## Chemical weathering in the Krishna Basin and Western Ghats of the Deccan Traps, India: Rates of basalt weathering and their controls

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Abstract—Rates of chemical and silicate weathering of the Deccan Trap basalts, India, have been determined through major ion measurements in the headwaters of the Krishna and the Bhima rivers, their tributaries, and the west flowing streams of the Western Ghats, all of which flow almost entirely through the Deccan basalts.

Samples (n = 63) for this study were collected from 23 rivers during two consecutive monsoon seasons of 2001 and 2002. The Total dissolved solid (TDS) in the samples range from 27 to 640 mg l<sup>-1</sup>. The rivers draining the Western Ghats that flow through patches of cation deficient lateritic soils have lower TDS (average: 74 mg l<sup>-1</sup>), whereas the Bhima (except at origin) and its tributaries that seem to receive Na, Cl, and SO<sub>4</sub> from saline soils and anthropogenic inputs have values in excess of 170 mg l<sup>-1</sup>. Many of the rivers sampled are supersaturated with respect to calcite. The chemical weathering rates (CWR) of "selected" basins, which exclude rivers supersaturated in calcite and which have high Cl and SO<sub>4</sub>, are in range of ~3 to ~60 t km<sup>-2</sup> y<sup>-1</sup>. This yields an area-weighted average CWR of ~16 t km<sup>-2</sup> y<sup>-1</sup> for the Deccan Traps. This is a factor of ~2 lower than that reported for the Narmada-Tapti-Wainganga (NTW) systems draining the more northern regions of the Deccan. The difference can be because of (i) natural variations in CWR among the different basins of the Deccan, (ii) "selection" of river basin for CWR calculation in this study, and (iii) possible contribution of major ions from sources, in addition to basalts, to rivers of the northern Deccan Traps.

Silicate weathering rates (SWR) in the selected basins calculated using dissolved Mg as an index varies between  $\sim 3$  to  $\sim 60$  t km<sup>-2</sup> y<sup>-1</sup>, nearly identical to their CWR. The Ca/Mg and Na/Mg in these rivers, after correcting for rain input, are quite similar to those in average basalts of the region, suggesting near congruent release of Ca, Mg, and Na from basalts to rivers. Comparison of calculated and measured silicate-Ca in these rivers indicates that at most  $\sim 30\%$  of Ca can be of nonsilicate origin, a likely source being carbonates in basalts and sediments.

The chemical and silicate weathering rates of the west flowing rivers of the Deccan are  $\sim 4$  times higher than the east flowing rivers. This difference is due to the correspondingly higher rainfall and runoff in the western region and thus reemphasises the dominant role of runoff in regulating weathering rates. The silicon weathering rate (SWR) in the Krishna Basin is  $\sim 15$  t km<sup>-2</sup> y<sup>-1</sup>, within a factor of  $\sim 2$  to those in the Yamuna, Bhagirathi, and Alaknanda basins of the Himalaya, suggesting that under favourable conditions (intense physical weathering, high runoff) granites and the other silicates in the Himalaya weather at rates similar to those of Deccan basalts. The CO<sub>2</sub> consumption rate for the Deccan is deduced to be  $\sim 3.6 \times 10^5$  moles km<sup>-2</sup> y<sup>-1</sup> based on the SWR. The rate, though, is two to three times lower than reported for the NTW rivers system; it still reinforces the earlier findings that, in general, basalts weather more rapidly than other silicates and that they significantly influence the atmospheric CO<sub>2</sub> budget on long-term scales.

#### 1. INTRODUCTION

Rivers carry the imprints of erosion on the continents in the form of dissolved and particulate materials. Most of the solutes in rivers are derived from chemical weathering of minerals contained in the rocks of the drainage basin. The proportion of various elements in the dissolved phase is a complex function of their relative abundances in minerals and of the mode and rate of their weathering. Chemical weathering of rocks involves consumption of CO<sub>2</sub>, a greenhouse gas that exerts strong influence on climate (Berner et al., 1983; Kump et al., 2000; Amiotte-Suchet et al., 2003; Dessert et al., 2003). Several parameters regulate the rate and intensity of chemical weathering and associated  $CO_2$  consumption. These include lithology of the drainage basin, runoff, temperature, vegetation, and relief. In terms of lithology, recent

works on basaltic provinces suggest that they weather more rapidly relative to granites and gneisses and that their weathering exerts important control on marine geochemical balances and global change (Meybeck, 1986; Bluth and Kump, 1994; Amiotte-Suchet and Probst, 1995; Louvat and Allegre, 1997; Dessert et al., 2001; Amiotte-Suchet et al., 2003; Dessert et al., 2003).

Deccan Traps (India) is one of the basaltic provinces studied (Dessert et al., 2001) for determining rates of weathering of basalts and the primary factors that control them. The work presented in this paper is also on the chemical weathering of Deccan basalts, carried out as a part of ongoing investigations on weathering of major lithological basins of India, based on chemical composition of rivers. These studies have been motivated by our quest to determine the role of major land forms in India such as the Himalaya and the Deccan Traps in contributing to dissolved fluxes of elements to oceans and to  $CO_2$  drawdown from the atmosphere (Sarin et al., 1989; Sarin et al., 1992; Krishnaswami et al., 1999; Dalai et al., 2002). More

specifically, the goals of this study are to (i) get baseline data on the major ion composition of rivers draining the Deccan Traps and identify their sources and processes contributing them, (ii) derive chemical weathering rates and associated  $CO_2$ consumption for the regions studied (southwestern and central Deccan), (iii) compare the present results with those available for the northern Deccan and other major river basins of India such as the head waters of the Ganga in the Himalaya, and (iv) determine the contribution of Deccan basalts to global riverine flux of major ions and atmospheric  $CO_2$  drawdown.

The earlier study on weathering of the Deccan Traps (Dessert et al., 2001) was based on the three watersheds: the Narmada, the Tapti, and the Wainganga-Wardha (tributaries of Godavari) in the northern region. The work described in this paper is based on the Krishna River system (the headwaters of the River Krishna and its tributaries all draining the southern and central Deccan Traps) and a number of small/medium rivers in the Western Ghats, many of which drain into the Arabain Sea. The headwaters of the Krishna and the Godavari are better suited for determining weathering rates of basalts as they flow almost entirely through the Deccan Traps. Though the Narmada-Tapti-Wainganga (NTW) rivers that have been studied (Dessert et al., 2001) predominantly drain Deccan basalts, a part of their basins are in the Indian shield, Vindhyan carbonates, sediments, and alluvial deposits. Further, the Narmada and Tapti Rivers flow through areas more prone to inputs from groundwater and hydrothermal waters. A number of hydrothermal springs have been reported along the Narmada-Tapti lineament (Minissale et al., 2000). Ramesh and Subramanian (1988) also had reported major ion composition of the Krishna River and in a few of its major tributaries as a part of their work to determine fluxes of various elements transported by this river system to the Bay of Bengal. Their sampling was focused more on the larger tributaries and along the lower stretches of the Krishna that predominantly drain Precambrian granites and metasediments, unlike this work that is on the headwaters of the Krishna and its tributaries draining the Deccan basalts.

## 2. MATERIALS AND METHODS

#### 2.1. Hydrogeology of the Region

The Deccan basalts, one of the largest volcanic provinces, is located in the western part of India, covering an area of  $\sim 5 \times 10^5$  km<sup>2</sup> with an estimated volume of  $\sim 10^6$  km<sup>3</sup> (Courtillot et al., 1986; Fig. 1a). These Traps have average elevation of 750 m and the thickness of lava pile varies from  $\sim 200$  m to  $\sim 2000$  m (Courtillot et al., 1986). Radiometric dating (K-Ar, Ar-Ar, and Re-Os) of these flows coupled with paleomagnetic data indicate that the bulk of these basalts erupted  $\sim 65$  to 67 Ma ago (Courtillot et al., 1986; Venkatesan et al., 1993; Allegre et al., 1999; Courtillot et al., 1999; Pande, 2002).

The Deccan Province experiences subtropical climate with highly variable rainfall, ~6200 mm y<sup>-1</sup> at Mahabaleshwar in the Western Ghats and ~700 mm y<sup>-1</sup> at Pune and the interior regions (Fig. 1b). The rainfall in the coastal belts, from Ratnagiri to Bombay, is around ~2500 mm y<sup>-1</sup>. Most of the rainfall (~85%) occurs during July to October, the monsoon period. The rainfall pattern is also reflected in the river discharge, the rivers of this region have >80% of their flow during monsoon (UNESCO, 1993). The surface air temperature of the sampling region ranges from 10° to 14°C in winter and between 31° to 37°C in summer, with a mean annual temperature of ~25°C.

The rivers sampled for this study are the headwaters of the Krishna River system from the state of Maharashtra and include the main River Krishna, and its tributaries; the Bhima, Koyna, Varna, Panchganga, Dudhganga, and the Ghataprabha (Table 1a; Fig. 1c). In addition, the major tributaries of the Bhima, the Ghod, Mutha, and the Nira, and a number of west flowing small rivers and streams of the Western Ghats (Fig. 1c) were also sampled. The headwaters of the Krishna, a major stretch of the Bhima, and their tributaries flow entirely through western and southwestern Deccan Traps (Fig. 1c). The rivers of the Krishna system flow eastwards and drain into the Bay of Bengal, whereas the small Western Ghat streams (Vashishthi, Shashtri, Kajli, Arjuna, Sukh, and Gad; Fig. 1c) flow west into the Arabian Sea. The characteristics of some of these river basins are given in Table 1a.

The Krishna River basin has a total drainage area of ~258,948 km<sup>2</sup> (Rao, 1975), of which  $\sim$ 66,810 km<sup>2</sup> (26%) lie in Deccan Traps. Its annual water discharge out of the Deccan Traps at Alamatti (16.33°N, 75.55°E; catchment area 36,286 km<sup>2</sup>) is  $1.73 \times 10^{13}$  l y<sup>-1</sup> (UNESCO, 1993). This translates to a runoff of  $\sim$ 476 mm y<sup>-1</sup> for the Krishna system in the Deccan Traps, similar to the runoff value of 452 mm y<sup>-</sup> for the Narmada basin (Borole et al., 1982) and 463 mm  $y^{-1}$  used by Dessert et al. (2001) for the northern Deccan Traps. The Bhima River, the largest tributary of the Krishna, has a catchment area of 33,916 km<sup>2</sup> in the Deccan Traps (Takli; 17.40°N, 75.85°E) and water discharge of  $7.2 \times 10^{12}$  l y<sup>-1</sup> (UNESCO, 1993). The Bhima and its tributaries (Ghod and Nira) have dams upstream of sampling locations that restrict their water flow, even during monsoon. The basins of the west flowing rivers experience much higher rainfall compared to the Krishna system in the Deccan interior (Fig. 1b). There is no data on their runoff; however, data are available for the Mandvi and Zuari rivers, ~100 km south of the River Gad. Subramanian (2000) has reported runoff of 1391 mm  $y^{-1}$  and 2000 mm  $y^{-1}$  for these rivers. A value of 1685 is derived for Mandvi from the discharge data of Shankar et al. (2004). In this work, for weathering rate calculations, runoff of 463 mm  $y^{-1}$  and 1690 mm  $y^{-1}$  is used for rivers predominantly draining east and west of the Western Ghats, respectively. These runoff values account for  ${\sim}65\%$  of the annual rainfall in these regions,  ${\sim}770$  and  ${\sim}2500~\text{mm}$  $y^{-1}$  (Fig. 1b; www.tropmet.res.in) average for the subdivision Madhya Maharashtra and Konkan and Goa, respectively.

The lithology of the drainage basins of the headwaters of the Krishna, Bhima, and the other rivers sampled are the Deccan Trap basalts, which are predominantly tholeiitic lavas. A detailed stratigraphy has been proposed for these based on field characteristics, mineralogical, chemical, and isotopic composition (Subbarao and Hooper, 1988). The lava flows of this region are composed of olivine, pyroxene, and plagioclase phenocrysts (Table 2). Mineralogical studies of some of these tholeiites suggest that olivines have forsterite between Fo<sub>77</sub> to Foss (Sen, 1980; Sen, 1986; Beane, 1988), plagioclase phenocrysts have 61 to 82% anorthite (Sen, 1986), and that augite and pigeonite are more common among pyroxenes (Sethna and Sethna, 1988). Another important but minor component of lithology of these basins is calcium carbonate. This occurs in river sediments and as calcareous tufas in the upland of the Bhima River basin (Pawar et al., 1988), formed mainly during the early Holocene through precipitation of CaCO<sub>3</sub> from groundwater springs. In addition, occurrences of calcite in some of the basalt flows also have been reported (Sukeshwala et al., 1972; Jeffery et al., 1988).

Black-coloured vertisols and laterites dominate the soils in the basins (Krishnan, 1982; Deshpande, 1998). The black soils are fine-textured with abundant smectite (Bhargava and Bhattacharjee, 1982). Some of these soils are salt-affected, containing chlorides, bicarbonates, and carbonates of Na, in different proportions (Fig. 1b; Bhargava and Bhattacharjee, 1982). Laterite soils are common in the low-lying coastal areas between Ratnagiri and Bombay and also occur in patches on the summits of the Western Ghats (Widdowson and Cox, 1996).

The natural vegetation of the Krishna Basin varies with geographic and climatic conditions. The high altitude regions of the Western Ghats with more rainfall have "tropical evergreen forest". The eastern part of the Western Ghats, which experiences semiarid to arid climate, has less forest cover and consists mainly of "tropical dry deciduous" vegetation (CPCB (90), 1990). In addition to this natural vegetation, the Krishna Basin is also one of the most intensely cultivated regions, with sugarcane and cereals being the major crops. The use of fertilizers for cultivation seems to have impacted upon the major ion chemistry of groundwater,  $NO_3$  in particular, in some of these regions (Pawar and Shaikh, 1995; Pawar et al., 1997).



Fig. 1. (a) Map of western India showing the Deccan Trap region. Major rivers and cities are also shown. (b) Map showing rainfall contours (values on the contour lines are annual rainfall in mm) and the distribution of saline soils (shaded) in the Deccan region. The rainfall map from Dr. Kolli (IITM, Pune) and the saline soil map modified from CSSRI (Karnal), India. (c) Sample locations, rainfall monitoring stations, and major cities. The rivers sampled in this study are from the Krishna system in the Deccan Traps and the west flowing Western Ghat rivers. The Western Ghats is shown as a shaded band running nearly parallel to the west coast.

## 2.2. Sampling and Analyses

River water and sediment samples were collected during peak monsoon periods of two consecutive yr, August 2001 and September 2002. The samples were collected from a total of 34 different locations (Table 1b and Fig. 1c). In addition to the Krishna and the Bhima, eight of their tributaries and seven small rivers that drain into the Arabian Sea were also sampled. Thus, this study is based on a total of 63 samples collected from 23 different rivers over a period of two consecutive yr.

The locations (latitude & longitude) of the sites and their altitudes are based mainly on GPS data. The initial characterization of river water samples was done at site by measuring their temperature, pH, and electrical conductivity. For alkalinity, river waters that appeared clear were sampled directly into ~125 mL bottles and stored unfiltered. River waters that were turbid were collected in ~1 L bottles and let stand for several h to allow particulate phases to settle down. The clear supernate was decanted into ~125 mL bottle. Samples for major ions were filtered through 0.4  $\mu$ m Nucleopore within ~6 h of collection. The filtered water was split into two aliquots. One fraction was unacidified and used for the analyses of Na, K, Cl, NO<sub>3</sub>, and SO<sub>4</sub>. The second split was acidified with high purity HNO<sub>3</sub> to pH  $\sim$ 2 and was used for the analyses of Ca and Mg. The major ion measurements were made by standard techniques: flame atomic absorbtion spectrophotometry (Na and K), inductively coupled plasma atomic emission spectrometry (Ca and Mg), ion chromatography (Cl, NO<sub>3</sub> and SO<sub>4</sub>), acid titration (HCO<sub>3</sub>), and spectrophotometry (Si). The precision of measurements of various cations and anions, determined based on repeat analyses, is generally better than 5%.

## 3. RESULTS

## 3.1. General Observations

The pH, temperature, electrical conductivity (EC), and the major ion concentrations of river waters analysed are given in

Table 1a. Basin characteristics of selected rivers in the Deccan Traps.

| River       |                    | Area <sup>b,c</sup><br>(km <sup>2</sup> ) | Rainfall <sup>a</sup> $(mm y^{-1})$ | Discharge <sup>c</sup><br>(10 <sup>13</sup> y <sup>-1</sup> ) |
|-------------|--------------------|---|-------------------------------------|---|
| Krishna     | Alamatti           | 36268                                     | 770                                 | 1 73  |
| Bhima       | Takli              | 33916                                     | 770                                 | 0.72  |
| Kovna       | Karad              | 1752                                      | 770                                 | 0.72  |
| Narmada     | Bharuch            | 90000                                     |                                     | 4.07  |
| Varna       | Sangli             | 2003                                      | 770                                 |   |
| Panchganga  | Krishna confluence | 2604                                      | 770                                 |   |
| Dudhganga   | Krishna confluence | 2554                                      | 770                                 |   |
| Ghataprabha | Krishna confluence | _   | 770                                 |   |
| Shashtri    | Sangameshwar       | 2174                                      | 2500                                |   |
| Vashisthi   | •                  | 2239                                      | 2500                                |   |
| Mandvi      |                    | 2032                                      | 2500                                | 0.34  |
| Zuari       |                    | 550                                       | 2500                                | 0.11  |

<sup>a</sup> Rainfall from www.tropmet.res.in.

<sup>b</sup> Area given is in Deccan Traps.

<sup>c</sup> Data on area and discharge from Rao (1975); Subramanian (2000), Shankar et al. (2004), and UNESCO (1993).

Tables 1b and 3. The pH of the samples varies from nearneutral to mildly alkaline, from 6.9 to 9.2, with most of them in the range of 7.0 to 8.0. The Bhima and its tributaries are the most alkaline. The range in EC of the samples is from 32 to 824  $\mu$ S cm<sup>-1</sup>. The lower values are in samples collected near the origin of rivers and/or due to dilution resulting from highrainfall events. The water temperature variations are from ~22 to 30°C.

The cationic charge  $(TZ^+)$  varies from ~290 to 8380  $\mu$ Eq, similar to the range reported for the NTW rivers (Dessert et al., 2001). The TZ<sup>+</sup> and TZ<sup>-</sup> are reasonably well balanced, TZ<sup>+</sup> =  $(0.96 \pm 0.003)TZ^- + 24$  (r<sup>2</sup> = 0.999). The extent of TZ<sup>+</sup> - TZ<sup>-</sup> charge imbalance, characterized in terms of NICB (normalized inorganic charge balance,  $(TZ^+ - TZ^-)/TZ^+$ ), is generally <5% (Table 3). The average NICB for all 63 samples is 3.1%, within the cumulative uncertainties in major ion measurements. It is also borne out from the NICB estimates that contribution of organic ligands such as oxalates, acetates, and humates is not significant to the charge balance as has been reported for some tropical rivers (Viers et al., 2000).

The dominance of HCO<sub>3</sub> in the anion budget (38-91% of TZ<sup>-</sup>) is evident from the ternary plot (Fig. 2a), which shows clustering of points near the HCO<sub>3</sub> apex. It is also seen from Figure 2a that many points lie along the mixing line of HCO<sub>3</sub> and (Cl+SO<sub>4</sub>) apices, with 9 to 62% contribution from (Cl+SO<sub>4</sub>). Generally, Cl is next in abundance (75–2333  $\mu$ Eq) to HCO<sub>3</sub>, accounting for 6 to 33% of anion charge; high-Cl concentrations are generally in rivers from basins with lesser rainfall. In five samples from the Bhima and four from the Nira, however,  $SO_4$  contribution to the total anion charge is more than that of Cl (Table 3). The sample near the origin of the Bhima River (BHM-1) has much higher Cl than SO<sub>4</sub> (Table 3) with Cl/SO<sub>4</sub> equivalent ratio of 3.5. The downstream Bhima samples, BHM-2, 3, 4, and 5 have both Cl and SO<sub>4</sub> abundances factors of 5 to 50 higher than BHM-1 (Table 3) with Cl /SO<sub>4</sub> equivalent ratio <1. This requires supply of both Cl and SO<sub>4</sub> to the river along its traverse with relatively more input of SO<sub>4</sub> compared to Cl. The NO<sub>3</sub> levels in the samples are generally  $<50 \ \mu\text{E}$  except in samples from the lower reaches of the Bhima, Nira, and the Ghod that also have higher Cl and  $SO_4$  (Table 3).

Ca is dominant among the cations, contributing 17 to 53% of TZ<sup>+</sup>. Mg follows Ca and accounts for 16 to 36% of cation charge. The contribution of alkali metals (Na+K) to TZ<sup>+</sup> is between 14 to 68% with Na making up most of it. These trends are evident in the ternary diagram for cations (Fig. 2b). Mg shows strong positive correlation with Ca, which has implications to their sources; these are discussed in the section on silicate weathering rates.

Dissolved silica is in the range of 91 to 685  $\mu$ M (Table 3; mean 323  $\mu$ M) and accounts for 4 to 28% of the total dissolved solids (TDS). The silica concentrations are similar to those in the NTW rivers (Dessert et al., 2001) and in others draining basalts such as those from Reunion Island (Louvat and Allegre, 1997) and Iceland (Steffansson and Gislason, 2001).

Silica shows an overall increasing trend with HCO<sub>3</sub>. The HCO<sub>3</sub>/SiO<sub>2</sub> ratios for the Western Ghat rivers (Table 3) flowing into the Arabian Sea and the Krishna tributaries (draining into the Bay of Bengal) have HCO<sub>3</sub>/SiO<sub>2</sub> molar ratios of  $\sim$ 2 to 3. These values are consistent with weathering of minerals in basalts to kaolinite/smectite. In the Bhima mainstream, its tributaries, and some of the Krishna mainstream samples, the HCO<sub>3</sub>/SiO<sub>2</sub> ratios are higher,  $\sim$ 5–10. These high ratios can result from supply of alkalinity from carbonates, salt affected soils, and anthrpogenic sources.

# 3.2. Spatial and Interannual Variation in TDS and Major Ions

The total dissolved solids (TDS) in the waters (Table 3) vary over a wide range, 27 to 640 mg l<sup>-1</sup> (Fig. 3), with a mean of 176 mg l<sup>-1</sup> (n = 63). This is similar to the range of ~13 to ~497 mg l<sup>-1</sup> for NTW rivers (Dessert et al., 2001), ~24 to ~580 mg l<sup>-1</sup> for rivers from Reunion Island (Louvat and Allegre, 1997), but higher than the range of ~39 to ~102 mg l<sup>-1</sup> for rivers from Iceland (Steffansson and Gislason, 2001). Variations in TDS among the sub-basins of the Krishna River system have been assessed by comparing their two yr average TDS, which decreases as: Ghod (337 ± 261, n = 3) ~ Bhima (318 ± 162, n = 8) > Krishna (185 ± 87, n = 12) > Western Ghats rivers (74 ± 28, n = 31). One obvious feature is the higher TDS in the Bhima and Ghod rivers as compared to the others, with abundantly high concentration of SO<sub>4</sub> in the Bhima (Table 3).

It is seen, based on average major ion abundances in the rivers analysed (Fig. 4), that the mean concentrations in 2002 samples (n = 29) are generally within  $\pm 20\%$  of the 2001 (n = 34) mean, for Cl (-20%), SiO<sub>2</sub> (+14%), HCO<sub>3</sub> (+9%), NO<sub>3</sub> (+11%), Na (-4%), Mg (+1.7%), and Ca (-1.5%). SO<sub>4</sub> shows higher variation ( $\sim -35\%$ ) resulting from its high and varying concentration in the Bhima River. The results of the Bhima at its origin, the Koyna, and the Ghataprabha (Fig. 4) show that interannual variability of major ions in these three rivers is generally <30%.

## 4. DISCUSSION

## 4.1. Sources of Major Ions

Determination of chemical and basalt weathering rates from the major ion composition of rivers requires data on their

## Table 1b. Location, altitude, temperature, pH, and electrical conductivity (EC) of Deccan Trap rivers sampled.

| Code          | River            | Year         | Lat.<br>(°N) | Long.<br>(°E) | Sampling location and remarks                       | Alt.<br>(m) | Temp.<br>(°C) | pH           | $\frac{\text{EC}}{(\mu \text{S cm}^{-1})}$ |
|---------------|------------------|--------------|--------------|---------------|---|-------------|---------------|--------------|--|
| Krichna me    | ainstroam        |              |              |               |   |             |               |              |  |
| KRS-1         | Krishna          | 2002         | 16.79        | 74.63         | Krishna before confluence with Panchganga           | 534         | 24.4          | 7.58         | 184  |
|               |                  | 2001         |              |               | 6. 6.   | 545         | 24.8          | 7.64         | 197  |
| KRS-2         | Krishna          | 2002         | 16.65        | 74.64         | Krishna after confluence with Panchganga            | 614         | 24.9          | 7.17         | 122  |
|               |                  | 2001         |              |               |   | 540         | 23.8          | 7.52         | 114  |
| KRS-3         | Krishna          | 2002         | 17.30        | 74.19         | Krishna after confluence with Koyna, near           | 564<br>572  | 25.5          | 7.76         | 189  |
| KRS-4         | Krishna          | 2001         | 17.40        | 74.11         | Karau<br>Krishna near Umbrai before confluence with | 583         | _             | 7.03         | 90<br>242                                  |
| KK5-4         | KIISIIIa         | 2002         | 17.40        | /4.11         | Kovna   | 575         | 24.0          | 8.01         | 187  |
| KRS-5         | Krishna          | 2002         | 16.80        | 74.57         | Krishna after confluence with Varna                 | 569         | 24.9          | 7.42         | 176  |
|               |                  | 2001         |              |               |   | -           | 24.5          | 7.62         | 182  |
| KRS-6         | Krishna          | 2002         | 17.94        | 73.90         | Krishna at Wai town, affected by                    | -           | 25.1          | 8.38         | 324  |
|               |                  | 2001         |              |               | anthropogenic activity.                             | 696         | 24.3          | 8.11         | 395  |
| Bhima Mai     | nstream<br>Dhime | 2002         | 10.02        | 72 62         | Divor Dhimo noor origin                             | 642         | 21.0          | 7 20         | 70   |
| BHM-1         | Bnima            | 2002         | 19.03        | /3.03         | River Bnima near origin.                            | 624         | 21.9          | 7.38         | 79   |
| BHM-2         | Bhima            | 2001         | 18 57        | 74 34         | Bhima before confluence with MTH-1                  | 517         | 25.3          | 8 39         | 538  |
| BHM-3         | Bhima            | 2002         | 18.57        | 74.38         | Bhima after confluence with MTH-1                   | 521         | 24.3          | 7.45         | 371  |
|               |                  | 2001         |              |               |   | 523         | 25.3          | 7.74         | 510  |
| BHM-4         | Bhima            | 2002         | 18.40        | 74.57         | Bhima after confluence with Ghod River              | 501         | 24.4          | 7.70         | 418  |
|               |                  | 2001         |              |               | (almost dry)  | 512         | 24.8          | 7.82         | 607  |
| BHM-5         | Bhima            | 2001         | 17.97        | 75.14         | Bhima after confluence with Nira (NIRA-2)           | 462         | 27.2          | 8.36         | 702  |
| Tributaries   | of Bhima         | 2002         | 10.00        |               |   | (77         | 22.0          | 7.00         | 010  |
| GHOD-1        | Ghod             | 2002         | 19.08        | 13.11         | River Ghod near origin.                             | 6//         | 22.8          | 7.99<br>8.00 | 213  |
| GHOD 2        | Ghod             | 2001         |              |               | Chod Piver before mixing Phima ( $\mathbf{PHM} A$ ) | 517         | 24.2          | 8.00         | 812  |
| MTH-1         | Mutha            | 2002         | 18 57        | 74 34         | Mutha before confluence with Bhima (BHM-            | 559         | 27.2          | 7.66         | 362  |
|               | mana             | 2002         | 10.57        | 71.51         | 2)  |             | 25.5          | 7.54         | 490  |
| NIRA-1        | Nira             | 2002         | 17.94        | 74.94         | Nira River at Baramati                              | 547         | 29.6          | 8.61         | 824  |
|               |                  | 2001         |              |               | Nira River, several check dams upstream             | 475         | 25.5          | 9.13         | 509  |
| NIRA-2        | Nira             | 2002         | 17.97        | 75.14         | Nira before confluence with Bhima (BHM-5)           | 474         | 27.8          | 8.54         | 345  |
|               |                  | 2001         |              |               |   | 451         | 28.6          | 9.20         | 373  |
| KUK-1         | Kukdi            | . 2002       | -            | -             | Kukdi River, a tributary of Ghod                    | -           | 25.0          | 8.69         | 481  |
| western gn    | ats and other 1  | rivers       |              |               |   |             |               |              |  |
| KYN-1         | Kovna            | 2002         | 17 27        | 74 18         | Kovna before confluence with Krishna                | 568         | 26.1          | 7 35         | 126  |
| IIII I        | noyna            | 2002         | 17.27        | ,             |   | 570         | 23.7          | 7.38         | 85   |
| KYN-2         | Koyna            | 2002         | 17.93        | 73.61         | Koyna at origin, near Mahabaleshwar                 | _           | 21.1          | 6.99         | 41   |
|               | •                | 2001         |              |               |   | 726         | 20.2          | 7.25         | 42   |
| VRN-1         | Varna            | 2002         | 16.87        | 74.36         | Varna River before mixing with Krishna              | 550         | 24.3          | 7.13         | 124  |
|               |                  | 2001         |              |               |   | 556         | 23.4          | 7.56         | 129  |
| PGN-1         | Panchganga       | 2002         | 16.69        | 74.60         | Panchganga before confluence with Krishna           | 541         | 24.4          | 7.12         | 95   |
| DCN 2         | Danahaanaa       | 2001         | 16 76        | 71.26         | (KKS-1)<br>Denehaanga naar Shanatha villaga         | 543         | 23.5          | 7.38         | 81   |
| GTP-1         | Ghataprabha      | 2002         | 16.70        | 74.20         | River Ghataprabha near Adkur village                | 710         | 24.7          | 7.03         | 93<br>40                                   |
| 011-1         | Ghatapraoha      | 2002         | 10.01        | /4.2/         | Kiver Ghataprabha hear Aukur vinage                 | 687         | 22.0          | 7.76         | 32   |
| HRN-1         | Hiranyakeshi     | 2002         | 16.36        | 74.35         | Hiranyakeshi River, Chandkhand-Gadinglaj            | 679         | 25.2          | 7.04         | 41   |
|               | 2                | 2001         |              |               | road  | 633         | 22.8          | 7.14         | 53   |
| TPN-1         | Tambrapani       | 2002         | 15.92        | 74.29         | Tambrapani River, Chandkhand-Belgaum road           | 747         | 23.4          | 7.12         | 55   |
| 5561          |                  | 2001         |              |               |   | 688         | 22.0          | 7.10         | 41   |
| DDG-1         | Dudhganga        | 2002         | 16.43        | 74.14         | River Dudhganga, near Gargoti                       | 546         | 24.7          | 7.03         | 109  |
| VDC 1         | Vadganga         | 2001         | 16.26        | 74 15         | Piwar Vadganga, naar Gargati                        | 558<br>611  | 23.4          | 7.35         | 144  |
| VDO-1         | veuganga         | 2002         | 10.50        | 74.15         | Kivel veugaliga, lical Gargoti                      | 562         | 27.4          | 7.00         | 70<br>69                                   |
| BGW-1         | Bhogwati         | 2001         | 16.50        | 74.05         | River Bhogwati near Amiai village                   | 632         | 23.8          | 7.06         | 85   |
|               |                  | 2001         |              |               |   | 561         | 22.8          | 7.10         | 57   |
| West flowing  | ng rivers        |              |              |               |   |             |               |              |  |
| ARJ-1         | Arjuna           | 2002         | 16.65        | 74.02         | River Arjuna near Rajapur                           | 28          | 26.2          | 6.92         | 76   |
| GAD-1         | Gad              | 2002         | 16.26        | 73.72         | River Gad near Kasal                                | 34          | 24.9          | 7.00         | 73   |
| SUKH-1        | Sukh             | 2002         | 16.56        | 73.63         | Sukh River near Khare patan village                 | 15          | 25.7          | 6.97         | 73   |
| KII 1         | Kaili            | 2001         | 16.02        | 73 51         | Kaili Diver near Laniba                             | 19          | 26.2          | 7.59         | /6   |
| AJL-1         | кајп             | 2002         | 10.95        | 15.51         | Kajii Kivei neai Lälijilä                           | - 23        | 20.1          | 7.01         | 94<br>85                                   |
| SHT-1         | Shashtri         | 2001         | 17.18        | 73.55         | Shashtri River near Sangameshwar                    | -           | 25.1          | 6.92         | 78   |
|               |                  | 2001         |              |               |   | 8           | 25.2          | 7.22         | 73   |
| VAT-1         | Vashishthi       | 2002         | 17.53        | 73.54         | Vashishthi River near Chiplun                       | _           | 25.8          | 6.99         | 83   |
|               |                  | 2001         |              |               | -   | 12          | 25.5          | 7.16         | 81   |
| <u>Others</u> |                  | <b>2</b> 00- |              |               | 4 1 1 D   |             | <b></b>       |              | 100  |
| AMB-1         | Ambika           | 2002         | -            | -             | Ambika River near Waghai                            | _           | 24.8          | 7.70         | 188  |
| MULA-1        | iviuia           | 2002         | 19.32        | /4.18         | KIVET MUIA, A INDUTARY OF GODAVARI RIVER            | 010         | 23.3          | 1.45         | 165  |

| Table 2. | Major | minerals |
|----------|-------|----------|

| Formation               |            | SiO <sub>2</sub> | CaO  | MgO  | K <sub>2</sub> O | Na <sub>2</sub> O | #Ca/Na | <sup>#</sup> Ca/Mg | Major<br>minerals <sup>@</sup> |
|-------------------------|------------|------------------|------|------|------------------|-------------------|--------|--------------------|--------------------------------|
| Poladpur (n = 4)        | Av.        | 49.8             | 10.7 | 6.16 | 0.20             | 2.40              | 2.50   | 1.26               | Ol + Pl                        |
|                         | $(\sigma)$ | 0.4              | 0.5  | 0.81 | 0.05             | 0.27              | 0.36   | 0.13               |                                |
| Ambenali $(n = 3)$      | Av.        | 48.1             | 11.1 | 6.08 | 0.23             | 2.48              | 2.49   | 1.32               | Ol + Pl                        |
|                         | $(\sigma)$ | 0.5              | 0.6  | 0.71 | 0.10             | 0.16              | 0.26   | 0.13               |                                |
| Mahabaleshwar $(n = 3)$ | Av.        | 48.7             | 10.7 | 5.56 | 0.35             | 2.64              | 2.25   | 1.39               | Ol + Pl                        |
|                         | $(\sigma)$ | 0.9              | 1.1  | 0.22 | 0.13             | 0.26              | 0.17   | 0.21               |                                |
| Bushe $(n = 3)$         | Av.        | 53.2             | 10.0 | 6.33 | 0.82             | 2.69              | 2.07   | 1.17               | Ol + Pl + Aug                  |
|                         | $(\sigma)$ | 1.0              | 0.6  | 1.58 | 0.32             | 0.26              | 0.3    | 0.22               | -                              |
| Thakurwadi (n = 9)      | Av.        | 51.5             | 9.7  | 6.49 | 0.53             | 2.19              | 2.58   | 1.07               | Ol + Pl + Aug                  |
|                         | $(\sigma)$ | 1.5              | 1.6  | 1.42 | 0.35             | 0.27              | 0.52   | 0.1                |                                |
| Bhimashanker $(n = 3)$  | Av.        | 50.3             | 9.8  | 5.95 | 0.66             | 3.18              | 1.70   | 1.18               | Ol                             |
|                         | $(\sigma)$ | 0.6              | 0.4  | 0.08 | 0.12             | 0.15              | 0.13   | 0.04               |                                |
| Overall av. $(n = 25)$  |            | 50.5             | 10.2 | 6.2  | 0.47             | 2.5               | 2.34   | 1.19               |                                |
|                         | $(\sigma)$ | 1.8              | 1.2  | 1.1  | 0.31             | 0.4               | 0.46   | 0.17               |                                |

Table 2. Major minerals and average abundances (wt%) of major element oxides in the Deccan basats.

\*Subbarao et al. (2000).

<sup>#</sup>Molar ratio.

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<sup>@</sup> Sen (2001).

Ol, Pl, and Aug refer to olivine, plagioclase, and augite in phenocrysts.

contributions from various sources to rivers. The chemical weathering of rocks and minerals present in the basin, dry and wet atmospheric deposition, and anthropogenic input are the primary sources of major ions to rivers. It is necessary to constrain the contributions from these sources to the major ion budgets to derive chemical weathering rates of the basin and associated  $CO_2$  drawdown.

## 4.1.1. Atmospheric supply

Contribution of major ions from atmospheric deposition can be determined from regional rainwater composition. Table 4a lists the major ion composition of rainwater from five locations of the Deccan region (Fig. 1c). Of these, three are from the monitoring stations of the Indian Institute of Tropical Meteorology (IITM), Pune (Parashar et al., 1996), and two single samples collected as a part of this study during August 2002. Among the three IITM stations, the one at Dona Paula (near Panaji; Fig. 1a), Goa, is a coastal site, therefore the rainwater chemistry at this station should reflect the oceanic end-member composition. The two other sites, Pune and Sinhagad, are urban stations situated  $\sim 100$  km inland off the west coast of India. Of the two sites sampled in this study, Ambolighat is near the origin of the Hiranyakeshi River, and Sangameshwar is on the banks of the Shastri River.

Cl concentration in rainwater from Goa is ~135  $\mu$ M, nearly identical (138  $\mu$ M) to that reported for rains from Bombay (Sequeria and Kelkar 1978; Sarin et al., 1989). The value decreases to 50  $\mu$ M and 51  $\mu$ M for the Pune and Sinhagad samples and 11 and 28  $\mu$ M for the Ambolighat and Sangameshwar samples (Table 4a). The Cl/Na molar ratios are the same within errors for the three IITM sites, with a value of ~1.17, typical of a marine end member. This suggests that there is no discernible contribution of Na from other sources, such as silicates, to these rain samples. Cl/Na ratios at Ambolighat and Sangameshwar are 0.64 & 1.07, respectively, indicating supply of dust derived Na to rain, particularly in the sample

from Ambolighat. All these inferences assume that there is no loss of Cl from sea salt.

In the six west flowing rivers collected within 10 to 20 km inland off the west coast, Cl is in the range of 101 to 117  $\mu$ M (Table 3). These values are marginally lower than Cl in rains at Goa and Bombay and suggest that in these streams Cl can be entirely from precipitation. Cl in rains from the interior Deccan average ~48  $\mu$ M (Table 4a), significantly lower than that in many rivers of the region. Considering an evapotranspiration enrichment of ~40% (based on average rainfall of ~770 mm y<sup>-1</sup> and runoff of ~463 mm y<sup>-1</sup>), the rainwater contribution of Cl to these rivers would be ~80  $\mu$ M. This accounts for 3 to 100% (average = 20%) of Cl in the east flowing Deccan Trap rivers. Table 4b presents the contribution to specific streams, however, can be different from the mean values given in Table 4b, as it would depend on the Cl content of local rain.

The supply of SO<sub>4</sub>, Na, Ca, and Mg from rains to the various groups of rivers has been estimated based on the relation given in the Appendix. These estimates (Table 4b) show that in the west flowing Western Ghat rivers, all SO<sub>4</sub> and a significant part of Na can be accounted for from rains. For Ca and Mg, the rainwater supply can account for a maximum of 15% (average 13%) and 13% (average 11%), respectively. Further, these calculations suggest that for many of the interior river samples, rainwater contribution of major ions, particularly Mg and Ca, forms only a minor component.

## 4.1.2. Other sources for Na, Cl and $SO_4$

Many of the Krishna and Bhima tributaries have Cl and  $SO_4$ in excess of that supported by rain (Tables 3 and 4b). Potential sources to balance the excess of these ions are evaporites, saline soils, and discharge from spring water or groundwater and anthropogenic inputs. In addition, for  $SO_4$ , pyrite oxidation can also be a source. There are no reports of halite exposure in these river basins, therefore, evaporites are an unlikely source for these ions. Recently, Naik et al. (2001) reported the major ion

Table 3. Major ion composition of rivers flowing through the Deccan Traps, India.

| Code              | River            | Ca<br>(µM) | Mg<br>(µM) | Na<br>(µM) | Κ<br>(μM) | HCO <sub>3</sub><br>(µM) | Cl<br>(µM) | SO <sub>4</sub><br>(µM) | NO <sub>3</sub><br>(μM) | $TZ^+$<br>( $\mu E$ ) | TZ <sup>-</sup><br>(µE) | Si<br>(µM) | TDS<br>(mgl <sup>-1</sup> ) | NICB<br>(%)  |
|-------------------|------------------|------------|------------|------------|-----------|--------------------------|------------|-------------------------|-------------------------|-----------------------|-------------------------|------------|-----------------------------|--------------|
| Krishna n         | nainstream       |            |            |            |           |                          |            |                         |                         |                       |                         |            |                             |              |
| KRS-1             | Krishna          | 454        | 270        | 484        | 20        | 1468                     | 287        | 90                      | 39                      | 1952                  | 1974                    | 334        | 168                         | -1.1         |
|                   |                  | 434        | 294        | 549        | 24        | 1418                     | 337        | 125                     | 29                      | 2029                  | 2034                    | 313        | 169                         | -0.2         |
| KRS-2             | Krishna          | 329        | 206        | 363        | 17        | 862                      | 262        | 69                      | 20                      | 1450                  | 1282                    | 291        | 114                         | 11.6         |
|                   |                  | 232        | 151        | 288        | 15        | 776                      | 230        | 58                      | 24                      | 1069                  | 1146                    | 228        | 96                          | -7.2         |
| KRS-3             | Krishna          | 490        | 295        | 410        | 19        | 1653                     | 221        | 46                      | 21                      | 1999                  | 1987                    | 350        | 172                         | 0.6          |
| WDG 4             | ** • •           | 206        | 141        | 219        | 11        | 802                      | 150        | 18                      | 8                       | 924                   | 996                     | 274        | 90                          | -7.8         |
| KRS-4             | Krishna          | 645        | 375        | 503        | 22        | 2226                     | 268        | 55                      | 29                      | 2565                  | 2633                    | 419        | 225                         | -2.7         |
| VDC 5             | Vrichno          | 460        | 311        | 415        | 18        | 10/2                     | 225        | 50<br>94                | 21                      | 1975                  | 2030                    | 341        | 1/3                         | -2.8         |
| ккэ-э             | KIISIIIia        | 390<br>307 | 247        | 408        | 17        | 1320                     | 279        | 116                     | 27                      | 1844                  | 1804                    | 302        | 155                         | -2.0<br>-2.1 |
| KRS-6             | Krishna          | 903        | 578        | 587        | 26        | 3252                     | 283        | 43                      | 81                      | 3575                  | 3702                    | 520        | 314                         | -3.6         |
| IIII U            | Kristina         | 1162       | 717        | 568        | 35        | 3995                     | 335        | 70                      | 92                      | 4361                  | 4562                    | 639        | 385                         | -4.6         |
| Bhima ma          | ainstream        | 1102       |            | 200        | 20        | 0770                     | 000        | 70                      | /=                      |                       |                         | 007        | 000                         |              |
| BHM-1             | Bhima            | 182        | 110        | 174        | 10        | 585                      | 133        | 19                      | 5                       | 768                   | 761                     | 309        | 75                          | 0.9          |
|                   |                  | 170        | 121        | 171        | 10        | 609                      | 140        | 20                      | 6                       | 763                   | 795                     | 300        | 76                          | -4.2         |
| BHM-2             | Bhima            | 795        | 628        | 2260       | 42        | 2162                     | 1313       | 886                     | 58                      | 5148                  | 5305                    | 293        | 385                         | -3.0         |
| BHM-3             | Bhima            | 768        | 479        | 1229       | 49        | 2464                     | 627        | 342                     | 89                      | 3772                  | 3864                    | 396        | 307                         | -2.4         |
|                   |                  | 932        | 618        | 1839       | 77        | 2815                     | 1094       | 598                     | 127                     | 5016                  | 5232                    | 379        | 396                         | -4.3         |
| BHM-4             | Bhima            | 822        | 547        | 1494       | 38        | 2499                     | 779        | 490                     | 65                      | 4270                  | 4323                    | 390        | 337                         | -1.2         |
|                   |                  | 1004       | 713        | 2444       | 73        | 2972                     | 1364       | 881                     | 13                      | 5951                  | 6111                    | 377        | 454                         | -2.7         |
| BHM-5             | Bhima            | 999        | 921        | 2950       | 77        | 2934                     | 2183       | 1054                    | 15                      | 6867                  | 7240                    | 323        | 511                         | -5.4         |
| <u>Tributarie</u> | es of Bhima      |            |            |            |           |                          |            |                         |                         |                       |                         |            |                             |              |
| GHOD-1            | Ghod             | 610        | 340        | 327        | 17        | 1999                     | 193        | 40                      | 61                      | 2244                  | 2333                    | 418        | 202                         | -4.0         |
|                   |                  | 493        | 278        | 291        | 18        | 1644                     | 212        | 38                      | 20                      | 1851                  | 1952                    | 390        | 170                         | -5.5         |
| GHOD-2            | Ghod             | 973        | 1206       | 3960       | 65        | 4624                     | 2333       | 752                     | 114                     | 8383                  | 8575                    | 563        | 640                         | -2.3         |
| MTH-1             | Mutha            | 771        | 464        | 1137       | 48        | 2501                     | 593        | 256                     | 95                      | 3655                  | 3701                    | 398        | 298                         | -1.3         |
|                   |                  | 990        | 593        | 1569       | 97        | 3125                     | 1003       | 370                     | 213                     | 4832                  | 5081                    | 429        | 395                         | -5.2         |
| NIRA-1            | Nira             | 672        | 641        | 5630       | 27        | 3631                     | 1397       | 1566                    | 62                      | 8283                  | 8222                    | 396        | 622                         | 0.7          |
|                   |                  | 468        | 448        | 2867       | 35        | 1934                     | 1068       | 1058                    | 0                       | 4734                  | 5118                    | 335        | 375                         | -8.1         |
| NIRA-2            | Nira             | 584        | 395        | 1498       | 39        | 2123                     | 654        | 423                     | 27                      | 3495                  | 3650                    | 336        | 284                         | -4.4         |
| 171117 1          | 77 1 1           | 459        | 416        | 1742       | 49        | 1856                     | 884        | 579                     | 0                       | 3541                  | 3898                    | 310        | 289                         | -10.1        |
| KUK-I             | Kukdi            | . /84      | 965        | 1685       | 32        | 4161                     | 886        | 129                     | 83                      | 5215                  | 5388                    | 506        | 428                         | -3.3         |
| western g         | gnat and other r | ivers      |            |            |           |                          |            |                         |                         |                       |                         |            |                             |              |
| I FIDULAFIE       | Vouno            | 200        | 201        | 276        | 10        | 1111                     | 176        | 10                      | 14                      | 1206                  | 1227                    | 252        | 122                         | 2.4          |
| KIN-I             | Koyna            | 205        | 122        | 270        | 10        | 712                      | 170        | 10                      | 14                      | 1500                  | 1557<br>801             | 222        | 122                         | -2.4         |
| KVN 2             | Kowna            | 203        | 133        | 194        | 0<br>5    | 300                      | 139        | 10                      | 15                      | 388                   | 305                     | 170        | 40                          | -1.5         |
| K11N-2            | Koyna            | 02         | 60         | 103        | 5         | 301                      | 86         | 10                      | 5                       | /00                   | 412                     | 165        | 40                          | -0.7         |
| VRN-1             | Varna            | 297        | 185        | 273        | 31        | 990                      | 195        | 37                      | 24                      | 1268                  | 1283                    | 292        | 114                         | -1.2         |
| VIXIN-1           | v arria          | 290        | 103        | 275        | 12        | 1045                     | 202        | 34                      | 29                      | 1266                  | 1344                    | 313        | 114                         | -63          |
| PGN-1             | Panchganga       | 208        | 125        | 239        | 15        | 611                      | 202        | 40                      | 12                      | 920                   | 911                     | 238        | 81                          | 1.0          |
| 10111             | i unengungu      | 175        | 115        | 190        | 12        | 585                      | 165        | 26                      | 11                      | 782                   | 813                     | 200        | 71                          | -4.0         |
| PGN-2             | Panchganga       | 212        | 138        | 210        | 11        | 680                      | 179        | 21                      | 27                      | 921                   | 928                     | 257        | 84                          | -0.8         |
| GTP-1             | Ghataprabha      | 74         | 52         | 127        | 6         | 212                      | 116        | 10                      | 16                      | 385                   | 364                     | 126        | 34                          | 5.5          |
|                   | - ····1 ··· ··   | 57         | 36         | 101        | 5         | 170                      | 100        | 9                       | 12                      | 292                   | 300                     | 91         | 27                          | -2.7         |
| HRN-1             | Hiranyakeshi     | 71         | 54         | 131        | 5         | 216                      | 120        | 11                      | 10                      | 386                   | 368                     | 128        | 34                          | 4.7          |
|                   | 5                | 107        | 71         | 132        | 10        | 337                      | 133        | 15                      | 11                      | 498                   | 511                     | 129        | 45                          | -2.6         |
| TPN-1             | Tambrapani       | 107        | 74         | 150        | 9         | 319                      | 146        | 14                      | 27                      | 521                   | 520                     | 166        | 48                          | 0.2          |
|                   |                  | 75         | 56         | 115        | 12        | 234                      | 119        | 11                      | 13                      | 389                   | 388                     | 117        | 35                          | 0.3          |
| DDG-1             | Dudhganga        | 289        | 168        | 223        | 10        | 835                      | 177        | 33                      | 35                      | 1147                  | 1113                    | 268        | 100                         | 3.0          |
|                   |                  | 373        | 232        | 264        | 19        | 1226                     | 215        | 33                      | 41                      | 1493                  | 1548                    | 344        | 136                         | -3.7         |
| VDG-1             | Vedganga         | 172        | 110        | 178        | 7         | 562                      | 148        | 13                      | 25                      | 749                   | 761                     | 247        | 71                          | -1.6         |
|                   |                  | 148        | 108        | 163        | 7         | 530                      | 136        | 12                      | 18                      | 682                   | 708                     | 241        | 66                          | -3.8         |
| BGW-1             | Bhogwati         | 193        | 128        | 192        | 9         | 603                      | 159        | 17                      | 46                      | 843                   | 842                     | 271        | 79                          | 0.1          |
|                   |                  | 124        | 80         | 144        | 8         | 395                      | 130        | 14                      | 19                      | 560                   | 572                     | 176        | 52                          | -2.1         |
| West flow         | ing rivers       |            |            |            |           |                          |            |                         |                         |                       |                         |            |                             |              |
| ARJ-1             | Arjuna           | 167        | 131        | 181        | 7         | 633                      | 115        | 11                      | 6                       | 784                   | 776                     | 366        | 80                          | 1.0          |
| GAD-1             | Gad              | 153        | 114        | 179        | 9         | 604                      | 108        | 12                      | 0                       | 722                   | 736                     | 323        | 75                          | -1.9         |
| SUKH-1            | Sukh             | 163        | 130        | 165        | 7         | 624                      | 102        | 12                      | 4                       | 758                   | 754                     | 332        | 77                          | 0.5          |
|                   |                  | 158        | 132        | 167        | 6         | 656                      | 115        | 12                      | 6                       | 753                   | 801                     | 341        | 80                          | -6.4         |
| KJL-1             | Kajli            | 162        | 128        | 168        | 6         | 633                      | 101        | 11                      | 4                       | 754                   | 760                     | 353        | 78                          | -0.8         |
| 01175 4           |                  | 196        | 151        | 180        | 5         | 755                      | 117        | 12                      | 2                       | 879                   | 898                     | 396        | 91                          | -2.2         |
| SHT-1             | Shastri          | 181        | 127        | 178        | 6         | 678                      | 111        | 12                      | 3                       | 800                   | 816                     | 386        | 84                          | -2.0         |
| 17.1 75.4         |                  | 163        | 126        | 160        | 5         | 623                      | 110        | 12                      | 3                       | 743                   | 760                     | 344        | 77                          | -2.3         |
| VA1-1             | Vashishthi       | 197        | 142        | 176        | 6         | 725                      | 104        | 12                      | 3                       | 860                   | 856                     | 391        | 88                          | 0.5          |
| 04                |                  | 173        | 137        | 167        | 6         | /16                      | 114        | 14                      | 5                       | /93                   | 863                     | 364        | 86                          | -8.8         |
| AMD 1             | A mahil          | 520        | 240        | 265        | 15        | 1076                     | 120        | 20                      | 1                       | 2056                  | 2062                    | 605        | 200                         | 1.0          |
| AMB-I<br>MULA 1   | Amoika           | 201        | 349<br>210 | 203        | 15        | 18/0                     | 150        | 28                      | 1                       | 2030<br>1714          | 2003                    | 224        | 200                         | -1.8         |
| WULA-I            | iviuia           | 391        | 510        | 504        | 0         | 1440                     | 199        | 42                      | 30                      | 1/14                  | 1/05                    | 554        | 132                         | -3.0         |



Fig. 2. Ternary plots for anions (2a) and cations (2b). The anions are dominated by  $HCO_3$ , showing a mixing trend with  $(Cl+SO_4)$ . The cations lean towards Ca, with most samples in Ca – (Na+K) region.

composition of several springs and groundwater in the Koyna River basin, one of the tributaries of Krishna (Fig. 1b), these have average Cl of  $\sim$ 310  $\mu$ M and SO<sub>4</sub> of  $\sim$ 38  $\mu$ M. From the distribution of springs in this basin, Naik et al. (2002) estimate that, on an average, there is one spring per km<sup>2</sup> of drainage area with an average flow of  $\sim 1.3 \times 10^7$  l y<sup>-1</sup>. This would contribute to a runoff  $\sim 13 \text{ mm y}^{-1}$ ,  $\sim 3\%$  of average river runoff for the region. If this estimate for the Koyna basin is representative of the rivers of the region, it would lead to infer that the maximum contribution of springs to the Cl and SO<sub>4</sub> budget of rivers is only  $\sim 10\%$ . An independent measure of groundwater input to these basins can be obtained by assuming that the river discharge during lean stage (April-May) is solely from groundwater. For the Krishna, at Alamatti, the April to May discharge averages  $\sim 10 \text{ m}^3 \text{ sec}^{-1}$ , compared to the annual average of  $\sim$ 550 m<sup>3</sup> sec<sup>-1</sup> (UNESCO, 1993). This is consistent with an earlier estimate based on Koyna spring data. Further, as the sampling was carried out during monsoon at the high-water stages of these rivers, the contribution from groundwater is expected to be minimal.

Salt-affected soils in the basin and anthropogenic inputs are



Fig. 3. Frequency distribution of total dissolved solids (TDS). The range in TDS, though, is wide (27 to 640 mg  $1^{-1}$ ); about half of the samples have TDS < 100 mg  $1^{-1}$ . The high TDS samples are from the lower reaches of the Bhima, Ghod, Nira, and the Kukdi, all of which have high Cl, SO<sub>4</sub>, and NO<sub>3</sub>.

other potential sources of Cl,  $SO_4$ , and Na to rivers. Occurrences of saline and alkaline soils containing NaCl and Na<sub>2</sub>SO<sub>4</sub> scattered in the Deccan Plateau have been reported (Bhargava and Bhattacharjee, 1982). Remote sensing studies (NRSA, 1998) also have documented the presence of salt-affected soils in Maharashtra, especially in the basins of the Bhima, Krishna, Nira, and Mutha rivers, and also along the coastal tracts of the Arabian Sea.

Dessert et al. (2001) attributed the high Cl in Kalimachak and Panjkra rivers of the Narmada-Tapti system to anthropogenic sources. Part of the Krishna Basin in Maharashtra is subject to intense agricultural activities, the main crops being sugarcane and cereals. Pawar et al. (1997), based on spatial and temporal variations of major ion chemistry of shallow ground waters near a sugarmill in Sonai, Deccan, show that the mill effluents can be a significant source of Cl and NO<sub>3</sub> to surface and groundwater. They also infer that urea and muriate of potash, used as fertilizers, can be source for these ions. Further, in the present study, the occurrence of high NO<sub>3</sub> with high Cl (and SO<sub>4</sub>) in some of the samples is an indication that anthropogenic activities may be influencing the composition of these rivers, the likely source for all these ions being fertilizers and sewage. This inference is also attested by the strong correlation among  $SO_4$ -Cl, and (Cl +  $SO_4$ )-Na (Figs. 5 a, b). Analysis of the data of Dessert et al. (2001) for the NTW rivers also show similar Cl-SO<sub>4</sub> and Na-(Cl +SO<sub>4</sub>) trends. It is tempting to interpret these observations in terms of a common source for Cl,  $SO_4$ , and Na, such as saline soils and anthropogenic inputs.

Estimation of individual contributions from salt-affected soils and anthropogenic sources to Cl,  $SO_4$ , and Na budgets of rivers draining the Bay of Bengal remains elusive. It is, however, possible to derive the total contribution from these two sources by assuming that all Cl in rivers in excess of that supplied from rains is from them (Appendix).

Such an approach would suggest that in the west flowing Western Ghat rivers, there is no discernible contribution of Cl and Na from these sources, whereas in the Krishna, the Bhima, and their tributaries, they can contribute  $\sim 70\%$  and  $\sim 90\%$  of



Fig. 4. Interannual variability in major ion abundances  $\blacksquare$  2001,  $\blacksquare$  2002: (a) average of all samples (n = 63), (b) Bhima River at its origin, (c) Koyna, and (d) Ghataprabha. The average variability is within  $\pm$  30%.

Cl and  $\sim 40\%$  to  $\sim 60\%$  of Na. In all these calculations, it is assumed that Cl derived from basalts is insignificant.

## 4.2. Chemical Weathering Rates

The amount of dissolved elements supplied to rivers via chemical weathering of the basin (X\* where X = Na, K, Ca, Mg, and SO<sub>4</sub>) is calculated by subtracting rain contribution to river water concentration (Appendix).

The total dissolved solids derived from chemical weathering of the basin, TDS\* (=( $\Sigma X_i^*$ ) +SiO<sub>2</sub>), varies from ~7 mg l<sup>-1</sup> to ~312 mg l<sup>-1</sup>, the high values, >80 mg l<sup>-1</sup>, are in samples

from the Bhima and its tributaries. The TDS\* estimate assumes that all alkalinity in the rivers is derived from atmospheric/soil CO<sub>2</sub>. Conversion of TDS\* to chemical weathering rates of the basins requires knowledge of runoff of individual rivers. These data being unavailable, particularly for the smaller rivers, the weathering rate estimates are based on average runoff of the major rivers of the region, ~463 mm y<sup>-1</sup> for the Krishna system and ~1690 mm y<sup>-1</sup> for rivers flowing into the Arabian Sea. The chemical weathering rates in the individual river basins over the two yr of sampling vary from ~3 to ~144 t km<sup>-2</sup> y<sup>-1</sup> (Fig. 6), with an average of ~36 t km<sup>-2</sup> y<sup>-1</sup>. This

Table 4a. Major ion composition of rainwater from the Deccan region.<sup>4</sup>

| Location              | n  | Na  | K  | Mg | Ca | Cl  | NO <sub>3</sub> | $SO_4$ | $\rm NH_4$ |
|-----------------------|----|-----|----|----|----|-----|-----------------|--------|------------|
| Inland stations:      |    |     |    |    |    |     |                 |        |            |
| Pune <sup>#</sup>     | 12 | 41  | 2  | 9  | 27 | 50  | 8               | 11     | 11         |
| Sinhagad <sup>#</sup> | 17 | 46  | 2  | 9  | 18 | 51  | 6               | 12     | 13         |
| Ambolighat*           | 1  | 17  | 8  | _  | 9  | 11  | 0               | 3      | 47         |
| Sangameshwar*         | 1  | 26  | 4  | _  | 10 | 28  | 6               | 8      | 0          |
| Mean <sup>@</sup>     |    | 42  | 2  | 9  | 21 | 48  | 7               | 11     | 13         |
| Coastal station       |    |     |    |    |    |     |                 |        |            |
| Goa <sup>#</sup>      | 6  | 115 | 3- | 15 | 23 | 135 | 6               | 16     | 7          |

n = number of samples.

<sup>†</sup> in units of  $\mu$ M.

<sup>@</sup> weighted mean based on n.

<sup>#</sup> Parashar et al. (1996).

\* Present study.

| Rivers  |        | C     | C .   | C* .  | $C^* / C (\%)$    |
|---|--------|-------|-------|-------|-------------------|
|   |        | $C_r$ | Crain | Crain | $C_{rain}/C_r(n)$ |
| West flowing $(n = 10)$                                 | Cl     | 110   | 135   | 135   | $\sim \! 100$     |
|   | $SO_4$ | 12    | 16    | 16    | $\sim 100$        |
|   | Na     | 172   | 115   | 115   | 67                |
|   | Ca     | 171   | 23    | 23    | 13                |
|   | Mg     | 132   | 15    | 15    | 11                |
| Krishna and Bhima tributaries (east flowing; $n = 31$ ) | Cl     | 398   | 48    | 80    | 20                |
|   | $SO_4$ | 181   | 11    | 18    | 10                |
|   | Na     | 790   | 42    | 70    | 9                 |
|   | Ca     | 338   | 21    | 35    | 10                |
|   | Mg     | 262   | 9     | 15    | 6                 |
| Krishna mainstream ( $n = 12$ )                         | Cl     | 267   | 48    | 80    | 30                |
|   | $SO_4$ | 69    | 11    | 18    | 26                |
|   | Na     | 445   | 42    | 70    | 16                |
|   | Ca     | 509   | 21    | 35    | 7                 |
|   | Mg     | 321   | 9     | 15    | 5                 |
| Bhima mainstream $(n = 8)$                              | Cl     | 954   | 48    | 80    | 8                 |
|   | $SO_4$ | 536   | 11    | 18    | 3                 |
|   | Na     | 1570  | 42    | 70    | 4                 |
|   | Ca     | 709   | 21    | 35    | 5                 |
|   | Mø     | 517   | 9     | 15    | 3                 |

Table 4b. Atmospheric contributions of major ions.

C = average concentration ( $\mu$ M), subscript r and rain refer to river and rain.

 $C_{rain}^*$  = rain water concentration corrected for evapo-transpiration.

average is identical to that reported by Dessert et al. (2001) for the NTW rivers draining the more northern regions of the Deccan Traps. A closer look at the distribution (Fig. 6) shows two main clusters, one at  $\sim 15$  t km<sup>-2</sup> y<sup>-1</sup> (belonging to the east flowing smaller tributaries of the Krishna) and the other at  $\sim 55$  t km<sup>-2</sup> y<sup>-1</sup>, comprised mainly of the west flowing Western Ghat rivers. Approximately 10% of the samples have values in excess of  $\sim 60$  t km<sup>-2</sup> y<sup>-1</sup>; these are the Bhima and its tributaries. Sources of uncertainties in the chemical weathering rates (CWR) estimates are:

- 1. Supply of Ca from carbonates. Carbonates in the form of calcite have been reported in some of the Deccan flows (Sukeshwala et al., 1972; Jeffery et al., 1988). To check on this further, carbonate content of 16 samples of Deccan basalts from Mahabaleshwar, Igatpuri, and Ambenali were measured by coulometry. The results show that many of the samples have measurable carbonate in them, with concentration between 0 to 0.92 wt% (mean 0.2 wt%). Similarly, bed sediments also have a few percent carbonate. Though low, the abundance of carbonates could be an additional source of Ca to selected rivers, as they weather more rapidly than silicates. If carbonates are important in Ca budget of rivers analysed, then a part of the alkalinity has to be derived from their weathering, making the CWRs calculated above lower limits. This is discussed in more detail in the next section.
- 2. Calcite precipitation. The removal of Ca from dissolved phase via calcite precipitation can also underestimate the CWRs. Calcite saturation indices (CSI; Langmuir, 1971) at 25°C were calculated (Drever, 1997) to check on the possibility of removal of Ca by calcite precipitation. The results show that 49 out of 63 samples are undersaturated in calcite (CSI: <0), while the remaining 14 show slight to moderate supersaturation. It is unclear if supersaturation would lead to calcite precipitation, as it may also depend upon other</p>

physicochemical conditions of rivers (Dalai et al., 2002). The Ca/Mg ratios of these calcite supersaturated rivers (as discussed in the next section), however, seem to indicate removal of Ca. It is interesting to mention that a similar calculation for streams from the NTW system (Dessert et al., 2001) show that a number of them are also supersaturated in calcite.

3. Anthropogenic supply. The impact of this source on Na and Cl abundances has already been considered. There could be other ions, such as SO<sub>4</sub>, which could also be derived from this source. The role of this source in major ion abundances, and hence CWRs of the basins, is difficult to quantify. Therefore, to avoid uncertainties in CWRs arising from this source and also in Ca budget due to calcite precipitation, CWRs were recalculated by excluding the data of the samples with high SO<sub>4</sub> (>100  $\mu$ M), Cl (>300  $\mu$ M), and CSI (>0). These include the Bhima in its lower reaches (BHM-2, 3, 4, and 5), its tributaries (the Ghod, Mutha, Nira, and the Kukdi), and some the Krishna samples (KRS-1, 4, and 5). This recalculation brings down the maximum CWR for the Krishna system rivers (n = 33; includes Ambika, Table 3) to  $\sim$ 34 t km<sup>-2</sup> y<sup>-1</sup> (mean: 14 t km<sup>-2</sup> y<sup>-1</sup>). The six west flowing Western Ghat rivers have higher and similar CWRs (48-60 t km<sup>-2</sup> y<sup>-1</sup>) compared to the east flowing Western Ghat rivers GTP-1, KYN-2, HRN-1, and TPN-1 that have CWR < 10 t km<sup>-2</sup> y<sup>-1</sup>. These results suggest that there is considerable variability in chemical weathering rates even among adjacent basins of the Deccan Traps.

Assuming that the average CWR for the Krishna system,  $\sim 14 \text{ t km}^{-2} \text{ y}^{-1}$ , as typical of the Deccan interior and  $\sim 54 \text{ t km}^{-2} \text{ y}^{-1}$  for the west of the Western Ghats ( $\sim 6\%$  of the total Deccan Trap area), the area weighted CWR for the Deccan Trap is calculated to be  $\sim 16 \text{ t km}^{-2} \text{ y}^{-1}$ . This translates to a chemical erosion flux (CEF) of  $\sim 0.8 \times 10^7 \text{ tons y}^{-1}$  and an erosion rate of 5.8 mm ky<sup>-1</sup> for the Deccan basalts. The present



Fig. 5. (a) Scatter plot of  $SO_4$  vs. Cl. The data shows an increasing trend with a good positive correlation. (b) Na vs. (Cl+SO<sub>4</sub>). The strong correlation between them is an indication that Na, Cl, and SO<sub>4</sub> may be derived from a common source.

day CEF, however, could be lower than that in the past, because of decrease in both chemical weathering over time due to development of soil cover (Bluth and Kump, 1994) and the aerial coverage of Deccan Traps.

## 4.2.1. Variability in CWRs among different Deccan Trap regions

The CWR for the Krishna system in the southern Deccan average  $\sim 14$  t km<sup>-2</sup> y<sup>-1</sup>, about four times lower than that for the west flowing rivers,  $\sim 54$  t km<sup>-2</sup> y<sup>-1</sup>, though their average TDS\* overlap. The major difference between these two regions is runoff, the western region has four times the runoff of the Krishna system. This, coupled with the observations that river water temperatures and physical weathering of the two regions are roughly similar, suggests that runoff determines the CWR in these basins. Similar inference on the coupling between CWR and runoff has been reported earlier (Bluth and Kump, 1994).

The CWR in the northern Deccan as deduced from the chemistry of NTW rivers (Dessert et al., 2001) is two to three times that for the Krishna system, determined in this study. This difference seems to result from higher intensity of chemical weathering of the NTW basins, rivers from this region have two to three times more TDS\* than the Krishna system rivers.

Possible explanations for the difference in TDS\*, and hence CWR between the north and the south Deccan, are (i) natural variability in intensity chemical weathering in the different regions of the Deccan Traps; (ii) underestimation of the weathering rates in this study because of sample selection criteria used in calculation (rejection of high Cl, SO<sub>4</sub>, and calcite supersaturated samples); and (iii) contributions from sources in addition to basalts in NTW rivers, which result in higher TDS\*. In this context, the role of easily weatherable Vindhayan carbonates/sediments of the basin, and groundwater/anthropogenic inputs in supplying major ions to the NTW rivers requires further scrutiny. The high NO<sub>3</sub> (>50  $\mu$ M), SO<sub>4</sub> (>100  $\mu$ M)



Fig. 6. Frequency distribution of chemical weathering rates (CWR). The peak between 50 to 60 t km<sup>-2</sup> y<sup>-1</sup> is from the west flowing Western Ghat rivers, which have a factor of ~4 higher runoff compared to the tributaries of the Krishna River. Rivers with >60 t km<sup>-2</sup> y<sup>-1</sup> CWR have very high Cl, SO<sub>4</sub>, and NO<sub>3</sub> and belong to the Bhima (lower levels and higher Na<sup>+</sup>/Mg<sup>+</sup> and Na<sup>+</sup>/Ca<sup>+</sup> in these waters relative to basalts are pointers to input from such sources.

#### 4.2.2. Silicate weathering rates

The rivers analysed in this study flow entirely through the Deccan basalts. It is, therefore, expected that the major ion abundances of these rivers (corrected for rain input) is from silicate weathering. If this is valid then the CWRs derived in the earlier section would be same as their silicate weathering rates (SWR). This approach to derive SWR can be in doubt if carbonates present in basalts and river sediments act as a significant source of Ca and alkalinity to rivers and if other sources (saline soils, anthropogenic supply) of major cations influence river water chemistry. It has been shown earlier that such inputs can be important for some of the rivers. Therefore, determination of SWRs has to depend on other approaches such as those based on elemental ratios in rivers and in basalts. SWRs are generally calculated using a suitable proxy (e.g., Na\* concentration in rivers) and assumptions regarding the release of various elements from rocks to water (Singh et al., 1998; Galy and France-Lanord, 1999; Dalai et al., 2002; Jacobson et al., 2002; Bickle et al., 2003). For some of the rivers sampled in this study, Na\* may not be a suitable proxy, as they may be receiving Na from saline soils and anthropogenic sources in addition to rain and basalts. Dessert et al. (2001) used HCO<sub>3</sub> as an index of basalt weathering to derive CO<sub>2</sub> consumption rates. This requires bicarbonate to be supplied entirely from silicate weathering, a requirement that needs to be verified considering that carbonates are present in basalts and in river sediments, and their weathering can also supply alkalinity to rivers. Alkaline soils can be another source of alkalinity to some of these rivers. The significance of this source, however, needs to be assessed.

In this work, dissolved Mg has been used as an index of silicate weathering, as it is expected to be supplied almost entirely from weathering of Deccan basalts. Dolomite weathering is another source of Mg, but there are no reports of its occurrence in the basins. Figure 7a, b shows scatter diagrams of Ca\* and Na\* vs. Mg\* in rivers with CSI < 0, Cl < 300  $\mu$ M, and SO<sub>4</sub><100  $\mu$ M (these rivers have been selected as they avoid ambiguities arising from calcite supersaturation, major anthropogenic and saline soil inputs). The plots show strong positive correlation between these elements, consistent with that expected if basalt weathering is the dominant source for them.

The silicate components of major cations in rivers are calculated using Mg as a proxy as follows

$$Mg_{sil} = Mg_r - Mg_{rr}$$
(1)

$$\mathbf{K}_{sil} = \mathbf{K}_r - \mathbf{K}_{rr} \tag{2}$$

$$Ca_{sil} = Mg_{sil} \times (Ca/Mg)_{sol}$$
(3)

$$Na_{sil} = Mg_{sil} \times (Na/Mg)_{sol}$$
(4)

where the subscripts *sil*, *r*, and *sol* are silicates, river and solution, respectively.  $Mg_{rr}$  (K<sub>rr</sub>) is the contribution of Mg (K) from rain to the river water (Appendix).

(Ca/Mg)<sub>sol</sub> and (Na/Mg)<sub>sol</sub> are the ratios with which Ca and Na are released relative to Mg, from basalts to rivers. These are calculated assuming that these elements are released to rivers in the same ratio as their abundances in basalts, Ca/Mg = 1.19and Na/Mg = 0.51 (Table 2). The accuracy of estimation of silicate derived Ca and Na in rivers depends critically on how well (Ca/Mg)sol and (Na/Mg)sol can be constrained. Independent estimates of these ratios are also made from Ca\*, Mg\*, and Na\* data of a few small rivers, VAT-1, SUKH-1, SHT-1, KJL-1, GAD-1, and ARJ-1 (Fig. 1c; Table 3). These rivers were selected as only two sources; rain and silicate weathering determine their major ion chemistry. Cl and SO<sub>4</sub> in these rivers can be accounted entirely by rain, <sup>87</sup>Sr/<sup>86</sup>Sr of most of them lie in the range of 0.705 to 0.707 similar to the range of  $^{87}$ Sr/ $^{86}$ Sr of basalts (Subbarao et al., 2000; Sen, 2001). The Ca\*/Mg\* and Na\*/Mg\* of these rivers are  $1.27 \pm 0.08$  and  $0.49 \pm 0.08$ respectively; these ratios overlap with the corresponding ratios in basalts.

Table 5 presents a comparison of Ca\*/Mg\* and Na\*/Mg\* ratios measured in selected samples of the Krishna, Bhima, and their tributaries (also includes Ambika and Mula) and west flowing rivers (CSI <0, Cl <300  $\mu$ M, and SO<sub>4</sub><100  $\mu$ M) with those expected based on chemical and mineralogical composition of the basalts. Among these, in some of the rivers, Na\* concentrations are quite low (Fig. 7b), and hence are subject to larger uncertainties.

These results show that the average Ca\*/Mg\* ratios in the Krishna and Bhima (and their tributaries) are marginally higher than those expected from basalts. This can be ascribed either to the presence of other source(s) of Ca to rivers or to a slight preferential mobility of Ca over Mg from basalts to water. Ca-rich minor phases in the basalts (such as carbonates), which are easily weatherable, can be the other sources for Ca. The close similarity of these ratios between basalts and river water, however, indicates near stoichiometric release of Ca, Mg, and Na to rivers from basalt. This is in contrast to the results from Reunion Island, where fractionation among Ca, Mg, and Na during weathering has been suggested, with preferential release



Fig. 7. (a) Scatter plot of  $Mg^*$  vs.  $Ca^*$ . The data shows very high correlation (b) plot of  $Mg^*$  vs.  $Na^*$ ; these elements also show a good correlation. These significant correlations coupled with their abundance ratios overlapping with those in basalts suggest that these elements are released to rivers from basalts without major fractionation.

of Na over Ca and Mg (Louvat and Allegre, 1997). In the samples analysed in this work, such fractionation is not evident.

Extension of this calculation to all rivers analysed brings out two other important observations: (i) the rivers that are supersaturated with calcite (e.g., NIRA-1, NIRA-2, GHOD-2,

| Table 5. Measured and ex | pected major | r ion ratios ( | n = 43). |
|--------------------------|--------------|----------------|----------|
|--------------------------|--------------|----------------|----------|

|   | Mea  | sured   |   |
|---|--|---|---|
| Ratio   | (1)  | (2)   | Expected  |
| Ca*/Mg*<br>Na*/Mg*<br>HCO <sub>3</sub> /Mg<br>Ca*/Na* | $\begin{array}{l} 1.38  \pm  0.21 \\ 0.48  \pm  0.18 \\ 5.85  \pm  0.59 \\ 3.34  \pm  1.5 \end{array}$ | $\begin{array}{l} 1.27  \pm  0.08 \\ 0.49  \pm  0.08 \\ 5.70  \pm  0.23 \\ 2.62  \pm  0.33 \end{array}$ | 1.15, 1.19 <sup>#</sup><br>0.51, 0.51 <sup>#</sup><br>6.40<br>2.25, 2.34 <sup>#</sup> |

(1) Krishna, Bhima and their tributaries (n = 33).

(2) West flowing rivers (n = 10).

<sup>#</sup> In basalts.

KUK-1, and BHM-5) show deficiency of Ca relative to its estimated supply from basalts. This finding is an indication that in these rivers, calcite precipitation may have influenced their Ca concentration; and (ii) Na\* in the Bhima in its lower reaches; Ghod, Mutha, Nira, and the Kukdi (Table 3) are quite in excess of Na<sub>sit</sub>. These rivers also have high Cl, SO<sub>4</sub>, which attests to the inference made earlier that Na contribution from saline/alkaline soils and anthropogenic sources might be important.

The total silicate cations  $\Sigma(Ca_{sil} + Mg_{sil} + Na_{sil} + K_{sil})$  in the above rivers (n = 43) range from 105 to 1652  $\mu$ E. This corresponds to ~36 and ~85% of TZ<sup>+</sup> (average: 66%), the balance being contributed by rain and other sources. The silicate fraction of cations in the Deccan rivers is much higher than those determined for the Ganga-Bramhaputra river system (Galy and France-Lanord, 1999; Krishnaswami et al., 1999; Dalai et al., 2002; Jacobson et al., 2002). This is expected as the basins of the Deccan rivers are covered almost entirely with basalts, whereas silicates, carbonates, and other sediments all occur in the drainage basins of the headwaters of the Ganga-Yamuna in the Himalaya.

### 4.2.3. Role of carbonates in Ca budget

It has been shown in some of the earlier studies on granite watersheds (Blum et al., 1998; White et al., 1999; Jacobson et al., 2002; Oliva et al., 2004) that Ca-rich minor phases such as calcite, apatites, and Ca-rich silicates present in these rocks can be a major source of Ca to rivers draining them. The role of such phases in contributing to Ca budget of Deccan rivers is evaluated below. In most of the rivers analysed, Ca\* is marginally in excess of  $Ca_{sil}$ . If this excess results from the supply of Ca from carbonates in basalts (or in the basin) to rivers, a limit on their contribution can be estimated as:

$$Ca_{c} = Ca_{r} - (Ca_{rr} + Ca_{sil})$$
(5a)

$$Ca_{r} = Ca_{r} - \left\{ Ca_{rr} + \left( Ca/Mg \right)_{sol} \times Mg_{sil} \right\}$$
(5b)

where subscript *c* refers to carbonate contribution ( $\mu$ M), and other subscripts are defined in the Appendix.

Ca<sub>c</sub> ranges from  $\sim$ 2 to  $\sim$ 145  $\mu$ M with a mean of 38  $\mu$ M in the 43 samples. This corresponds to  $\sim 1$  and  $\sim 29\%$  of measured Ca in these rivers. Measurement of  $\delta^{13}C$  of dissolved inorganic carbon (DIC) in these waters also attests to the contribution of carbonate derived DIC in them.  $\delta^{13}C$ values in these waters vary from  $\sim -20$  to -8%, with a strong inverse correlation with 1/HCO<sub>3</sub> and Si/HCO<sub>3</sub>. These are interpreted in terms of mixing of two DIC end members, generated from silicate and carbonate weathering with CO<sub>2</sub> from C<sub>3</sub> vegetation. The  $\delta^{13}$ C of the west flowing rivers is the most negative consistent with the inference that their major ion composition is determined by basalt weathering. Samples enriched in  ${}^{13}C$ , -13 to -8%, have higher carbonate component of DIC. These samples are at or above calcite supersaturation or have signatures of anthropogenic inputs (high Cl and  $SO_4$ ). The major uncertainty in Ca<sub>c</sub> estimate is the value of (Ca/Mg)<sub>sol</sub>. If this is different from the value used in calculation, (Ca/Mg) abundance ratio in basalts, Ca<sub>c</sub> would also vary accordingly.

The maximum Ca contribution from carbonates is  $\sim 29\%$ for the rivers used in calculation This is unlike granites/ gneiss watersheds, where Ca supply from such minor phases are reported to be more significant (Blum et al., 1998; White et al., 1999; Oliva et al., 2004). This difference is attributable to high Ca in basalts, relative ease of their weathering, and their relatively low carbonate content. Further, though carbonates may weather orders of magnitude higher than basalts in natural environments, the weathering of calcites contained in silicate rocks would be limited by the rate of their exposure. Carbonates dispersed in sediments can also be a potential source of Ca.

## 4.2.4. Comparison of silicate weathering rates

The silicate weathering rates in the Krishna system and the west flowing Western Ghat rivers are presented in Figure 8a and summarized in Table 6. The SWR of the Krishna at Alamatti (KRS-2) is  $\sim$ 14 t km<sup>-2</sup> y<sup>-1</sup>. The west flowing

Western Ghat rivers have SWR of  $\sim$ 53 t km<sup>-2</sup> y<sup>-1</sup>, a factor of  $\sim$ 4 higher than those of the Deccan interior, caused mainly by their higher runoff of similar proportion (Table 6). This reemphasises the importance of runoff in determining weathering rates (Bluth and Kump, 1994; Amiotte-Suchet and Probst, 1995; Louvat and Allegre, 1997; Kump et al., 2000). Further, this study also has shown that in some basins of the Deccan Trap, the SWR can be low (<10 t km<sup>-2</sup> y<sup>-1</sup>), possibly due to "transport limitation" resulting from their soil cover (Stallard, 1995).

Comparison of SWRs of the south and western regions of the Deccan Traps based on this study with the reported results from northern region (Dessert et al., 2001) is strictly not possible, as only CWR data are available for the latter. The estimation of SWR for the northern Deccan region needs better understanding on the role of Vindhayan carbonates/sediments and anthropogenic/saline soils and supersaturation of calcite in contributing to the major ion budget of the rivers draining this region.

The data in Table 6 show that the SWRs of the Krishna system are within a factor of  $\sim 2$  of the Ganga headwaters (the Yamuna, Bhagirathi, and the Alaknanda) in the Himalaya, though these two sets of rivers flow through quite different climatological and lithological basins. The Yamuna and the Ganga basins in the Himalaya are multi-lithological, with a significant fraction of their basins being covered by lithologies other than silicates such as carbonates, whereas the Krishna and the Western Ghat basins are covered almost exclusively with Deccan basalts. Among the silicates of the Yamuna-Ganga basin, granites/gneisses is a significant lithology (Valdiya, 1980). The similarity in SWRs among these basins seems to suggest that under "favourable conditions" (i.e., high physical erosion, runoff), silicate weathering rates of granite/granitoid drainage basins can also be as high and/or similar to those of basalts.

## 4.3. CO<sub>2</sub> Consumption Rates

The calculated CO<sub>2</sub> consumption rates for different regions of the Deccan and the Himalaya are given in Figure 8b. For the rivers draining into the Arabian Sea, the CO<sub>2</sub> consumption rates cluster around  $\sim 1 \times 10^6$  mol km<sup>-2</sup> y<sup>-1</sup>, whereas the Krishna system rivers show much wider range, from 0.05 to  $0.76 \times 10^6$ mole km<sup>-2</sup> y<sup>-1</sup>. Many streams that have low-silicate weathering rates have  $\rm CO_2$  consumption rate  $< 0.1 \times 10^6$  mole km<sup>-2</sup>  $y^{-1}$ , similar to some of the lowest values reported for other basaltic regions (e.g., Hawaiian basalts; Bluth and Kump, 1994). The area-weighted CO<sub>2</sub> consumption rate for the Deccan Traps is  $0.36 \times 10^6$  moles km<sup>-2</sup> y<sup>-1</sup>, much lower than the reported average value of  $1.26 \times 10^6$  mole km<sup>-2</sup> y<sup>-1</sup> for the NTW rivers (Dessert et al., 2001). In a more recent publication, however, Dessert et al., (2003), report a lower value of 0.74  $\times$  $10^6$  mole km<sup>-2</sup> y<sup>-1</sup> for the Deccan Traps. The average annual  $CO_2$  drawdown by Deccan Traps (area 5 × 10<sup>5</sup> km<sup>2</sup>) based on  $\mathrm{CO}_2$  consumption rates determined in this study is ~0.18 imes $10^{12}$  moles, ~1.5% of the annual global CO<sub>2</sub> consumption  $(11.7\times10^{12}\mbox{ moles y}^{-1})$  by silicate weathering (Gaillardet et al., 1999). The proportion of CO<sub>2</sub> consumption by Deccan basalts is a factor of  $\sim$  4 more than its fractional area of continental drainage. This reinforces the earlier findings (Dessert et al., 2001; Amiotte-Suchet et al., 2003) that Deccan Traps



Fig. 8. (a) Distribution of silicate weathering rates in selected samples of the Krishna system ( $\blacksquare$ ) and the west flowing Western Ghat rivers (ℤ, WFWR). The SWR in the WFWR are much higher than those of the Krishna system and are a result of higher runoff in the region. The chemical weathering rate based on the results of northern Deccan (Dessert et al., 2001), the area-weighted average SWR for the Deccan basin in the present study, and the global silicate weathering rate are also shown for comparison. (b) CO<sub>2</sub> consumption rates due to silicate weathering in selected basins of the Krishna system ( $\blacksquare$ ) and in WFWR (ℤ). The area-weighted average CO<sub>2</sub> consumption rate for the entire Deccan basin based on these results is  $\sim 3.6 \times 10^5$  moles km<sup>-2</sup> y<sup>-1</sup>. The reported CO<sub>2</sub> consumption rate based on results of northern Deccan (Dessert et al., 2001; Dessert et al., 2003) and the global CO<sub>2</sub> consumption rate due to silicate weathering (Gaillardet et al., 1999) are also shown for comparison.

(and basalts in general) are consuming  $CO_2$  disproportionately more than their aerial coverage during their chemical weathering.

## 5. SUMMARY AND CONCLUSION

A detailed and systematic geochemical study of the headwaters of the Krishna and the Bhima and a number of medium and small rivers draining the southwest Deccan Traps (India) has been carried out to determine rates of chemical and silicate weathering of their basins and Deccan basalts in general. This study is based on repeat sampling of about two dozen rivers over two monsoons, 2001 and 2002. The rivers selected for this work flow entirely through Deccan tholeiites but have significant differences in rainfall, soil cover, and altitude among the basins, which provide an opportunity to evaluate their role in influencing weathering processes. The important findings of the study are:

- 1. The waters are neutral to mildly alkaline, with TDS in the range of  $\sim 27$  to 640 mg l<sup>-1</sup>; however, nearly half of the samples have TDS <100 mg l<sup>-1</sup>. The high TDS are in the Bhima and its tributaries and are a result of abundant Cl, SO<sub>4</sub>, and Na concentrations.
- 2. (Ca+Mg) and HCO<sub>3</sub> are the most abundant cations and anions in a majority of the rivers. Fourteen (out of 63) samples are supersaturated with respect to calcite, many of these samples also have high Cl, SO<sub>4</sub>, and TDS. Rivers with high Cl also have high SO<sub>4</sub>; in general, there is a strong correlation between them and also with Na. If these obser-

Table 6. Silicate weathering rates in the Deccan Traps and in the Himalaya.

| River basin                      | Location        | Runoff (mm $y^{-1}$ ) | TDS(s) (mg l-1) | $\frac{\text{SWR}}{(\text{t km}^{-2} \text{ y}^{-1})}$ | Reference                  |
|----------------------------------|-----------------|-----------------------|-----------------|--|----------------------------|
| Deccan Traps                     |                 |                       |                 |  |                            |
| Krishna (KRS-2)                  | Alamatti        | 463                   | 30              | 14   | This work                  |
| West flowing rivers <sup>@</sup> | Western Deccan  | 1690                  | 32              | 53   | This work                  |
| Krishna system (east flowing)    | Deccan          | 463                   | 28              | 13   | This work                  |
| Narmada-Tapti-Godavari           | Northern Deccan | 463                   | 81              | 37*  | Dessert et al. (2001)      |
| Himalaya                         |                 |                       |                 |  |                            |
| Yamuna                           | Batamandi       | 1125                  | 25              | 28   | Dalai et al. (2002)        |
| Bhagirathi                       | Devprayag       | 1064                  | 14              | 15   | Krishnaswami et al. (1999) |
| Alaknanda                        | Bhagwan         | 1195                  | 9               | 10   | Krishnaswami et al. (1999) |

 $TDS(s) = \Sigma(Na + K + Mg + Ca)_{sil} + SiO_2$ ; TDS(s) and SWR are rounded off.

\* Chemical weathering rate.

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vations are interpreted in terms of supply from saline soils and anthropogenic sources, their average contribution to the tributaries of the Krishna and the Bhima and the Krishna and Bhima mainstream would be  $\sim$ 70 to 90% of Cl, and  $\sim$ 40 to 60% of Na, respectively.

- 3. Chemical weathering rates (CWR) of rivers (with CSI <0, Cl <300  $\mu$ M and SO<sub>4</sub>< 100  $\mu$ M) range from ~3 to ~60 t km<sup>-2</sup> y<sup>-1</sup>. Silicate weathering rates (SWR) in these rivers, calculated using Mg as an index, varies from  $\sim 3$  to  $\sim 60$  t  $km^{-2} y^{-1}$ , making up ~95% of CWR. This suggests that major ion abundance in these selected rivers is almost entirely of silicate origin. The Ca\*/Mg\* and Na\*/Mg\* in these rivers closely match their ratios in basalts, suggesting their near stochiometric release from basalts to rivers. Estimates of contribution of Ca from carbonates in basalts and in the basin show that it can be  $\sim 13\%$  on average, though in some rivers it can be up to  $\sim 30\%$  of the Ca budget. The CWR and SWR of west flowing Western Ghats rivers are ~4 times those of the east flowing rivers. This difference is in proportion to their runoff and attests to the major role of runoff in determining chemical and silicate weathering rates.
- 4. The area-weighted average  $CO_2$  consumption rate from silicate weathering in the Deccan Traps is  $3.6 \times 10^5$  mole km<sup>-2</sup> y<sup>-1</sup>. The CO<sub>2</sub> drawdown by Deccan basalts is estimated to be  $1.8 \times 10^{11}$  moles y<sup>-1</sup>. This is ~1.5% of CO<sub>2</sub> consumed by continental silicate weathering, ~4 times higher than the fractional area of exposure of Deccan basalts, and reaffirms the earlier observation that basalts weather more rapidly and thus contribute to higher CO<sub>2</sub> drawdown.
- 5. The CWR, SWR, and  $CO_2$  consumption of rivers analysed in this study from the southwest Deccan Traps are two to four times lower than those reported for the Narmada-Tapti-Wainganga (NTW) systems from the more northern region of Deccan. Spatial variations in weathering rates, calculation of CWR and SWR in this study based on selected rivers, and possible supply of major ions to NTW system from sources other than basalts all are potential causes for the observed differences. The SWR for the Deccan Traps derived in this study are comparable to those reported for the Ganga-Yamuna headwaters in the Himalaya. This suggests that weathering of granites/gneisses can be similar to those of

basalts under favourable conditions of higher physical weathering and higher runoff.

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#### APPENDIX

(A). Supply of Na, Ca, Mg, and  $\mathrm{SO}_4$  from rains to rivers is calculated using the relation

$$X_{rr} = (X/Cl)_{rain} \times Cl_{rain} / f_{et}$$
(1a)

where  $X_{rr}$  is the contribution of rain ( $\mu$ M) to rivers; (X/Cl) is the molar abundance ratio in rains;  $f_{et}$  is the correction factor for evapo-transpiration. For the west flowing Western Ghat rivers, in which all Cl and SO<sub>4</sub> can be from rain,  $f_{et} \approx 1$ , for the interior Deccan,  $f_{et} \approx 0.6$  has been used.

(B). The contribution of Cl and Na from anthropogenic and salt-affected saline soils ( $\mu M$ ) to rivers of Deccan interior can be derived from

$$Cl_s = Cl_r - Cl_{rain}/0.6$$
(2a)

$$Na_s = Cl_s$$
 (2b)

where subscripts s and r refer to salt-affected plus anthropogenic sources and rivers, and 0.6 is the evapotranspiration factor.

(C). The dissolved major ions in rivers  $(\mu M)$  resulting from chemical weathering of the basin (X\*) are calculated as

Case 1: For rivers flowing into the Arabian Sea, all Cl can be accounted for from rain. In these samples

$$\mathbf{X}^* = \mathbf{X}_r - \mathbf{X}_{rr} \tag{3a}$$

where X = Na, K, Ca, Mg, and SO<sub>4</sub>;  $X_{rr}$  is calculated based on Appendix Eqn. 1.

Case 2: For the rivers draining into the Bay of Bengal (Deccan interior)

X\* for K, Ca, Mg, and SO<sub>4</sub> can also be calculated based on the above relation (1) and  $f_{et} = 0.6$ .

For Na, additional correction is needed because of its input from saline soils/anthropogenic sources. Na\* is given by

$$Na^* = Na_r - (Na_{rr} + Na_s) \tag{4a}$$

$$Na^* = Na_r - Cl_r + \left\{1 - (Na/Cl)\right\} \times Cl_{rain}/f_{et}$$
(4b)

where Na<sub>r</sub> and Cl<sub>r</sub> are the concentrations in rivers, the second term on RHS of Appendix Eqn. 4 is a result of  $(Na/Cl)_{rain}$  being  $\neq 1$ .