mining sites are a threat to these rivers. FeS_2, also known as pyrites are often found in conjunction with valuable metals and in most of the cases the acids released in these rivers come from oxidation of these pyrites. The sulphuric acid-mediated weathering in these two rivers also evident from their high SO_4/HCO_3 ratios compared to other Archean rivers (Mahanadi, Nethravathi; Table 3). The acid formed, mainly sulphuric acid, mediate can mediate the process of chemical weathering in these rivers. In such a case there is no CO_2 consumption from the atmosphere, instead it acts as a source of CO_2. Chemistry of these rivers need to be studied for better understanding of weathering process in these rivers. CO_2 consumption in Kaveri is low (0.9×10^5 moles/km^2/yr) compared to other rivers flowing in peninsular India. Heterogeneity of the lithology in these regions needs to be taken into account when quantifying chemical weathering rates in such a river and designation of proper end member values can give a more reliable estimates for the weathering process occurring in such rivers.

Table 4. Results from forward model for the silicate weathering rates (SWR) and CO_2 consumption in peninsular Indian rivers. For comparison, the corresponding global average values for rivers (Gailardet et al., 1999) are also given.

Rivers	CO_2 consumption(10^5 moles/Km2/yr)	SWR (tons/km^2/yr)
Narmada	5.99	10.5
Tapi	4.51	7.9
Godavari	2.18	4
Krishna	11.49	20.9
Mahanadi	2.53	5.1
Nethravathi	2.53	5.1
Subernarekha	7.95	15.8

Damodar	6.97	14.1
Kaveri	0.97	1.9
Sabarmati	2.56	5.1
Mahi	4.66	8.9
Global average	0.9	5.4

Efforts are also made in this study to apportion the various sources using an inverse model. This model has been used, to quantify the contribution of ions from different sources and estimate the chemical weathering rate and associated CO_2 consumption for these rivers.

3.3. Inverse model

Inverse model has also been successfully used to quantify the contribution of cations from different sources (Negrel et al., 1993; Gaillardet et al., 1999; Millot et al., 2003; Wu et al., 2005; Moon et al., 2007; Tripathy and Singh, 2010; Moon et al., 2014). Unlike the forward model, the inverse model also gives an estimate of the elemental ratios of the end members. The calculations are based on a set of mass balance equations as give below

$$(X/Na)_r = \sum_{i=1}^{n} \left(\frac{X}{Na}\right)_i * f_i\,(Na) \qquad (10)$$

$$[(^{87}Sr/^{86}Sr)*\left\{\frac{Sr}{Na}\right\}]_r = \sum_{i=1}^{n} \left(\frac{87Sr}{86Sr}\right) i * \left(\frac{Sr}{Na}\right) * fi\ (Na) \qquad (11)$$

$$\sum_{i=1}^{n} fi(Na) = 1 \qquad (12)$$

Where, f_i (Na) represent the mixing proportion of Na from each reservoir. The equations (10-12) can be written in the form of d=g (p), where d and p are the data and the model spaces respectively. These mass balance equations can then be solved by iterative techniques to estimate the best f_i values for each reservoir and the reservoir constraints $(X/Na)_I$. These so called posteriori values are then used to calculate other elemental fractions and weathering rates.

3.3.1. A Priori value of the end members

The rivers draining the peninsular India flow through region with highly variable geomorphology. The end members contributing to the solute load are not the same for all the rivers. Hence different end members have been assigned to rivers draining different regions. Table 5 list the elemental ratios for various end members used for the source apportionment in the peninsular Indian rivers.

Table 5: A priori molar ratio of various end members with their uncertainties

	Rain (a)	Carbonates (b)	Deccan (a)	Archean (c)	Saline-Alkaline (d)	Anthropogenic (e)
Cl/Na	1.52 ±0.32	0.001±0.001	0.001±0.001	0.001±0.001	0.241±0.093	0.583±0.0017
Ca/Na	0.52±0.30	50±20	2.34±1.19	0.24±0.07	0.0133±0.0002	0.567±0.0016
Mg/Na	0.23 ± 0.63	20±8	1.966±1.075	0.08±0.05	0.013±0.00043	0.325±0.0005
HCO_3/Na	1.49 ± 2.49	100±40	8.612± 5.14	0.64±0.148	0.289±0.145	1.486±0.0110

(a) Das et al., 2005
(b) Moon et al., 2007
(c) Pattanaik et al., 2013 ,(d) Rai et al., 2010,(e)Negral et al., 2007

3.3.2. Simulated Annealing

In order to make the best estimate for the fraction (fi) and the end-member ratios (X/Na)I defined in the equations (10-12), we have used a Simulated Annealing (SA) algorithm. The SA optimization algorithm is a global optimization technique which helps the algorithm to escape from a local minimum by adding random fluctuations (Kirkpatrick, 1983). The concept of SA has been taken from statistical mechanics. For a hot metallic body, the motion of atoms is controlled by the thermal fluctuations. When the body is allowed to cool, the system finally attains a configuration of minimum energy. In the SA algorithm, temperature is analogous to a defined parameter T and the error is similar to energy. The SA involves following steps-

- The algorithm begins with a trial model m_a and an error associated with it is calculated. The error function, E_a, can be defined as the difference between the observed and the predicted parameters.
- The trial model is perturbed by adding an increment Δm to m_a and error ΔE is evaluated.
- If $\Delta E < 0$, the new model is accepted and if $\Delta E > 0$, the new model is accepted with a probability proportional to exp $(-\Delta E/T)$.

The above process is repeated number of times, following a cooling schedule until the error becomes a constant.

The figure 5 depicts typical representation of the running SA algorithm estimating the global optimal solution following a cooling schedule. The first representation with Error on the y-axis and iteration on the x axis is shown and it shows the misfit (Error) getting reduced with more number of iterations.

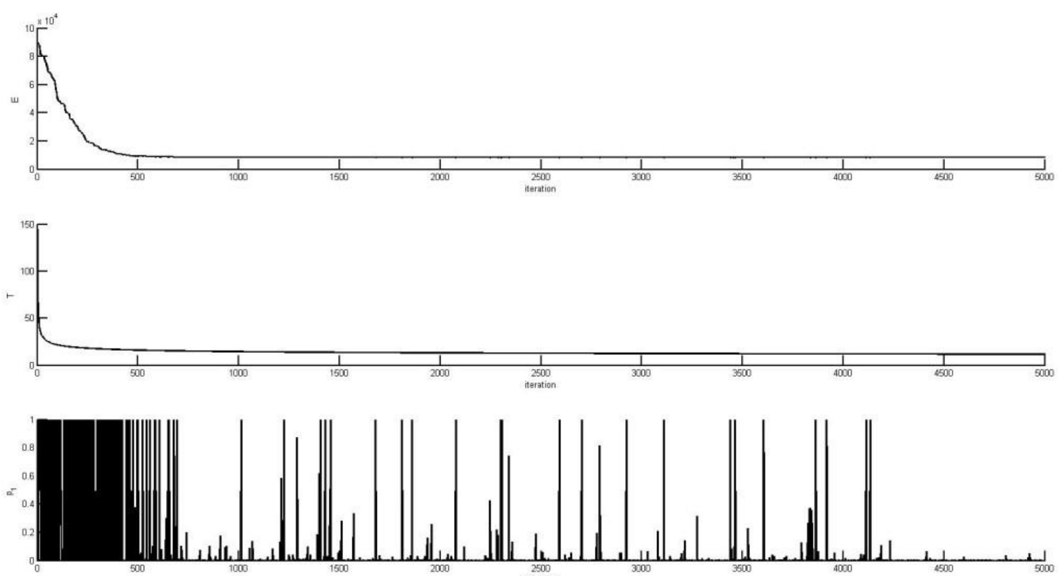

Figure 5: *Schematic representation of Simulated Annealing*

The Fig. 5 (second inset from top) also shows the cooling schedule which drives the algorithm. The temperature is reduced very slowly and attains a minimum once the error is least. The bottom inset in the Fig. 5 shows the variation in the probability of the acceptance of new models in successive iterations. It can be seen that more models are selected in the initial stages (dark band can be seen). As the iteration increases, lesser models are accepted (lines can be seen separate), an as the algorithm progresses the best model is selected.

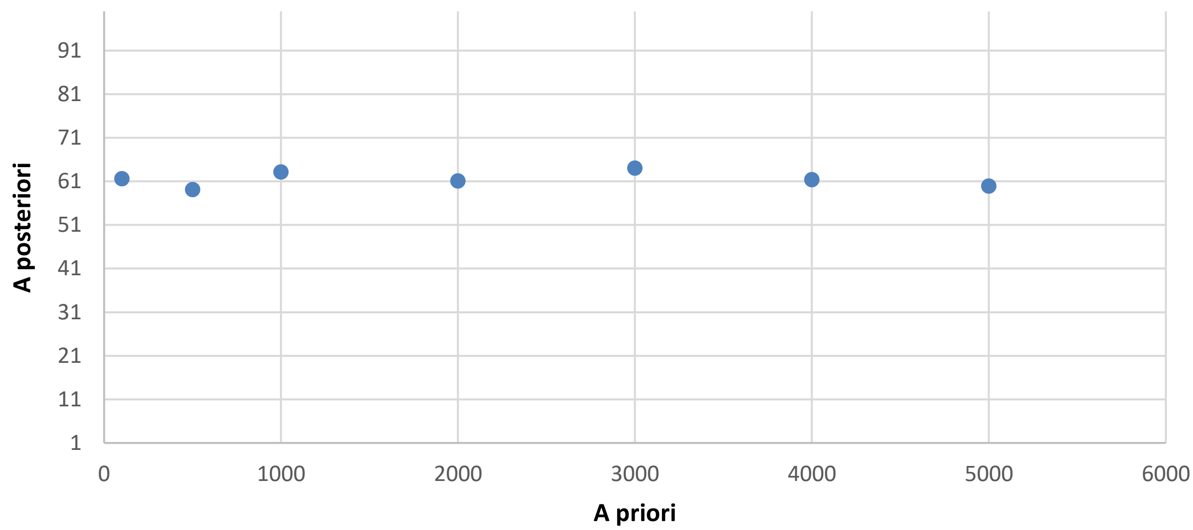

Figure 6: *Sensitivity test of the SA algorithm. The inverse model efficiently converges to similar a-posteriori results for about three order magnitude change in the a-priori data.*

3.3.3. Sensitivity test for the Inverse model

To assess the performance of the proposed algorithm (SA) a sensitivity test of the inverse model was done. A wide range of a priori values were chosen and algorithm was run to check the convergence of the posterior value. Also analysis of Rishikesh river data using the present analysis and the one used by Tripathy and Singh (2010) was done and a good correlation was observed between the two, indicating consistency of the model.

We carried out a sensitivity test of the inverse model by varying the a-priori Ca/Na of carbonates by three orders of magnitude from 50 to 5000 (Fig. 6). The a-posteriori results for Ca/Na in all the cases converge to same ratio of around 55, which establishes the robustness of the model in searching the global optimization (Fig. 6).

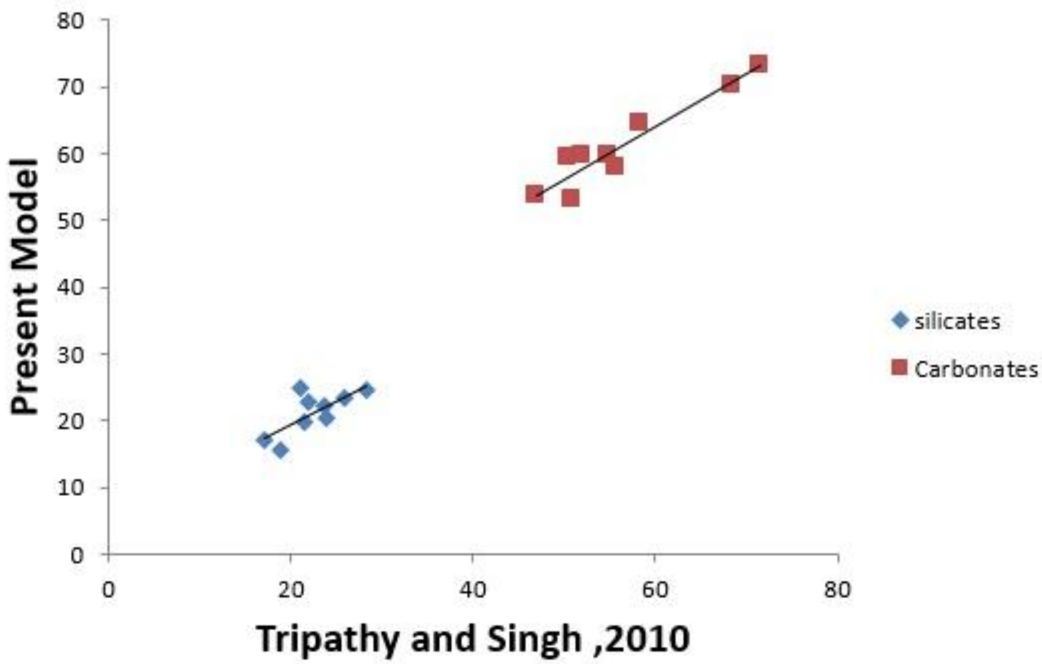

Figure 7: *Comparison of inversion results obtained for the [resent model and the Quasi-Newton algorithm used by Tripathy and Singh (2010). The plot shows contribution of cations from silicate and carbonates using the same river water chemistry data in both the models.*

In addition to this, we re-run the data from Tripathy and Singh (2010) for the Ganga river water chemistry. Fig. 7 compares the results obtained for same dataset for the percentage of cations from silicates and carbonates by using our model and that of the Quasi-Newton approach followed by Tripathy and Singh, 2010.

Table 6 shows the a-posterior values obtained from the inversion procedure for the Peninsular Indian samples. A close observation on the a-priori and the a-posteriori values can tell us how closely they are to each other, an information which may be crucial in understanding the ongoing weathering type (incongruent/congruent) in the basin. Thorough investigation of these preliminary results from the inverse model is in progress.

Table 6: A-posteriori results for different river basins resulted from inversion method.

Narmada and Tapti				
	Rain	**Carbonates**	**Deccan**	**Archean**
Cl/Na	0.702±0.0005	0.0009±0.000013	0.003±0.000028	0.001±0.0000093
Ca/Na	0.012±0.000006	2.484±0.100698	2.767±0.00323	0.098±0.001043
Mg/Na	0.0007±0.00000004	1.475±0.01631	2.678±0.0092	0.070±0.000761
HCO3/Na	0.118±0.00013	13.215±0.04565	9.793±0.06992	0.650±0.005095
Krishna and Godavari				
	Rain	**Carbonates**	**Deccan**	**Archean**
Cl/Na	0.739±0.00023	0.003±0.000076	0.0009±0.0000058	0.003±0.000052
Ca/Na	0.021±0.000012	5.788±0.083988	2.698±0.004731	0.126±0.001565
Mg/Na	0.0005±0.00000025	3.598±0.23621	0.991±0.00799	0.147±0.002477
HCO3/Na	0.085±0.000163	38.166±0.28127	5.802±0.045428	0.661±0.002739
Saline alkaline				
Cl/Na	0.245±0.0001			
Ca/Na	0.011±0.000071			
Mg/Na	0.013±0.00091			
HCO3/Na	0.409±0.00023			
Damodar, Subernarekha and Mahanadi				
	Rain	**Carbonates**	**Archean**	**Anthropogenic**
Cl/Na	0.579±0.0024	0.001±0.000058	0.0007±0.00003	1.762±0.07587
Ca/Na	0.015±0.00036	1.104±0.000029	0.287±0.000016	0.252±0.03611
Mg/Na	0.0008±0.000012	1.115±0.02619	0.162±0.005158	0.742±0.007214
HCO3/Na	0.097±0.00000044	5.143±0.03234	1.414±0.001528	2.000±0.00854
Kaveri, Nethravati, Sabaramati, Mahi, Ponnaiyar and Palar				
	Rain	**Carbonates**	**Archean**	**Anthropogenic**
Cl/Na	0.716±0.000003	0.001±0.004308	0.0003±0.000062	0.746±0.000903
Ca/Na	0.015±0.0000002	3.580±0.0348	0.088±0.000279	0.301±0.00106
Mg/Na	0.001±0.000008	3.778±0.09959	0.086±0.000224	0.288±0.001195
HCO3/Na	0.158±0.000012	16.016±0.0627	0.316±0.000629	1.331±0.000738

The ion concentration at the outflow of the river can gives us an overall estimate of the cationic flux from the river to the ocean. Table 3 lists the typical ion concentrations of rivers draining the peninsular India, sampled at their outflow. These values are used to further calculate the ionic budget from each source and also the cation contribution to the river from different reservoirs.

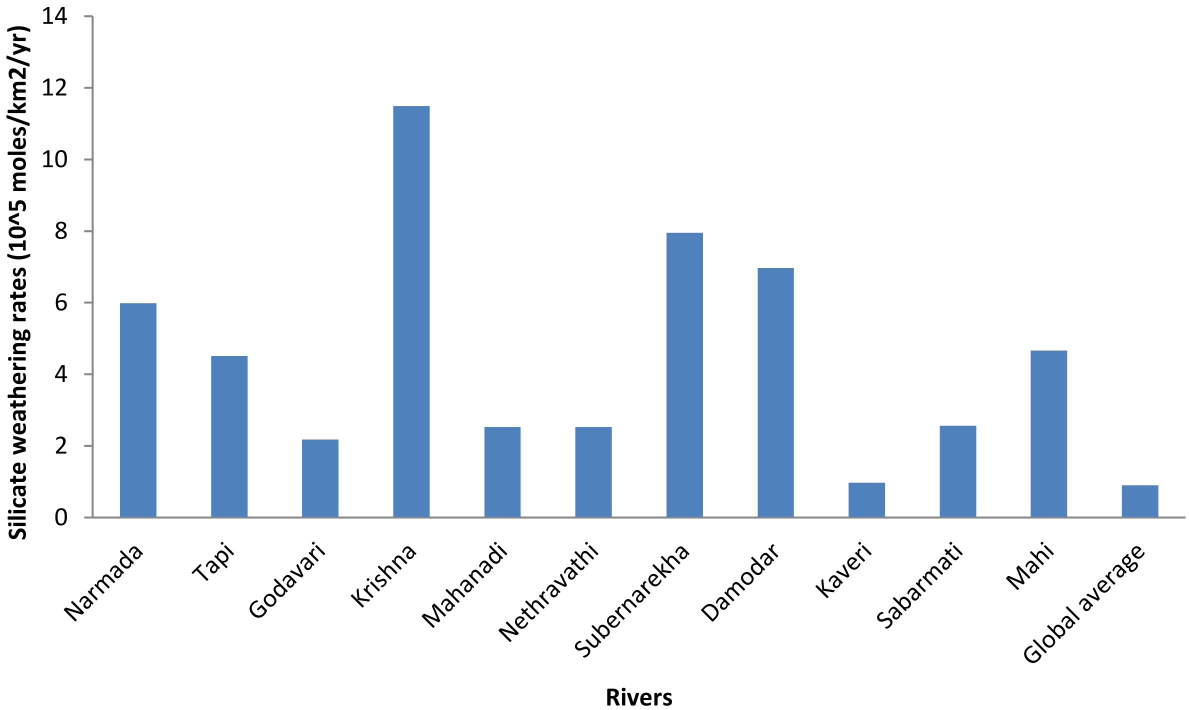

Figure 8: *Comparison of silicate and carbonate weathering rates in Peninsular Indian Rivers using forward model. The global average data is from Gaillardet et al. (1999).*

The a-posteriori results obtained for different river basins were found to be significantly different (Table 6). These elemental ratios are also different when compared to that used in forward models. These differences can be attributed to preferential release of elements from the bedrock to the streams and warrants precise information on source compositions for constraining the erosion rates. These preliminary results from inverse model need to be evaluate thoroughly for better understanding of the weathering pattern and rates of the basins.

We estimated the silicate weathering rates for different river basins by using results from forward model (Fig. 8). The silicate weathering in the rivers draining the peninsular India is found to be higher when compared to the global average. The SWR obtained for the Krishna river basin is found comparable with that reported by earlier study (Das et al., 2005). The dominance of carbonate weathering in Mahanadi has been attributed to the dissolution of the limestones present in the upper reaches of the basin (Panigrahy and Raymahashay, 2005) and our results are in good accordance with the previous observations made on River Mahanadi. River Godavari drains almost half of the region in the Deccan and other half in the Archean region. The silicate weathering rate estimated using the forward model found to be comparable with the global average. River Subarnarekha and Damodar, which flow through regions rich in industrial and mining activities, show higher SWR (Fig. 8). These higher SWR for these two rivers is primarily due to intense chemical weathering mediated by H_2SO_4 acids. These sulphuric acids seem to be formed either by oxidation of sulphides and/or supplies from anthropogenic inputs. These two rivers are also have higher SO_4/HCO_3 ratio compared to other Archean flowing rivers, pointing to sulphuric acid mediated weathering in their basins. It must be mentioned here that the carbonates weathering mediated by sulphuric acid act as a source for atmospheric CO_2. Rivers Sabarmathi and Mahi flowing through similar lithology have silicate weathering rate more than the global average.

Chapter 4

Summary and Conclusions

The present study attempts to provide a comprehensive picture of chemical weathering pattern of the Peninsular Indian river basins. For this, available literature geochemical data for rivers were compiled and reanalyzed using forward and inverse models. These analyses were carried out to apportion the sources for the dissolved solutes and also, to estimate the weathering rates of the river basins. The chemical compositions of these rivers are dominantly regulated by weathering of carbonates, and the silicate weathering play a sub-ordinate role. This indicates that the weathering kinetics of minerals and climate play important role in these tropical regions, whereas lithology seems to be only a minor contributor for chemical weathering pattern of the Peninsular Indian river basins.

The inversion modeling approach is based on mass balance equation for various chemical elements and uses a probabilistic approach and an optimization algorithm (simulated annealing) to apportion the sources. The method is advantageous as it allows us to take into account the uncertainties in the a-priori and a-posteriori values to be addressed. To implement the inversion technique, computational aid was required and a code in MATLAB was developed to run the algorithm. Sensitivity of the algorithm and the program developed was tested by using the algorithm on previously published results and it was noticed that the results are reliable. Forward model as well as inverse model approach were used to estimate the chemical weathering rates for the peninsular Indian rivers. In the forward model calculation only the release ratios $(Ca/Na)_{sol}$ and $(Mg/Na)_{sol}$ for Deccan and Archean regions were used and it did not provide information on contributions from other significant end members for each rivers. The inverse model employed has taken into account contributions from different end members and the estimated weathering rates and the associated CO_2 consumption are found to be more reliable compared to the forward model.

The silicate weathering rates, carbonate weathering rates and the associated CO_2 consumption rate was calculated using the available data and it was found that the rivers in the total Silicate weathering rates in the peninsular India are higher when compared to global average values for rivers. These weathering rates vary in different river basins and basin slope and runoff of the rivers seem to drive the intensity of the weathering in different basins. Higher SWR and SO_4/HCO_3 ratios are observed for two Archean rivers (Suberanrekha and Damodar) when compared to other Archean rivers; these higher ratios and SWRs are mainly due to intense weathering in these basins driven by sulphuric acids. The proton-donating sulphuric acids in these basins seem to be supplied mainly from the mining activities. Therefore, man-made activities in these basins supply strong acids and their involvement in chemical weathering processes can act as a source of atmospheric CO_2.

Outcomes of this study critically depend on the source compositions and uncertainties associated with them. Future studies should precisely evaluate the source composition of the rocks, atmospheric and anthropogenic inputs from these basins to better constrain of sources and improve our understanding of the weathering pattern of these tropical rivers.

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