## Radium isotopes and Rare Earth Elements in Indian Rivers and the Bay of Bengal

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By

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## Certificate

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any university or institution.

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# DEDICATED TO THE FOND MEMORIES OF MY PARENTS

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### Statement

#### **1.1 Introduction**

This thesis discusses (i) the determination of lateral and vertical diffusive mixing parameters in the surface waters of the Bay of Bengal and the Arabian Sea using radium isotopes, <sup>228</sup>Ra and <sup>226</sup>Ra and (ii) processes influencing the abundance and distribution of uranium and Rare Earth Elements (REE) in dissolved and particulate phases of the Chambal and the Yamuna rivers. As these topics address two distinctly different issues, viz. circulation in the coastal waters of the Bay of Bengal and the Arabian Sea and weathering and transport of river sediments in the Himalaya and the Vindhyan plains, these results are presented and discussed as two separate sections. **Part A** deals with radium isotopes in the surface waters of the Bay of Bengal and transport of uranium and REE in the Chambal and Yamuna rivers.

#### A. Radium isotopes in seawater

Ra isotopes have found extensive applications in seawater circulation studies. Especially <sup>228</sup>Ra has found widespread application in studies of coastal ocean and upper thermocline circulation. This isotope, with a half-life of 5.75 y serves as a chronometer to study circulation and water mixing occurring on decadal time scales (Moore, 1969, 1972; Knauss et al., 1978; Yamada and Nozaki, 1986). <sup>226</sup>Ra (half-life = 1620 y) is used to study large-scale ocean mixing using a vertical advection-diffusion model to describe its distribution in the water column (Chung and Craig, 1980; Ku et al., 1980). In this study, these Ra isotopes are measured in seawater from surface to 500 m depth to study the upper ocean circulation of the Arabian Sea and the Bay of Bengal.

The Arabian Sea is a unique oceanic region characterized by the wellknown annual reversal in the atmospheric and upper ocean circulations (Qasim, 1982; Madhupratap et al., 1996). This, in turn, leads to significant variability of surface water properties during different seasons. During the southwest monsoon (June-September), Somali region of the Arabian Sea experiences intense upwelling which causes in very high levels of biological production in these regions, particularly the western Arabian Sea both in the coastal waters off Somalia and Arabia and in the open ocean northwest of the Findlater jet (Qasim, 1982; Madhupratap et al., 1996). These high rates of biological production export significant quantities of organic matter to the intermediate waters leading to the development of intense oxygen minimum at intermediate depths (Naqvi, 1994).

The Bay of Bengal is another distinctive oceanic region wherein seven large rivers from the Himalava and peninsular India annually discharge  $\sim 10^{15}$  L of water and  $\sim 10^{15}$  g sediment, a major fraction of this being contributed by the Ganga-Brahmaputra river system itself (Milliman and Syvitski, 1992). The sources of Ra isotopes to the surface ocean are from river water, desorption from particles and from the decay of Th isotopes (<sup>232</sup>Th and <sup>230</sup>Th) contained in the coastal and shelf sediments followed by upward diffusion via pore waters. Ra is released from suspended sediments to the estuarine waters at increasing ionic strengths at mid-chlorinities (Li et al., 1977; Elsinger and Moore, 1984). In case of the Bay of Bengal, in addition to the high sediment input which supplies Ra to seawater,  $(1-3) \times 10^{15}$  dpm y<sup>-1</sup> of dissolved <sup>228</sup>Ra is added to the Bay of Bengal from the Ganga-Brahmaputra river system (Sarin et al., 1990). With the large component of riverine Ra isotope input, coupled with the sedimentary flux of Ra isotopes from shelf sediments, it should be easily possible to study time scales of open ocean circulation using Ra isotopes in both the surface and upper oceans (depth <500 m) of the Bay of Bengal and the Arabian Sea.

The concentration of Ra isotopes, particularly <sup>228</sup>Ra is quite low (ranging between 6.2 to 42.1 dpm/100kg at the sampled locations) in surface and upper ocean waters and hence needs to be preconcentrated from 50-100 L of seawater for its measurement. This was done by adsorbing Ra on Mn fibres (Moore, 1976). Towards this, seawater samples of 60-100 L was passed through Acrilan fibre coated with MnO<sub>2</sub>, Ra isotopes were acid leached from these fibres, coprecipitated with BaSO<sub>4</sub>, and their gamma activities were assayed using HPGe well detector. A total of 68 surface seawater samples for Ra isotopes were

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collected from four cruises to the western Bay of Bengal. In addition, 42 seawater Ra isotope profiles consisting of samples from surface to 500 m depth from the Arabian Sea and the Bay of Bengal were collected on board FORV Sagar Sampada during seven different cruises. The <sup>228</sup>Ra concentration in the surface waters was modelled to determine the lateral and vertical advection and eddy diffusion rates. The eddy diffusivities derived are the first sets of such measurements in the Bay of Bengal. These values are compared with those obtained from the Arabian Sea to bring out the salient aspects of upper ocean circulation of these two basins.

#### B. Uranium and Rare Earth Elements in rivers

The geochemistry of sedimentary rocks has considerable consequence for our understanding of the earth and the processes that shape it. The processes of weathering, erosion, sediment sorting and diagenesis, essentially involve water/rock interaction. The composition of riverine sediments may provide useful insights into the mechanisms of element mobility in crustal environments.

Large ion lithophile (LIL) or incompatible elements include K, Rb, Cs, Sr, Ba, REE, Th and U. All these elements are strongly concentrated in the continental crust. Of these, U is relatively more soluble during surficial weathering because of its ability to form uranyl carbonate complex, UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>-4</sup>. Analysis of dissolved uranium concentration and <sup>234</sup>U/<sup>238</sup>U activity ratio in the Yamuna and the Chambal rivers was undertaken to determine the source of U in these rivers and the relative contribution of the Himalayan and Chambal basins to the dissolved U concentration of the Ganga river. Earlier studies carried out by Sarin et al. (1990) had shown a distinct difference in <sup>234</sup>U/<sup>238</sup>U activity ratio between the lowland rivers (Chambal, Betwa, Ken, Son) draining predominantly the Indo-Gangetic plains and the highland waters (Gandak, Ghaghra and the upper reaches of Ganga) flowing through the Himalaya. This difference is attributed to variations in the geology of their drainage basins and the type of weathering processes. The near equilibrium value of <sup>234</sup>U/<sup>238</sup>U activity ratio in the highland rivers was explained in terms of their release, to surface waters, from

weathered materials from which most of the mobile  $^{234}$ U has already been lost or by the congruent weathering of rocks in the basin. In contrast,  $^{234}$ U/ $^{238}$ U activity ratios > 1 in the lowland rivers was explained in terms of weathering of silicates where radiogenic  $^{234}$ U is preferentially leached relative to  $^{238}$ U.

The REE form a unique chemical group wherein the gradual decrease in ionic radius across the series leads to systematic changes in geochemical behaviour (Henderson, 1984). Their transport through rivers from the continents to the oceans play an important role in the geochemical cycle of REE in the ocean and in the development of the REE pattern of seawater. For this reason several investigations have recently been made on the geochemical behaviour of REE in rivers, estuaries and coastal seas (Drever, 1988; Gouveia et al, 1993; Keasler and Loveland, 1982; Tricca et al., 1999). Earlier studies indicate that solution and surface chemistry play a major role in establishing the REE Both the concentration and the extent of composition of fresh waters. fractionation of dissolved REE in river waters are dependent on pH and on the presence of colloidal particles (Sholkovitz, 1995). Although REE behave as an unusually coherent group of elements, the Lanthanide contraction affects the stability of the carbonate complexes of REE cations. The heavy rare earth elements (HREE; Gd-Lu) form stronger complexes with carbonate (e.g.,  $K_{Er}=10^{5.6}$ ) than the light rare earth elements (LREE; La-Sm) (e.g.,  $K_{Nd}=10^{5.2}$ ). This leads to enrichment of HREE in the aquatic phase and to enrichment of LREE in the surface adsorbed fraction. High pH waters have the lowest REE concentrations and the most fractionated composition (HREE enriched). Studies of REE in river waters and sediments also provide information on the distribution of the sources of weathered materials (Gaillardet et al., 1997). Correlations of La/Yb normalized ratio with pH and dissolved La concentrations are observed for the Congo Basin, Amazon and Mississippi rivers. These relations tend to indicate that pH of river waters has a major control on the shape of the dissolved REE patterns and thus REE fractionation in the dissolved load. This study provides new data set on REE from high altitude rivers of the Yamuna system in

the Himalaya and that in one of its tributaries, the Chambal draining the Vindhyan plains.

#### 1.2 Objectives of the thesis

Objectives of this thesis are:

- I. To obtain the distribution of <sup>228</sup>Ra and <sup>226</sup>Ra isotopes in the surface and upper ocean waters of the Bay of Bengal and the Arabian Sea.
- II. To estimate the mixing parameters viz eddy diffusivities and advection velocities using radium isotopes in the surface and upper ocean waters of the Bay of Bengal and to compare them with those of the Arabian Sea.
- III. To study the major ion chemistry and trace metal abundances of the Chambal river basin and assess the relative contributions of various lithologies in controlling the solute budgets.
- IV. To characterize the nature and extent of chemical weathering in the two river basins viz the Chambal and the Yamuna basins and infer the differences due to lithology, relief and climate.
- V. To measure uranium and REE in the dissolved phase of the Chambal and the Yamuna rivers and identify the sources of these elements to river waters and their fluxes out of the basin.
- VI. To obtain the concentrations and downstream trend of REE of the bed sediments of the Chambal and the Yamuna rivers and to identify the sources and the evolution of REE pattern in these rivers and the Ganga River in the plains.

Objectives I and II are discussed in the section Part A while III to VI are discussed in the section Part B.

#### **1.3 Structure of the thesis**

This thesis is divided into eight chapters. Chapters 1-3 deals with "Radium isotopes in the seawater" and Chapters 4-7, with "Uranium and Rare Earth Elements in the rivers". Chapter 1 introduces the first of the two thesis topics, namely, Ra isotope studies in the Bay of Bengal and the Arabian Sea and the problems to be addressed in the present study.

Chapter 2 details the study areas in the Bay of Bengal and the Arabian Sea, sampling and analysis carried out for Ra isotope study. This chapter also focuses on the general oceanography of the Bay of Bengal and describes sampling of seawater, analytical methods employed to carry out various measurements as well as precision and accuracy of Ra isotope measurements.

Chapter 3 presents and discusses Ra isotopes in the Bay of Bengal and the Arabian Sea. Distribution of Ra isotopes is modelled to derive mixing parameter for the surface circulation and bring out mesoscale features of the Bay of Bengal and the Arabian Sea.

Chapter 4 provides introduction to the second thesis topic, namely, the study of REE and uranium in the Chambal and the Yamuna rivers in conjunction with the major ion chemistry. This chapter also gives a detailed background on the extent of studies carried out on this topic and discusses the nature of debates existing on the issues.

Chapter 5 details the study area of the Yamuna and Chambal river catchments, sampling and analysis carried out for this study. This chapter describes the geology of the Yamuna and Chambal river catchments, sampling protocols for river waters, sediments and source rocks, analytical methods employed for various measurements, their precision and accuracy. This chapter provides a detailed description of the techniques and analytical procedures used for sampling, ICPAES and FAAS analyses of the major elements (AI, Fe, Mn, Mg, Ca, Na and K) and REE in the river waters and bed sediments.

In Chapter 6, abundances of major ions, trace elements in Chambal river waters and sediments are presented. This chapter also contains measured concentrations of REE in the Yamuna and the Chambal river waters and bed sediments. These data have been used to assess the nature and extent of contemporary chemical weathering in these catchments and to characterize sources of major ions and REE in river waters.

In Chapter 7, uranium concentrations and isotopic ratios in the Yamuna and Chambal river waters are discussed with emphasis on the role of various lithologies in contributing to U isotopic ratios of the Yamuna and the Chambal rivers.

Synthesis of the results obtained in these two studies and broad conclusions drawn from them are presented in Chapter 8. Future work that needs to be carried out to address some of the issues that are borne out of this work has been outlined.

Part A. Radium isotopes in the Bay of Bengal and the Arabian Sea

**Chapter 1** 

Introduction

#### **1.1 Introduction**

Oceans sustain life on this planet by moderating its temperature and climate. It drives the climate of Earth by transferring heat from one region to another within itself and also by exchanging with the atmosphere. The transport of heat and materials in the ocean is through lateral and vertical mixing. Surface mixing is driven primarily by winds, which maintain it at a state of constant turbulence and motion. The surface currents generated through wind stretch far and wide over length scales of several hundreds of kilometers. The ocean surface layer is important as an interface of material and energy transfers between the oceans and the atmosphere. The use of geochemical tracers holds great promise as a means of learning about ocean circulation and mixing. Tracer distribution in the ocean is controlled by the location of sources and sinks and the action of the circulation and mixing in transferring the tracer. In order to study the mixing by mesoscale physical processes such as motions due to currents and waves, stable tracers eg., salinity, nutrients, oxygen, heat are useful (Defant, 1961). The environmental radioactive isotopes as tracers, with their characteristic half-lives, can additionally provide timescales of mixing. <sup>228</sup>Ra and <sup>226</sup>Ra are used as tracers to study upper ocean circulation of the Bay of Bengal and the Arabian Sea.

The fate of dissolved material brought by rivers delivered to the coastal ocean depends on its reactivity and the rate at which it is mixed offshore. Ra isotopes are introduced to coastal waters by rivers and to a small extent by groundwater input and desorption from coastal sediments and suspended particles (Moore, 1997). Within the decay series of uranium and thorium are <sup>226</sup>Ra and <sup>228</sup>Ra derived from decay of thorium parents. Because thorium remains tightly bound to sediment particles, sediments provide a continuous source of Ra isotopes to marine waters at rates set by the decay constants of the Ra daughters.

#### 1.2 Ocean circulation

Oceans are in a state of perpetual motion by winds in the surface layer and by density differences in the deeper layers. Understanding and accurate parameterization of these stirring and mixing mechanisms is important for general ocean circulation model (GCM). Values of lateral and vertical mixing coefficients presently used in large-scale numerical models are based mainly on interpretation of the major patterns of currents observed in the ocean (Defant, 1961). The mixing of physical and chemical constituents of water in the oceans is considered to occur through diffusion and advective processes (Munk, 1966). The steady-state mass balance equation for temperature, T, in the ocean, where this tracer behaves conservatively, can be expressed as

$$K_{x}\frac{\partial^{2}T}{\partial x^{2}} + K_{y}\frac{\partial^{2}T}{\partial y^{2}} + K_{z}\frac{\partial^{2}T}{\partial x^{2}} - w_{x}\frac{\partial T}{\partial z} - w_{y}\frac{\partial T}{\partial y} - w_{z}\frac{\partial T}{\partial z} = 0 \quad \dots [1.1]$$

where x, y and z refer the zonal, meridional directions (coordinates) and depth respectively. In a simple one-dimensional, vertical model, which neglects all lateral mixing processes the equation for the distribution of temperature is given by:

$$K_{v} \frac{d^{2}T}{dz^{2}} - w_{v} \frac{dT}{dz} = 0 \qquad \dots [1.2]$$

where  $K_v$  is the vertical diffusivity and  $w_v$  vertical advection rate and the scale height  $K_v/w_v$  of the exponential solution of this equation is matched to a value of about 1 km appropriate to the ocean interior. If upwelling at velocity  $w_v$  is attributed to formation of bottom water in the polar regions (mainly Antarctic) at a rate of about 10<sup>-3</sup> of the volume of the oceans per year, one can calculate  $w_v$  and  $K_v$  as follows:

Let volume of the oceans be  $x \text{ km}^3$  and average depth be 4 km.

Ocean area = (x/4) km<sup>2</sup>.

Then,  $w_v = (volume of bottom water formed) / area$ 

= (x.  $10^{-3}$ )/(x/4) = 4 m y<sup>-1</sup> This gives K<sub>v</sub>  $\approx 10^{-4}$  m<sup>2</sup> s<sup>-1</sup>.

This value does not apply to those parts of the ocean above isopycnals, which outcrop at the surface away from the regions of bottom water formation (Munk, 1966; Garrett, 1979). An independent check on the values of  $w_v$  and  $K_v$  is obtained by applying equation 1.2, with a decay term on the right hand side, to radioactive geochemical tracers, and fitting the mathematical solutions to observed <sup>14</sup>C and <sup>32</sup>Si profiles (Craig 1969; Sarmiento et al., 1976; Somayajulu et al., 1991). The above simple one-dimensional model (1-D) can be suitably extended for studying lateral and vertical mixing in the zonal and meridional directions.

Recently Prasad et al. (2002) reported retrieving sea surface advection rates using sediments as a tracer from the suspended sediment maps derived from the sequential Ocean Colour Monitor (OCM) data around 20°N, 87°E from the Indian remote sensing satellite IRS-P4). The method is based on matching suspended sediment dispersion patterns in sequential two-time lapsed images.

#### **1.3 Measurement of Ra isotopes**

Earlier <sup>226</sup>Ra was measured in the seawater using the <sup>222</sup>Rn (half-life = 3.8 d) emanation technique (Mathieu, 1988). The detection of <sup>228</sup>Ra is usually accomplished through beta counting of its daughter <sup>228</sup>Ac (= 6.1 h) or alpha spectrometry of its granddaughter <sup>228</sup>Th (= 1.9 y), since <sup>228</sup>Ra itself is only a weak beta emitter. In this study, Ra isotopes in the Bay of Bengal and the Arabian Sea are measured in the surface as well as upper ocean depth profiles between surface and 500 m and are used to determine the horizontal and vertical mixing rates using the 1-D and 2-D advection-diffusion models with a new approach. The use of High-purity germanium well detectors has proven to be easier to measure simultaneously <sup>228</sup>Ra and <sup>226</sup>Ra without going into tedious separation procedures as mentioned above.

# **Chapter 2**

# **Methods and Approaches**

#### 2.1 Introduction

The stress exerted by monsoon winds on the surface ocean drives the circulation in the Bay of Bengal and the Arabian Sea. The occurrence of the southwest and the northeast monsoons over the Indian Ocean implies that the winds are strongly seasonal. The Bay of Bengal is well known as a source of cyclonic storms for about 75% of the year (Fein and Stephens, 1987). These tropical and subtropical cyclones account for stormy winds and heavy rainfalls over the north Indian Ocean and surrounding areas in these monsoon seasons and thus become important for the study of surface mixing. Both lateral and vertical mixing rates are computed using concentrations of <sup>228</sup>Ra and <sup>226</sup>Ra in the surface and upper ocean seawater samples to the advection-diffusion model in order to bring out the effect of wind-generated surge forced by frequent tropical cyclones in the Bay of Bengal and the Arabian Sea.

This chapter discusses general oceanography of the Bay of Bengal and the Arabian Sea and describes sampling of seawater, analytical methods employed to carry out Ra isotope measurements.

#### 2.2 Oceanographic features of the western Bay of Bengal

The Bay of Bengal is the northeastern arm of the Indian Ocean, located between peninsular India and Myanmar (Fairbridge, 1966). It is 2,090 km long and 1,610 km wide and covers about 2.2 x  $10^6$  km<sup>2</sup> and is bordered on the north by the Ganga and Brahmaputra River deltas, on the east by the Burmese peninsula and the Andaman and Nicobar Islands, on the west by India and Srilanka, and on the south by the Indian Ocean. The Bay of Bengal is the freshwater region in the Indian Ocean by virtue of both direct monsoon rainfall and by large riverine input. The onset of summer monsoon rainfall occurs on the eastern side of the bay (near to the outflow of the Irrawaddy River) and over parts of Myanmar and Thailand and then spreads toward the northwest. The seasonal runoff from the rivers in summer monsoon is 9.43 x  $10^{11}$  m<sup>3</sup> compared to that in winter, 1.04 x  $10^{11}$  m<sup>3</sup> (UNESCO, 1971). During the summer southwest

monsoon, river runoff doubles the surface freshwater input (precipitation P + runoff R - evaporation E) into the bay to nearly 18.3 x 10<sup>11</sup> m<sup>3</sup> (Varkey et al., 1996; Schott and McCreary, 2001). The surface salinity and density fields show marked variations both spatially and temporally as a result of large freshwater inputs, variable monsoon winds and associated upwelling/downwelling, and advection from the west and south of high salinity water masses. Sea surface salinity shows strong meridional gradients on the western side of the Bay developing in June-September, with salinity dropping by more than 6 units from the mouth of the Ganga-Brahmaputra estuarine region to about 15° N. The gradient decreases in subsequent months. In addition to the large fresh water forcing, with phase lags between precipitation and river input, the circulation of the bay undergoes changes due to strong seasonal variations in upwelling/downwelling, locally generated Rossby and coastal Kelvin waves, and Ekman flow associated with monsoonal winds. Mc Creary et al., (1993) reported the modeled coastal currents to be affected more by wind stress forcing within the Bay except on the eastern side. The five major rivers that empty into the Bay of Bengal are the Krishna, the Godavari, the Mahanadi, the Ganges and the Irrawady (Fig. 2.1) all forming fertile, heavily populated deltas (Howden and Murtugudde, 2001). Sediment from the rivers has made the Bay a shallow sea, and the inflow of freshwaters reduces the salinity of surface waters along the shore. The average depth is around 3000 m with maximum depths reaching over 4000 m in the southern parts. The effect of riverine input in the Bay is not confined to the surface waters. A pool of cold anomaly (-1° C) and freshwaters are centered near 100 m depth in the center of the Bay (90°E) with the riverine input (Thadathil et al., 2002). This cold pool beneath the mixed layer allows entrainment cooling of the mixed layer to be more effective, even though mass entrainment is lower relative to the case neglecting river input (Howden and Murtugudde, 2001).

Many workers (La Fond and La Fond, 1968; Wyrtki, 1971; Potemra et al., 1991; Vinaychandran, 1995; Shetye et al., 1996) have described the physical

oceanography of the Bay of Bengal. The monsoon winds that sweep across the north Indian Ocean force considerable seasonal changes in surface circulation. Though winds over the north Indian Ocean are much stronger during the southwest monsoon (June-September), the circulation along the coast of India is well set-up during the northeast monsoon (November-January) (Shetye, 1999).



Fig. 2.1. River water inputs to the Bay of Bengal. Rivers plotted are the Ganga-Brahmaputra (diamonds), the Irrawady (squares), the Godavari (pluses), the Mahanadi (crosses) and the Krishna (circles) (Howden and Murtugudde, 2001).



Fig. 2.2. A schematic representation of identified current branches during the Southwest monsoon (top) and Northeast monsoon (bottom). Currents indicated are SouthEquatorial Current (SEC), South Equatorial Countercurrent (SECC), Northeast and Southeast Madagascar Current(NEMC and SEMC), East African Coast Current (EACC), Somali Current (SC), Southern Gyre (SG) and Great Whirl (GW). Associated upwelling wedges are Sacotra Eddy (SE), Ras al Hadd Jet (RHJ), West Indian Coast Current (WICC), Laccadive High and Low (LH and LL), East Indian Coast Current (EICC), Southwest and Northwest Monsoon Current (SMC and NMC), South Java Current (JC) and Leeuwin Current (LC) (Adapted from Schott and McCreary, 2001).

The East India Coastal Current (EICC) is best developed in March-April, when winds in the region of the current are the weakest during the year. The current carries low-salinity waters that originate in the northern Bay due to river runoff, especially from the Ganga-Brahmaputra rivers. The EICC transports these waters all the way to the southwest coast of India after turning around Sri Lanka. From there the western India Coastal Current (WICC) carries them northward along the West Coast of India (Fig. 2.2). The currents in the basin are primarily due to free and forced tropical Rossby waves, equatorial Kelvin waves and coastal Kelvin/shelf waves triggered by both SW and NE monsoons whose winds can be represented as the sum of annual and semi-annual components (Shetye, 1999). The monsoon wind variations and the resulting circulations also serve to induce upwelling near the coasts during the spring (with the northward current) and the piling up of surface water along the coasts during the late fall and early winter (with the southward currents). Thus the isopycnals tilt upwards and downwards towards the shore the spring and late fall. The annual mean SST for the region is ~28.5° C, although upwelling can reduce this to 25-27° C during spring. The salinities are kept lower than normal oceanic values (especially in the western parts) by extensive monsoon river runoff (Fairbridge, 1966; Tomczak and Godfrey, 1994).

The Bay of Bengal Water (BBW) is the water mass that originates in the northern Bay of Bengal. It is a low salinity water mass that spreads across the Bay in an approximately 100 m thick layer that produces a strong halocline beneath and keeps the surface salinity in the eastern parts of the Bay below 33.0 throughout the year. There are no variations in temperature through the BBW layer, salinity variations below 50 m in the BBW has been observed due to lack of mixing under the prevailing weaker winds. The main thermocline layer of the ocean is in general treated as a layer that is excluded from seasonal variability, because it is situated well below the seasonal surface layer. Between these two layers, there is a density transition, which Defant (1961) called the "barrier layer".

The low salinity surface water to the west of India, sometimes called East Arabian Sea Water (EAW), is usually subsumed under the BBW rubric due to its nearly identical properties (Tomczak and Godfrey, 1994).



Fig. 2.3. Map showing bathymetric contours (dotted lines) and mean annual surface salinity variations (grey shade contours) in the Bay of Bengal (Varkey et al., 1996; Levitus, 2001).

The mixed layer depth ( $D_{ml}$ ) in the western Bay of Bengal varies from ~ 40 m to ~100 m but averages around 50 m for the most part of the year (Wyrtki, 1971; Shetye, 1993; Varkey et al., 1996). It is shallower toward the coast than farther offshore. Average values of temperature and salinity observed in the region are 27° C and 32, respectively (Shetye et al., 1996). The mean annual-surface-salinity distribution in the Bay of Bengal in general is unique. The north, northwestern and northeastern regions are noted for maximum freshwater discharge which results in low salinity waters ( $\leq$ 31) which increases to ~34 south towards equator (Fig. 2.3). Overall, the surface salinity patterns do not significantly change during different seasons (Wyrtki, 1971; Levitus, 2001). Temperature-salinity-time diagrams for the surface layer show the semi-annual cycle in the salinity in the Bay of Bengal and in the temperature of the Arabian Sea (Carvalho, 1998, Fig. 2.4).

The Bay of Bengal is well known as a source of cyclonic storms for about 75% of the year. These storms generally move into Bangladesh and the east coast of India (Pant and Rupa Kumar, 1997). Abnormal increases in the elevation of the sea surface above its mean level have led to well-documented cases of flooding with consequential loss of life and property in the low-lying areas adjacent to the Bay of Bengal. These increases can be produced by a combination of effects of the astronomical tides, wind-generated surges forced by tropical cyclones and freshwater outflow from the river systems (Johns, 1981). While returning to the Bay such tidal waters can bring in Ra isotopes leached from the soil and suspended sediments but these are not perennial like river discharges. All these features suggest that the surface waters of the Bay of Bengal are fairly turbulent for a large part of the year.



Fig. 2.4. Surface water mass regions of the Indian Ocean based on water type time diagrams for the surface layer. (a) Bay of Bengal Surface Water, (b) Arabian Sea Surface Water, (c) Equatorial Indian Ocean Surface Water, (d) South Indian Ocean Surface water. The regions are defined on temperature, salinity, chlorophyll, Ekman pumping velocity, net fresh water flux, zonal and meridional wind stress component. The diagram on the left gives typical T-Stime diagrams for the four regions. Dots indicate months. Note the prominence of the semi-annual cycle in the salinity in the Bay of Bengal (a) and in the temperature of the Arabian Sea (b) (Carvalho, 1998).

#### 2.3 Oceanographic features of the Arabian Sea

The Arabian Sea is northwestern part of the Indian Ocean, covering a total area of about  $3.86 \times 10^6 \text{ km}^2$  and forming part of the principal sea route between Europe and India (Fairbridge, 1966). It is bounded to the west by the Horn of Africa and the Arabian Peninsula, to the north by Iran and Pakistan, to the east by India, and to the south by the remainder of the Indian Ocean. It has a mean depth of 2,734 m. The Indus River is the principal river draining into the sea followed by the Narmada and Tapi, all the three are recently dammed for irrigation. Stretching southeastward from Socotra is the submarine Carlsberg Ridge, which coincides with the belt of seismic activity in the Indian Ocean that divides the Arabian Sea into two major basins - the Arabian Basin to the east and the Somali Basin to the west (Fairbridge, 1966).



34.4 34.6 34.8 35.0 35.2 35.4 35.6 35.8 36.0 36.2 36.4 Fig. 2. 5. Map showing mean annual surface salinity variations in the Arabian Sea (Levitus, 2001).

The Arabian Sea has a monsoon climate. Minimum air temperatures of about 24° to 25° C at the sea's surface occur in the central Arabian Sea in January and February, while temperatures higher than 28° C occur in both June and November. The surface salinity distribution is shown in the Fig. 2.5. During the rainy season, which occurs when the southwest monsoon winds are dominant (April to November), salinities of less than 35 have been recorded in

the upper 50 m of the sea, while during the dry season (November to March), when the northeast monsoon winds prevail, salinities of more than 36 have been recorded at the surface over the entire Arabian Sea north of latitude 5° N, except off the Somali coast (Fig. 2.5). Because evaporation exceeds the combined precipitation and riverine input, the sea exhibits a net water loss annually. A thick  $D_{ml}$  of 110 m was observed at 10°N, which dropped to 40 m around 20°N (Madhupratap et al., 1996; Muraleedharan and Prasanna Kumar, 1996; Prasanna Kumar et al., 2001).

The Arabian Sea is unique among the world's oceans in that the winds over the ocean basin reverse semi-annually, blowing from the southwest during the northern summer, and from the northeast during the northern winter (the southwest and the northeast monsoons). The periodic reversals in the winds drive corresponding reversals in the currents of the upper ocean (Fig. 2.2). A striking feature of the upper ocean is the deepening and cooling of the mixed layer in the Arabian Sea during both monsoons (Rao et al., 1989). During the SW monsoon, occurring during the summer, the strong winds of the Findlater Jet are found in the western Arabian Sea where they blow to the northeast along the coast of the Arabian peninsula; the climatological mean surface currents include strong northeastward western boundary currents and eastward flow in the central region (Knox, 1987; Rao et al., 1989). During the NE monsoon, which occurs during the winter, the surface winds are moderate in strength over a broad region and the climatologically mean surface currents are to the west.

These seasonal reversals of the wind and surface circulation over such a vast area are remarkable when compared to the seasonal signals in the Atlantic or Pacific oceans. For example, the Somali current has surface velocities and mass transport that exceed those of the Gulf Stream but that changes directions every six months (Fig. 2.2). There are numerous eddies in the Arabian Sea that recur on a seasonal basis. The currents in the Arabian Sea evolve rapidly into a very complex pattern of eddies with the onset of the southwest monsoon. The

higher primary productivity of NE monsoon results from cool, dry continental air brought by prevailing northeast trade winds that intensify evaporation leading to surface cooling (Madhupratap et al., 1996; Prasanna Kumar and Prasad, 1996). This combined with reduced incoming solar radiation and high ambient salinity (>36.0), drives convective mixing in the northern Arabian Sea, resulting in the upward transport of nutrients from the base of the mixed layer and upper thermocline.

The complex Somali Current, which attains high velocities (~13 km hr<sup>-1</sup>) off the coast of Socotra, becomes part of a clockwise circulation system that in summer continues to the northeast along the coast of Arabia and turns south along the coast of India to 10° N. At that point it merges with the Southwestern Monsoon Current, flowing east between 5° and 10° N. Pronounced upwelling of deeper waters occurs along the Somali and Arabian coasts in summer (Fig. 2.2). The Somali Current weakens and reverses direction during the northeast (winter) monsoon. Of the five water masses that have been distinguished in the upper 1,000 m of the north Indian Ocean, three have been identified as originating in the Red Sea, the Persian Gulf, and the Arabian Sea, respectively.

Some regions of the Arabian Sea are rich in nutrients and high in biological productivity due to intense upwelling caused by periodic reversal of wind regimes. The southwest monsoon winds blow along the coast of Somalia and Oman creating a clear movement of the surface waters away from the shore (Ekman transport) and consequently, deep waters are upwelled in the coastal areas of Somalia and Oman. These upwelled, nutrient-rich waters produce phytoplankton blooms. Later (December-January), the wind picks up again, but from the NE with enough strength to change the circulation pattern of the sea. This physical forcing also produces elevated primary production compared to inter-monsoon periods, although this may be explained by downwelling of surface waters cooled (heavier) by inland winds from the Himalayan Plateau. Some of the organic particles produced are transported to the interior of the sea where they are degraded or remineralized. This natural biogeochemical process

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causes an extreme depletion of oxygen from intermediate waters (between 100-1200 m depth) generating a widespread oxygen minimum zone, OMZ (Naqvi, 1991 and 1994; Naqvi et al., 2000). Thus the interplay between wind patterns, water mixing and surface productivity makes the Arabian Sea a very unique basin, where the biogeochemical features may be responsible in part of the biogeochemical signatures of global ocean water masses that interact in this tropical ocean basin (Banse, 1987; Madhupratap et al., 1996; Smith et al., 1998).

#### 2.4 Sample sites, collection and Analytical Methods

#### 2.4.1 Sampling of Ra isotopes in the Bay of Bengal and the Arabian Sea

Radium isotope measurements were made on 72 surface seawater samples collected in the western Bay of Bengal during five different cruises. These were G-200 (August-September 1988) on board R/V Gaveshani, SK-63 (March-April 1991) and SK-70 (December 1991) both on board ORV Sagar Kanya, SS-152 (February 1997) and SS-172 (February 1999) both on board FORV Sagar Sampada (Fig. 2.7). The SK-63 cruise covered most of the EEZ of the Bay of Bengal coast of India whereas the SK-70 cruise taken during December 1991 covered the southern part of the area. A rosette attached with eight PVC Go Flo bottles of 30 L capacity and an underwater CTD unit (Sea Bird Electronics) was used for temperature-salinity profiling and seawater sampling (Fig. 2.6). Usually ~100 L seawater was collected from each depth by tripping four Go Flo bottles each at the desired depth.

A total of 42 seawater depth profiles from surface to 500 m for Ra isotopes from the Arabian Sea and the Bay of Bengal were collected on board FORV Sagar Sampada during seven different cruises. They were SS98 (Feb 1992), SS117 (February 1995), SS118 (March 1995), SS132 (February 1996), SS152 (February 1997), SS164 (March 1998) and SS172 (February 1999). The sample locations during these cruises are given in Fig. 2.7.

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Fig. 2.6. Sampling of seawater onboard FORV Sagar Sampada. Rosette attached with eight 30 L PVC Go Flow bottles and SBE (underwater CTD unit) being lowered for temperature-salinity profiling and seawater sampling. Usually two samples were collected from each cast, by tripping four bottles at the desired depth.

During all these cruises, 100 L surface water samples were collected using either 100 L GoFlo bottles fixed on a hydrographic wire or four GoFlo bottles of 30 L capacity fixed on a rosette and these samples were transferred into clean plastic drums. From these waters Ra isotopes were extracted by adsorbing onto  $MnO_2$ fibres (Moore, 1976). Towards this, seawater was passed through two plexiglas columns in series (2 cm diameter x 20 cm length) which were packed with  $MnO_2$  fibre at the rate of ~2 to 3 L h<sup>-1</sup>. After passing seawater, fibre samples were washed repeatedly in distilled water and brought to the laboratory. These  $MnO_2$  fibres preferentially extract Ra from seawater and thus provide an ideal preconcentration technique. It is established earlier that at low flow rates of 2 - 3 L  $h^{-1}$ , the extraction is nearly quantitative. Seawater Ra isotope concentrations were derived from the measured activity of these isotopes in the fibre and the volume of seawater passed through it.

## 2.4.2 On board measurements

Continuous profiles of temperature and salinity were obtained using a Seabird CTD instrument. The system consists of SBE 9 underwater unit mounted with sampling rosette (Fig. 2.6) and a SBE 11 deck unit for receiving the digital data. The CTD salinity values were calibrated using the values measured by Guildline Autosal salinometer (Model 84000A). The instrument determines the conductivity ratio (K<sub>15</sub>) of a sample – defined by the ratio of conductivity of a sample at 15° C and 1 atmosphere pressure, to that of KCl solution containing 32.4356 g of KCl in 1 kg of solution. R<sub>t</sub> is the conductivity ratio at t° C. The instrument displays twice the R<sub>t</sub> values, from which salinity was determined using an empirical relationship (UNESCO, 1978) using SEACALC software. The salinometer was calibrated using IAPSO Standard Seawater. The precision of salinity measurements by Autosal was typically  $\pm$  0.0005, based on repeat measurements of seawater samples.



Fig. 2.7. Map showing sample locations for Ra isotopes in the Arabian Sea and the western Bay of Bengal. Sample location details are given in Table 3.1 and 3.4. Coast-to-open-ocean tracks A to H of SK-63 and SK-70 cruises are indicated along the coast. During G200, SK-63 and SK-70, surface seawater Ra samples are collected. During SS98, SS117, SS118, SS132 SS152, SS164 and SS172 cruises, depth profiles of Ra isotopes from surface to 500 m collected on board FORV Sagar Sampada.

#### 2.4.3 Analysis of Ra isotopes

The MnO<sub>2</sub> fibre samples containing Ra isotopes were boiled with 2M HCl to dissolve Mn and Ra isotopes. Ra from the solution was co-precipitated with BaSO<sub>4</sub>. For this, Ba carrier (equivalent to 500 mg BaSO<sub>4</sub>) was added, homogenized and BaSO<sub>4</sub> was precipitated using H<sub>2</sub>SO<sub>4</sub>. The precipitate was filtered, dried, weighed and sealed in a plastic vial and was assayed for Ra isotopes after at least three weeks from sealing the vial to allow <sup>222</sup>Rn and its daughters to grow into equilibrium with <sup>226</sup>Ra. Samples were counted in a Canberra Model GCW 2523 coaxial well type, intrinsic HPGe detector with a well depth of 35 mm and diameter of 20.5 mm which was calibrated using standards of known concentrations of Ra isotopes (Moore, 1984; Somayajulu et al., 1999). Data acquisition was done with Canberra Series 35 multi channel analyzer. Standards were made from BaSO<sub>4</sub> doped with U (4 and 2%) and monazite NBS standards as well as calibrated <sup>226</sup>Ra solution. They were counted periodically to check the constancy of the efficiencies of the gamma detector during the counting period. Table 2.1 gives the gamma ray energies of the isotopes used for the determination of <sup>226</sup>Ra and <sup>228</sup>Ra activities, gamma yield and counting efficiencies (Fig. 2.8) for the HPGe well detector. This table also gives the backgrounds measured in each of these regions of the spectra after correcting for the Compton continuum. As given in Table 2.1, <sup>228</sup>Ra and <sup>226</sup>Ra were determined by measuring  $\gamma$  rays of three different energies each from their progenies. The mean of these values and their standard deviation were used for calculating their activities. The detector is shielded with 15-cm thick lead to reduce the background. BaSO<sub>4</sub> blanks (500 mg recovered using the same procedure without passing seawater) were also counted periodically. The resolution of the detector is 1.4 keV (FWHM) at 1.22 MeV. Precision of this analytical technique is  $\pm$  5% (1 $\sigma$ ) based on multiple analyses of several standards used for calibration. Typical spectra of the background, sample and standard are shown in Fig. 2.9. Whenever there was a delay between sample collection and counting (by more than one month) the <sup>228</sup>Ra data were decay corrected to the date of collection. Since the time delay was less than ~2 years in extreme cases, no corrections were necessary for <sup>226</sup>Ra.

Generally, it took 3-4 days counting time to achieve a precision better than 10%  $(1\sigma)$  on the Ra isotope concentrations (Chapter 3, Appendices 3.1 and 3.2).

Isotope	Energy* (KeV)	γ-ray yield*	% efficiency	Background (cph)	
For <sup>226</sup> Ra					
<sup>214</sup> Pb	295	0.189	30.3±0.5	0.837±0.71	
<sup>214</sup> Pb	351	0.367	25.2±0.4	1.311±0.723	
<sup>214</sup> Bi	609	0.461	7.4±0.1	3.013±0.569	
For <sup>228</sup> Ra					
<sup>228</sup> Ac	338	0.113	22.4±0.6	-	
<sup>228</sup> Ac	911	0.272	7.2±0.2	0.739±0.429	
<sup>228</sup> Ac	964-969	0.213	6.7±0.2	-	

Table 2.1. Gamma rays and counting efficiencies for the HPGe well detector used in the measurement of radium isotopes.

\* From Lederer and Shirley (1978).



Fig. 2.8. Calibration curve for HPGe well detector.



Fig.2.9. Typical spectra of background (A), sample (B), U standard (C) and Th standard (D). Ra isotopes are measured using the peaks marked in the spectrum (Table 2.1).

## **Chapter 3**

# Ra isotopes in seawater

#### 3.1 Introduction

Within the U-Th decay series (Fig. 3.1), <sup>228</sup>Ra (half-life = 5.75 y) and <sup>226</sup>Ra (= 1622 y) are derived from decay of thorium parents. These isotopes are introduced to coastal waters via rivers, groundwater input, desorption from suspended sediments and diffusion from shelf sediments. Thorium, the parent of Ra isotopes, remains tightly bound to particles. Ra isotopes, produced in the sediments from the decay of Th, are recoiled into pore spaces from where they diffuse out. Thus sediments provide a continuous source of Ra isotopes to seawater. This chapter presents the discussion on Ra isotope data collected from the surface and upper layers of the Bay of Bengal and the Arabian Sea and using this data, lateral and vertical eddy diffusivities and advection velocities are derived from 1-D and 2-D advection-diffusion models.

#### 3.2 Marine chemistry of Ra isotopes

Because of the nature of the source function of Ra, viz. supply from river water and at sediment water interface, its concentration decreases away from the source region. This was first observed by direct measurements of <sup>228</sup>Ra in seawater by Moore (1969). Subsequent studies documented that <sup>228</sup>Ra decreased horizontally away from the coasts and vertically away from the seafloor. Consequently, many attempts have been made to determine oceanic mixing rates using the distribution of this nuclide (Moore, 1972; Kaufman et al., 1973; Sarmiento et al., 1976; Yamada and Nozaki, 1986).

As with <sup>228</sup>Ra, the primary source of <sup>226</sup>Ra is also bottom sediments, especially the slowly accumulated pelagic sediments with enriched <sup>230</sup>Th (the progenitor of <sup>226</sup>Ra). Using Ba as a stable analogue for radioisotopes of Ra, attempts have been made to apply <sup>226</sup>Ra as a tracer for studying large-scale oceanic circulation and mixing in the deep sea (Chung and Craig, 1980; Ku and Luo, 1994).

Although <sup>228</sup>Ra and <sup>226</sup>Ra have similar source terms and the same processes control their distributions in the water column, the data on the concurrent measurement of these two isotopes are rather sparse in the literature. This is because they can be

used independent of each other in different oceanic regimes, viz. coastal and open ocean regions and the differences in analytical methods and sample sizes required for their analysis. On the other hand, data available for both nuclides could provide additional information regarding water mixing in a given oceanic area.

Element	<sup>238</sup> U series				<sup>232</sup> Th series		
Uranium	<sup>238</sup> U 4.47x10 <sup>9</sup> y	*	<sup>234</sup> U 2.48x10 <sup>5</sup> y				
Protacti- nium	•	<sup>234</sup> Pa 1.18 min	¥				
Thorium	<sup>234</sup> Th 24.1 d		<sup>230</sup> Th 7.52x10 <sup>4</sup> y		<sup>232</sup> Th 1.40x10 <sup>10</sup> y		<sup>228</sup> Th 1.91y
Actinium			↓		↓	<sup>228</sup> Ac 6.13 h	¥
Radium			<sup>226</sup> Ra 1600 y		<sup>228</sup> Ra 5.75 y		<sup>224</sup> Ra 3.66 d
Francium			↓				↓
Radon			<sup>222</sup> Rn 3.82 d				<sup>220</sup> Rn 0.15 s
			÷	<b>↓</b>	Alpha decay		÷
Lead			<sup>206</sup> Pb stable	×	Beta decay		<sup>208</sup> Pb stable

Fig. 3.1. Isotopes of uranium and thorium decay series showing the lineage of Ra isotopes.

## 3.3 Relation of Ra isotopes with salinity

## 3.3.1 Bay of Bengal

The measured concentrations of <sup>228</sup>Ra and <sup>226</sup>Ra along with (<sup>228</sup>Ra/<sup>226</sup>Ra) activity ratio (henceforth denoted as [228/226]) in the surface waters of the western Bay of

Bengal collected during the five cruises are given in Appendix 3.1. Though samples were collected at least 10 km away from the coastline to avoid localized and fluctuating Ra sources, one still notices some localized high values especially for <sup>228</sup>Ra and [228/226] as evident in samples, G-200/4892 and SK-70/A-1. It is possible that submarine groundwater discharge (Moore, 1996; Buddemier, 2000; Somayajulu et al., 2003) may be contributing to the high Ra values especially in the region south of 12°N. The range and mean surface concentrations of Ra isotopes and [228/226] in the Bay of Bengal are given in Table 3.1. Frequency distribution of the concentration of <sup>226</sup>Ra in the surface samples are given in Fig. 3.2 and the contour plots of the surface <sup>228</sup>Ra and <sup>226</sup>Ra concentrations are shown in the Fig. 3.3. It is evident that the concentration <sup>228</sup>Ra peaks near the source regions, at the mouths of Ganga-Brahmaputra and Godavari rivers.



Fig. 3.2. Frequency plot <sup>226</sup>Ra in the surface waters of the Bay of Bengal. The peak concentrations lie between 8.5 and 9.5 dpm/100 kg in the Bay of Bengal.



*Fig. 3.3.* <sup>228</sup>*Ra (top) and <sup>226</sup>Ra (bottom) concentrations in the Bay of Bengal surface waters.* 

A few high <sup>228</sup>Ra, <sup>226</sup>Ra and [228/226] values were reported by lyengar et al. (1989) close to Kalpakkam, the site of major nuclear complex. These are very shallow waters too close to the coast and their effect is not discernible beyond the sampling site. The <sup>226</sup>Ra concentration of the Indian Ocean surface waters by earlier workers viz. 9-10 dpm/100 kg fall in the overall range obtained in the present study (viz. 6-16.7 dpm/100 kg) except for one unusually high value of 41.9 dpm/100 kg near Visakhapatnam Port which receives a large amount of sewage from the city (Appendix 3.1). In general, during different seasons, <sup>228</sup>Ra and [228/226] decrease from coast to open, especially in the north south direction. The <sup>226</sup>Ra concentrations do not show such a clear decrease. A better way to understand these changes is through plots of isotope concentration and [228/226] as a function of salinity. Such plots are shown in Figs. 3.4a, b and c. Regression analysis of the data (n=71) in the measured salinity range of 27 to 35 yields the following equations:

$$\begin{array}{ll} & \label{eq:rescaled} & \label{eq:re$$

It is seen that both <sup>228</sup>Ra concentration and [228/226] decrease with increasing salinity in the range of 27 to 35. Desorption of Ra by the increased salt content in the mixing zone drastically changes the dissolved Ra contributed to the ocean by rivers (Li et al., 1977; Hanor and Chan, 1977; Somayajulu et al., 2002). The best fit lines through the data (Figs. 3.4a, b and c) yield <sup>228</sup>Ra and <sup>226</sup>Ra concentrations of ~107 and 21.2 dpm/100 kg respectively and [228/226] = 6.9 at salinity = 13 where Ra isotope concentrations reach their maximum values in the Ganga-Brahmaputra estuarine region (Carroll, 1990). Generally it is in this low to mid salinity region that Ra isotopes show high concentrations (Elsinger and Moore, 1983). The predicted and measured values in this estuarine region (Carroll, 1990; Somayajulu et al., 2002) are in reasonable agreement. In the case of <sup>226</sup>Ra, there is no significant variation in its concentration with salinity (Fig. 3.4b). It is reasonable to assume that <sup>226</sup>Ra is about uniformly distributed in the Bay of Bengal surface waters

averaging 9.2 $\pm$ 2.2 dpm/100 kg (Table 3.1, Fig. 3.2) irrespective of seasons. This is expected in view of the long half-life of <sup>226</sup>Ra and rapid mixing of the Bay of Bengal surface waters due to monsoons and cyclones. Significant variations are seen for short-lived <sup>228</sup>Ra, indicating mixing timescales of comparable magnitude to the mean-life of <sup>228</sup>Ra. Since the change in <sup>226</sup>Ra concentration is small, the [228/226] is expected to follow the distribution of <sup>228</sup>Ra, which is evident from Figure 3.4c. Even in estuaries (salinity = 2-20) where Ra isotopes are excessively released into the seawater, the [228/226] values do not exceed 3-5 (Elsinger and Moore, 1983; Somayajulu et al., 2002).

## 3.3.2 Arabian Sea

Fifteen vertical profiles from the Bay of Bengal and around twenty from the Arabian Sea (between 5 m and 400 m) were processed for Ra isotopes during the seven cruises on board FORV Sagar Sampada. Concentrations of <sup>228</sup>Ra and <sup>226</sup>Ra along with [228/226] in seawater profiles of the Bay of Bengal and the Arabian Sea are given in Appendix 3.2. The range and mean concentrations of Ra isotopes and [228/226] in the surface waters of the Arabian Sea are given in Table 3.1. The frequency distribution of surface concentration of <sup>226</sup>Ra in the Arabian Sea is presented in the Fig. 3.5 and contour plots of surface <sup>228</sup>Ra and <sup>226</sup>Ra in the Arabian Sea is shown in Fig. 3.6. As the Indus river is dammed, river input of Ra isotopes are almost reduced to minimum in the northern Arabian Sea as EICC brings water from the Bay of Bengal. <sup>228</sup>Ra, <sup>226</sup>Ra and [228/226] vs. salinity of the surface samples are plotted in Fig. 3.7. Regression analysis of the data (n=28) in the measured salinity range of 33-36.5 gives the following equations:

 ${}^{228}\text{Ra}(\text{dpm}/100 \text{ kg}) = (-2.558\pm0.118) \text{ x salinity} + (99.904\pm3.832)$  [r=-0.518, P<0.005]  ${}^{226}\text{Ra}(\text{dpm}/100 \text{ kg})=(-0.424\pm0.043) \text{ x salinity} + (22.260\pm1.515)$  [r=-0.265, P<0.010]  $[228/226]=(-0.313\pm0.015) \text{ x salinity} + (11.742\pm0.518)$  [r=-0.744, P<0.005]



Fig. 3.4 (a-c). Plots of <sup>228</sup>Ra (dpm/100 kg) (a), <sup>226</sup>Ra (dpm/100 kg) (b) and [228/226] (c) as a function of salinity in the surface waters of the western Bay of Bengal. Notice the change of scale in y-axis for different plots.

	n*	<sup>228</sup> F dpm/ 1	Ra 00 kg	<sup>226</sup> Ra dpm/ 100 kg		[228/226]	
		Range	Mean	Range	Mean	Range	Mean
Bay of Bengal	71	6.8-42.1	17.8±7.9	6.0-16.7	9.2±2.2	0.8-3.4	1.9±0.5
Arabian Sea	30	0.93-11.7	5.3±2.8	4.3-9.5	7.3±1.4	0.17-1.42	0.75±0.37

Table 3.1. Range and mean of concentrations of <sup>228</sup>Ra and <sup>226</sup>Ra and [228/226] of the surface waters of the Bay of Bengal and the Arabian Sea.

\* n refers to number of samples



Fig. 3.5. Frequency plot <sup>226</sup>Ra in the surface waters of the Arabian Sea. Two prominent peaks are seen at concentrations 7.5 and 9.0 dpm/100 kg.



Fig. 3.6. <sup>228</sup>Ra (top) and <sup>226</sup>Ra (bottom) concentrations in the Arabian Sea surface waters.



Fig. 3.7 (a-c). Plots of (a) <sup>228</sup>Ra (dpm/100kg), (b) <sup>226</sup>Ra (dpm/100 kg) and (c) [228/226] as a function of salinity in the surface waters of the Arabian Sea.

Poor correlation coefficients for the above equations are due to (a) low salinity water with high concentration of Ra isotopes entering the Arabian Sea from the Bay of Bengal and (b) the semi-annual reversal of the wind regimes caused by southwest and northeast monsoons, which subsequently makes impact on the upper ocean circulation and cause intense upwelling in the Arabian Sea (Qasim, 1982; Madhupratap et al., 1996).

### 3.4 Advection-diffusion modeling of surface Ra isotopic data

As seen in the previous sections, the surface salinity in the Bay of Bengal shows a dominantly increasing trend from north to south. The west to east trend is not as clearly discernible since the freshwater discharge from the Indian peninsular rivers is much less than that of the Ganga-Brahmaputra system. This kind of consistent trend across the bay (from north to south) is a result of the mixing of low salinity waters entering from the Ganga-Brahmaputra estuarine system with the high salinity waters in the south. As it is shown that Ra isotopes especially <sup>228</sup>Ra (and <sup>228</sup>Ra/<sup>226</sup>Ra) are decreasing from their source regions to the open ocean, one can use the Ra isotope distribution to evaluate time scales of mixing of surface waters.

## 3.4.1 One-dimensional lateral model:

<sup>228</sup>Ra can be used as a tracer to estimate eddy diffusivity of coastal waters across the shelf. Several studies have reported on the expediency of the distribution of <sup>228</sup>Ra in continental shelf waters to determine horizontal mixing rates across the shelf (Kaufman et al., 1973; Brewer and Spencer 1975; Knauss et al., 1978). The observed gradient in <sup>228</sup>Ra concentrations in surface water between coastline and open ocean sites reflects eddy diffusion of <sup>228</sup>Ra. In the simplest case, the <sup>228</sup>Ra distribution can be treated as a balance between eddy diffusion and radioactive decay of <sup>228</sup>Ra. At steady state,

$$K_{h} (d^{2}C/dx^{2}) - \lambda C = 0$$
 ...[3.4]

where C is the concentration of <sup>228</sup>Ra,  $\lambda$  the decay constant of <sup>228</sup>Ra (3.83 x 10<sup>-9</sup> s<sup>-1</sup>) and x is the distance offshore. With boundary conditions C=C<sub>0</sub> at x=0 and C=0 at x= $\infty$ , the solution of equation [3.4] is

$$K_{h} = [x/ln(C_{0}/C)]^{2} .\lambda$$
 ...[3.6]

x is the distance between the two points,  $x^*$  the scale length and  $K_h$  the effective lateral eddy diffusivity.

It should be pointed out here that in this simplistic model, change in Ra concentration is taken to be depending on lateral mixing and radioactive decay, i.e., advection, both in horizontal and vertical directions, and any input/removal of Ra, is neglected. It is known that in the near-coastal regions there can be deepening of the mixed layer with distance from the coast, which is also neglected in this model. The straight-line trajectories in the west-east direction from seven coastal locations have been taken and the plots of <sup>228</sup>Ra versus distance from the coast are shown in Fig. 3.8. These are the trajectories along which physical oceanographic data were collected during SK-63 and SK-70 cruises (Shetye et al., 1996). In two of the later cruises SS-152 and SS-172, surface samples collected from the study region in the same month/season along these transects have also been used in the plots (Appendix 3.1). The K<sub>h</sub> values in the west-east direction (for the transects A-D, G and H), calculated using equation [3.6] are shown in Table 3.2, range from  $5.1 \times 10^6$  to  $2.5 \times 10^7$  cm<sup>2</sup> s<sup>-1</sup> with a characteristic scale length of ~114-323 km comparable to the size of the study area. As seen from Table 3.5, the coast to open ocean cruise tracks are in the E-W, NW-SE direction. Available data for the N-S direction in the open ocean are also collected and the K<sub>h</sub> value is calculated to be 5.6x10<sup>7</sup>  $cm^2 s^{-1}$ . The overall range of K<sub>h</sub> is between 5.1x10<sup>6</sup> and 56x10<sup>6</sup> cm<sup>2</sup> s<sup>-1</sup>. These values derived using <sup>228</sup>Ra fit well with the empirical diffusion diagram shown by Okubo (1971) using dye-release experiment data in the upper mixed layer of the North Sea. Data from the two transects E and F (Chapter 2, Fig. 2.7) could not be used, as there is no decrease of <sup>228</sup>Ra with distance from the coast. The lack of <sup>228</sup>Ra decrease suggests the assumptions made in this model are perhaps not correct and that it cannot be applied on a regional basis. Since there is a concentration gradient along six transects (Fig. 3.8) it is used to get an estimate of K<sub>h</sub> values. Eddy diffusivity values obtained during March 1991 are higher than those obtained during December 1991 because EICC is best developed during March-April, when winds in the region of the current are weakest of the year (Shetye, 1999). The current carries low-salinity waters that originate in the northern bay



due to river runoff, most notably from the Ganga and Brahmaputra. Moore (1987) tried to use 1-D diffusion model in the south Atlantic without success due to similar problems.

## **Distance from shore (km)**

Fig. 3.8. Plots showing <sup>228</sup>Ra versus distance from the coast along the six coast-to-open ocean tracks denoted by letters A to H. H-A denotes north to south track comprising <sup>228</sup>Ra data from all available samples on this track. Data (especially in panels A, C, D) show considerable scatter. See Fig. 2.3 for the cruise tracks.

		Eddy Diffusivity (10 <sup>6</sup> cm <sup>2</sup> s <sup>-1</sup> )				
Direction	Leg	SK-63 March 1991	SK-70 Dec. 1991	Both Data		
W-E	А	17.2 <sup>+</sup>	4.0	15.7		
W-E	В	12.7	1.7	6.2		
W-E	С	11.0	1.9	7.9		
NW-SE	D	24.7	1.2	39.0		
NW-SE	G	31.7	-	-		
NNW-SSE	Н	5.1	-	-		
N-S		56	-	-		

 Table 3.2. Effective eddy diffusivities using lateral transects from the shore of the

 Bay of Bengal.

<sup>+</sup> This value is calculated combining the data from SS-152 and SS-172 cruises (Table 3.1).

Lateral mixing can be brought about both by diffusion and advection. A positive advection (away from the shore) is likely to make  $K_h$  higher. In the surface ocean at locations away from the coastal sediment <sup>228</sup>Ra source, vertical mixing tends to dilute the <sup>228</sup>Ra concentration at the surface. This tends to lower the value of  $K_h$ . The effect of the vertical mixing is such that it steepens the horizontal gradient, which makes  $K_h$  lower. Thus the two opposing effects may more or less cancel each other such that the modelled  $K_h$  values adequately describe the lateral mixing in the study area (Huh and Ku, 1998).

To resolve this better, Ra isotope data should be applied in a 2-D model with the inclusion of currents/advection in the lateral directions. Earlier, an attempt in this direction was made by Somayajulu et al. (1996) where a 2-D diffusion model was used for [228/226] data from the Arabian Sea. Huh and Ku (1998) also applied a similar model to <sup>228</sup>Ra data from the northeast Pacific region (off Baja California).

## 3.4.2 Two-dimensional lateral model:

For surface measurements of Ra isotopes, a steady-state 2-D lateral model is

appropriate to deduce the mixing parameters since the mean annual salinity field of the western Bay of Bengal is a permanent feature (Chapter 2, Fig. 2.3) and upwelling that brings low <sup>228</sup>Ra, <sup>226</sup>Ra waters to the surface (Sarin et al., 1994) is not a dominant phenomenon in the Bay of Bengal compared to the Arabian Sea. It is therefore not unreasonable to assume steady state conditions. It is mentioned in the previous sections that the shoaling of D<sub>ml</sub> does not arise once the near coastal region is avoided. The two-dimensional steady-state mass balance equation for <sup>228</sup>Ra in the surface of the ocean, where this tracer behaves conservatively, can be expressed as

$$K_{x}\frac{\partial^{2}C}{\partial x^{2}} + K_{y}\frac{\partial^{2}C}{\partial y^{2}} - w_{x}\frac{\partial C}{\partial x} - w_{y}\frac{\partial C}{\partial y} - \lambda C = 0 \quad \dots [3.7]$$

where C is the <sup>228</sup>Ra concentration (dpm/100 kg) in seawater; x and y refer the E-W (zonal) and S-N (meridional) directions (coordinates), respectively, positive eastward and northward and  $\lambda$ C is the radioactive decay term. Besides radioactive decay, the <sup>228</sup>Ra budget is affected by transport into and out of a volume element, described in terms of lateral eddy diffusivity (K<sub>h</sub>) and lateral advection (w) in both zonal and meridional directions. We proceed as follows: In the first instance, mixing is assumed to be diffusion dominated; i.e., advection terms are neglected. Later the diffusion terms are neglected making advection the dominant mixing process and finally both diffusion and advection are taken into account.

#### 3.4.2.1 2-D diffusion model:

Neglecting advection terms, equation [3.7] reduces to

$$K_{x} \frac{\partial^{2} C}{\partial x^{2}} + K_{y} \frac{\partial^{2} C}{\partial y^{2}} - \lambda C = 0 \quad \dots [3.8]$$

The dominant source regions of Ra isotopes to the Bay of Bengal are distributed all along the coast with several rivers, making it difficult to fix boundary values for the <sup>228</sup>Ra concentrations (like for example, those for the western Arabian Sea, (Somayajulu et al.,

1996)). To avoid this problem, the solution to equation [3.8] in the analytical form is assumed to be

$$C_{(x,y)} = C_{\theta} e^{-Ax} \cdot e^{-By}$$
 ....[3.9]

This can be rewritten as

$$logC_{(x,y)} = logC_0 - By - Ax$$
 .....[3.10]

By fitting the analytical form to the data, A, B and C<sub>0</sub> are estimated using least squares method (Bevington, 1969). This model is applied to the <sup>228</sup>Ra data from the western Bay of Bengal and the distribution of measured and the model-based <sup>228</sup>Ra concentration are shown in Figures 3.9 and 3.10. Six data points with high values of <sup>226</sup>Ra (>14 dpm/100 kg) near the coast and the corresponding <sup>228</sup>Ra values are not considered for the model. These high concentrations may be due to the groundwater recharge into the Bay of Bengal during the lean-flow period (Moore, 1996 and 1997). Distances in both x and y directions are calculated by taking 22°N 88°E as origin (indicated by asterisk in Fig. 3.9) and the  $C_{o}$ value obtained for <sup>228</sup>Ra is 18.5 dpm/100 kg which is close to the values measured in this region viz., H-2, H-3 and H-4 of SK-63 (Salinity = 31.1) (Table 3.1). Since the Ganga-Brahmaputra estuarine waters as well as those of the Hooghly river have the highest <sup>228</sup>Ra, <sup>226</sup>Ra and [228/226] (Carroll, 1990; Carroll et al., 1993; Somayajulu et al., 2002), the choice of the location as origin is reasonable. Except for the coastal high values, other features are reasonably well reproduced by the model (Fig. 3.9 and 3.10). Using for <sup>228</sup>Ra distribution in the Bay of Bengal, values obtained for A and B are 0.3067 x 10<sup>-6</sup> and -0.4234 x 10<sup>-6</sup> m<sup>-1</sup> respectively. The estimated errors (Topping, 1972) on these values are about ~40%; not surprising from the uneven distribution of the sampling locations in the western Bay of Bengal. It should be mentioned here that the choice of origin has no effect on the model-derived data as well as on the deduced mixing parameters (K, w or both) and reproduces the contours of the measured <sup>228</sup>Ra data.



Fig. 3.9. Contour maps of the distribution of a) measured and b) model-derived <sup>228</sup>Ra concentration (dpm/100 kg) in the surface waters of the western Bay of Bengal. Model reproducibility is good.



Fig. 3.10. Contour maps of the distribution of (a) measured and (b) model-derived <sup>226</sup>Ra concentration (dpm/100 kg) in the surface waters of the western Bay of Bengal. Whereas measured values range from 8-12 dpm/100 kg, model contours range from 8-9 dpm/100 kg.

A and B are obtained independent of the chosen origin. One can select origin anywhere and the C<sub>o</sub> concentrations as well as constants A and B are computed by the least square fit. In the case of <sup>226</sup>Ra, the model values are in a narrow range, 8.4 - 8.8 dpm/100 kg, which are lower than the measured ones (6-14 dpm/100 kg) (Figs. 3.10). This is probably not unexpected considering the difficulty in statistical fitting of the dispersed data with small differences in the measured values of <sup>226</sup>Ra. In order to set up two equations to determine K<sub>x</sub> and K<sub>y</sub>, it was considered <sup>226</sup>Ra to be more suitable than other conventional oceanographic parameters.

Substituting  $C_{(x,y)}$  in the equation [3.8], the estimated constants A and B can be related to eddy diffusivities as:

$$K_x A^2 + K_y B^2 = \lambda$$
 .....[3.11]

By using the distribution of  $^{228}$ Ra and  $^{226}$ Ra concentrations in the Bay of Bengal the following two equations are obtained so that the two unknowns K<sub>x</sub> and K<sub>y</sub> can be determined.

$$K_x A_{226}^2 + K_y B_{226}^2 = \lambda_{226} \qquad \dots [3.13]$$
$$K_x A_{228}^2 + K_y B_{228}^2 = \lambda_{228} \qquad \dots [3.12]$$

where subscripts 228 and 226 correspond to the values derived from <sup>228</sup>Ra and <sup>226</sup>Ra data respectively. A<sub>228</sub>, B<sub>228</sub>, A<sub>226</sub> and B<sub>226</sub> obtained for the western Bay of Bengal data are  $0.3067 \times 10^{-6}$ , -0.4234  $\times 10^{-6}$ , 0.7642  $\times 10^{-7}$  and -0.1718  $\times 10^{-7}$  m<sup>-1</sup> respectively,  $\lambda_{228}$  is 3.83 x  $10^{-9}$  s<sup>-1</sup> and  $\lambda_{226}$  is 1.3725 x  $10^{-11}$  s<sup>-1</sup>. By solving these two equations, K<sub>x</sub> and K<sub>y</sub> are obtained to be  $1.3 \times 10^{7}$  and  $2.1 \times 10^{8}$  cm<sup>2</sup> s<sup>-1</sup> respectively. These are higher by a factor of 0.7 and 16 respectively over their Arabian Sea counterparts (Somayajulu et al., 1996). The high meridional eddy diffusivities K<sub>y</sub> in the Bay of Bengal can be explained due to the high river water input and the salinity gradient from north to south direction (Chapter 2, Fig. 2.3). Also the effective lateral eddy diffusivity, K<sub>h</sub> derived from lateral transects in the Bay of Bengal (Section 3.4.1) ranged from 0.51  $\times 10^{7}$  to 5.6  $\times 10^{7}$  cm<sup>2</sup> s<sup>-1</sup> are comparable to the K<sub>x</sub> values.

Eddy diffusivities in the tropical Pacific Ocean have recently been derived by Bauer et al. (2002) using the Lagrangian surface drifting buoy data obtained from EPOCS (Equatorial Pacific Ocean Climate Study) and TOGA (Tropical Ocean Global Atmosphere) studies. The zonal eddy diffusivities ( $K_x$ ) ranged from 5 x 10<sup>7</sup> to 7.6 x 10<sup>8</sup> cm<sup>2</sup> s<sup>-1</sup> higher than the meridional eddy diffusivities ( $K_y$ ) which varied from 2 x 10<sup>7</sup> to 9 x 10<sup>7</sup> cm<sup>2</sup> s<sup>-1</sup>. The  $K_x$  and  $K_y$  derived for the western Bay of Bengal are in the same general range; only the meridional mixing appears faster than the zonal when compared with the tropical Pacific Ocean. It is significant to note that the synoptic measurement values are matching well with those obtained from time-averaged radiotracer methods.

## 3.4.2.2 2-D Advection model:

By neglecting the influence of diffusion and assuming the distribution of the Ra isotopes in the western Bay of Bengal is due to lateral advection and radioactive decay only, one can obtain by substituting  $C_{(x,y)}$  in equation [3.4] the following relation:

$$w_x A + w_y B = \lambda \qquad \dots [3.14]$$

As before two equations for <sup>228</sup>Ra and <sup>226</sup>Ra are set up.

 $w_x A_{226} + w_y B_{226} = \lambda_{226}$  ....[3.15]  $w_x A_{228} + w_y B_{228} = \lambda_{228}$  ...[3.16]

Solving equations [3.15] and [3.16], w<sub>x</sub> and w<sub>y</sub> are determined to be -0.2 and -1.1 cm s<sup>-1</sup> respectively implying their directions are west to east and south to north respectively. The negative sign indicate (in both w<sub>x</sub> and w<sub>y</sub>) that the effective advection is in the N-S and E-W directions. The distances in both x and y directions are computed by taking 22°N 88°E as origin. Like eddy diffusivity, the advection velocity too is higher in meridional direction relative to zonal direction. Surficial currents (depth  $\leq$  5m) in the Bay of Bengal mainly depend on wind intensities and are deduced to be in the region of 1-5 cm s<sup>-1</sup> (McCreary et al., 1996) where as surface currents in the Bay of Bengal derived from satellite tracked Lagrangian surface drifting buoy data by Shenoi et al. (1999) are < 10 cm s<sup>-1</sup>, are about an order of magnitude faster than the ones deduced presently. Note the distinction that

comparison is between advection measured for a short period and that averaged over the mean-life of <sup>228</sup>Ra, viz. ~8 y (present study).

#### 3.4.2.3 Error analysis:

To evaluate accurately the effect of physical processes, such as horizontal advection/diffusion, from the distribution of Ra isotopes in a coastal marine environment is easier especially when there are large gradients in concentration of Ra isotopes over small spatial scales. It is not the case in the Bay of Bengal. The uncertainties involved in the derived values of horizontal advection rates and eddy diffusivities are estimated through the propagation of errors on A and B obtained from <sup>228</sup>Ra (See Section 3.4.2.1) using the following equation (Bevington, 1969) with  $\delta$  as the notation for errors.

$$(\delta X)^2 = \left(\frac{\partial X}{\partial A}\right)^2 (\delta A)^2 + \left(\frac{\partial X}{\partial B}\right)^2 (\delta B)^2 \qquad \dots [3.16a]$$

where  $X = K_x$ ,  $K_y w_x$  and  $w_y$ . The partial differential terms are evaluated for the equations [3.11] and [3.14]. The uncertainty estimates thus obtained are ~5 % for  $w_x$  and  $w_y$  and ~18 % for  $K_y$ . This failed to yield realistic errors for  $K_x$ . This is due to the unequal distribution of the sampling stations in the Bay of Bengal as well as due to the strong coastal currents, which changes directions in the two different monsoon periods. The samples are at times as far as 100-300 km from each other. Further studies should aim for systematic and closer sampling (1° x 1° grid size) covering the two different seasons in conjunction with data from CTD profiles and current meter measurements. Such an approach would reduce the uncertainties in estimating eddy diffusivities especially in the zonal direction in the model calculations using Ra isotopes.

#### 3.4.2.4 2-D Advection-Diffusion model:

To see the effect of advection/current, advection terms are included in equation [3.11]

$$K_x A^2 + K_y B^2 = \lambda - w_x A - w_y B$$
  
 $K_x A^2 + K_y B^2 + w_x A + w_y B = \lambda$  ....[3.17]

$$K_{x} = \frac{\lambda - w_{x}A - w_{y}B}{A^{2}} - \frac{K_{y}B^{2}}{A^{2}}$$
$$K_{x} = \frac{\lambda - w_{x}A - w_{y}B}{A^{2}} \left[ 1 - \frac{K_{y}B^{2}}{\lambda - w_{x}A - w_{y}B} \right]$$

Similarly,

$$K_{y} = \frac{\lambda - w_{x}A - w_{y}B}{B^{2}} \left[ 1 - \frac{K_{x}A^{2}}{\lambda - w_{x}A - w_{y}B} \right]$$

or 
$$K_x = \frac{k_1}{A} \left[ \frac{\lambda}{A} - w_x - \frac{w_y B}{A} \right]$$
 ......[3.18]  
 $K_y = \frac{k_2}{B} \left[ \frac{\lambda}{B} - w_y - \frac{w_x A}{B} \right]$  ......[3.19]

where  $\lambda$ =3.83 x 10<sup>-9</sup> s<sup>-1</sup>, A=0.3067 x 10<sup>-6</sup> m<sup>-1</sup>, B=-0.4234 x10<sup>-6</sup> m<sup>-1</sup> (A and B are obtained using <sup>228</sup>Ra data) and  $k_1 + k_2 = 1$ . Giving equal weightage to  $k_1$  and  $k_2$  (i.e. 0.5), one can vary  $w_x$  and  $w_y$  over a wide range of values to see the effect of w on K. The term that fixes K is  $\lambda$ /A (also  $\lambda$ /B) which has the dimension of velocity, the values are  $\lambda$ /A= 1.2 cm s<sup>-1</sup> and  $\lambda$ /B= -0.90 cm s<sup>-1</sup>. Only when ( $w_x + w_y$ ) <  $\lambda$ /A and ( $w_x + w_y$ ) <  $\lambda$ /B will the K<sub>x</sub> and K<sub>y</sub> reduce from 10<sup>8</sup> cm<sup>2</sup> s<sup>-1</sup> to lower values. Variations of K<sub>x</sub> and K<sub>y</sub> are considered with varying  $w_x$  and  $w_y$ . Here directions too are important, two cases are considered.

- i. Zonal advection velocity, w<sub>x</sub> is west to east (i.e. positive value) and meridional velocity w<sub>y</sub> is north to south (negative value). The variations of K<sub>x</sub> and K<sub>y</sub> are shown in Figures 3.11a and b, respectively. The eddy diffusivities decrease with increasing velocities, the decrease per unit change is slower in the zonal direction (Fig. 3.11a).
- Both w<sub>x</sub> and w<sub>y</sub> are kept positive (i.e in west to east and south to north directions, respectively). K<sub>x</sub> (Fig. 3.11c) and K<sub>y</sub> (Fig. 3.11d) steeply increase with increasing w values, w<sub>y</sub> having more effect on both K<sub>x</sub> and K<sub>y</sub>.



Fig. 3.11. 3-D plots of K versus  $w_x$  and  $w_y$ . In (a) and (b)  $K_x$  and  $K_y$  variations are shown, respectively, with increasing  $w_x$  (west to east) and  $w_y$  (north to south). With the increase in  $w_x$  and  $w_y$ , K decreases in both cases.  $K_x$  and  $K_y$  variations are shown with increasing  $w_x$  (west to east) and  $w_y$  (south to north) in (c) and (d) respectively. Notice the y-axis scales are reversed (compared to (a) and (b)) to show the abrupt increases in  $K_x$  and  $K_y$ . See text for discussion.

## 3.5 Advection-diffusion modeling of water column profiles of Ra isotopes

In all the Ra depth profiles of the Arabian Sea and the Bay of Bengal from thermocline region (Appendix 3.2), [228/226] varied between 0.077±0.048 to 2.48±0.12. The lowest ratio was found at 13°4'N 94°6'E (SS172/4036) at 405 m depth and the highest ratio was observed at 10°48'N 94°46'E (SS172/4037) at 6 m depth both in the Bay of Bengal. <sup>228</sup>Ra, and [228/226] decrease from surface to deeper waters. <sup>226</sup>Ra concentration does not show such a variation, below ~200 m, it starts increasing all the way to the sediment-water interface, which is the source region (Chung, 1987; Sarin et al., 1994).

Table 3.3. List of GEOSECS stations reoccupied during FORV Sagar Sampada cruises.

Location	GEOSECS sta. #	Present cruise #	
Arabian Sea			
13°22'N 53°16'E	413	SS164/4018	
19°45.5'N 64°37'E	416	SS164/4016	
12°58.3'N 64°28.8'E	417	SS164/4021	
6°11.2'N 64°25.3'E	418	SS164/4020	
3°57.1'N 56°48.2'E	419	SS164/4019	
Bay of Bengal			
8°31.4'N 86°2.5'E	445	SS152/3829	
12°31.5'N 84°30.7'E	446	SS152/3844	
0°1.1'N 80°3.3'E	448	SS152/3846	

Depth distributions of <sup>226</sup>Ra in the Bay of Bengal and the Arabian Sea are illustrated in Figs. 3.12 and 3.13 respectively, which show profiles of <sup>226</sup>Ra taken in 1998 and in 1978, ~20 years ago during the Indian Ocean GEOSECS cruises (Table 3.3; NSF, 1987). Water column profiles of <sup>226</sup>Ra at all stations are fairly similar and show an increasing trend with depth from 4.3-10.1 dpm/100 kg at the surface to ~13 dpm/100 kg at 500 m depth in the Arabian Sea and the Bay of Bengal (Appendix 3.2). Our measured <sup>226</sup>Ra activities also compare favourably (within ±20%) with those reported at the nearby GEOSECS stations. Some temporal changes of this order in surface water <sup>226</sup>Ra are not unexpected near ocean boundaries due to variability caused by seasonal upwelling.



Fig. 3.12. Plot of <sup>226</sup>Ra against depth in the upper water column of the Bay of Bengal. The solid circles represent samples collected at the GEOSECS stations and open circles correspond to nearby stations presently sampled.



Fig. 3.13. Plot of <sup>226</sup>Ra against depth in the upper water column of the Arabian Sea. The solid circles represent samples collected at the GEOSECS stations and open circles correspond to nearby stations presently sampled.

Cruise	Station code	K₂ cm² s⁻¹	
SS-98	2496	5.6	
SS-117	3101	0.66	
	3102	1.25	
	3104	0.56	
	3111	0.71	
SS-118	B8	1.9	
	F9	5.7	
	H1	0.12	
SS-132	3269	0.71	
	3271	4.4	
	3273	1.7	
	3275	1.31	
SS-152	3827	4.0	
	3829	1.44	
	3831	0.32	
	3833	0.011	
	3838	2.2	
	3844	1.15	
	3846	0.38	
SS-164	4016	5.8	
	4018	6.2	
	4019	0.43	
	4020	1.8	
	4021	10.3	
SS-172	4028	1.1	
	4030	0.78	
	4031	0.54	
	4034	0.28	
	4036	0.75	
	4037	0.91	
	4039	1.1	
	4041	3.7	

Table 3.4. Effective vertical eddy diffusivities obtained using seawater depth profiles of <sup>228</sup>Ra in the Bay of Bengal and the Arabian Sea.

## 3.5.1 1-D vertical model

Using the relationship [3.6] and taking depth instead of the horizontal distance, <sup>228</sup>Ra profile data can be used to derive effective vertical eddy diffusivity. Vertical diffusivities obtained from the seawater profiles of <sup>228</sup>Ra are given in Table 3.4. Vertical eddy diffusivities in the Arabian Sea and the Bay of Bengal ranged between 0.12 to 10.3  $cm^2 s^{-1}$  and 0.011 to 3.7  $cm^2 s^{-1}$  respectively. Higher values in the vertical eddy diffusivities obtained in the Arabian Sea can be explained by the presence of intense upwelling regions in the Arabian Sea relative to the Bay of Bengal.

## 3.6 Conclusions

To the <sup>228</sup>Ra and <sup>226</sup>Ra concentrations measured in the surface waters during five cruises to the western Bay of Bengal, a 2-D advection-diffusion model is applied to derive the surface mixing parameters. Eddy diffusivities (K<sub>x</sub> and K<sub>y</sub>) ranging from ~10<sup>7</sup> to ~10<sup>9</sup> cm<sup>2</sup> s<sup>-1</sup> and advection velocities ranging from ~10<sup>-2</sup> to ~1 cm s<sup>-1</sup> are needed to maintain the surface Ra isotope distribution which translates into the observed mean annual salinity distribution in the western Bay of Bengal. One needs more measurements covering the entire Bay during at least two seasons, viz. southwest monsoon and non-monsoon seasons to better understand the surface mixing processes. Measured <sup>226</sup>Ra activities also compare favourably (within ±20%) with those reported at the nearby GEOSECS stations ~20 years ago. Vertical diffusivities from 0.011 to 10.3 cm<sup>2</sup> s<sup>-1</sup> are obtained from the seawater <sup>228</sup>Ra profiles of the Bay of Bengal and the Arabian Sea. Higher values in the vertical eddy diffusivities measured in the Arabian Sea can be explained by the presence of intense upwelling regions in the Arabian Sea relative to the Bay of Bengal.

Station	Location	Temp °C	Salinity	<sup>228</sup> Ra (dpm/100kg)	<sup>226</sup> Ra (dpm/100kg)	[228/226]	
G-200 (August-September 1988)							
4884	15°44.7'N 83°51.6'E	29.4	33.01	12.9±1.2	9.9±0.8	1.31±0.05	
4886	16°47.0'N 82°51.7'E	29.7	29.36	39.1±3.5	14.9±0.6	2.62±0.21	
4890	16°27.8'N 82°17.6'E	28.7	33.60	33.8±2.0	13.8±0.7	2.45±0.09	
4892	16°6.5'N 81°51.5'E	28.8	31.90	41.9±3.0	16.7±0.6	2.51±0.16	
4893	15°52.3'N 82°09.1'E	28.7	33.60	15.5±1.3	9.9±0.8	1.56±0.06	
4895	15°07.9'N 83°05.6'E	29.6	33.85	11.5±1.8	9.4±0.3	1.22±0.19	
4897	14°57.0'N 81°37.0'E	29.2	33.61	10.1±0.6	7.7±0.3	1.31±0.05	
4898	15°26.5'N 81°06.0'E	28.5	33.83	12.5±3.0	9.8±0.4	1.27±0.17	
4900	15°04.5'N 80°18.7'E	29.5	33.80	11.6±0.6	8.6±0.4	1.34±0.04	
4901	14°31.2'N 80°18.0'E	29.4	33.80	14.7±2.4	8.7±0.7	1.69±0.24	
4906	12°8.1'N 81°28.0'E	29.6	33.94	11.2±2.7	8.6±0.4	1.29±0.31	
4908	13°30.0'N 83°10.0'E	29.2	33.16	11.2±1.1	8.5±0.3	1.33±0.17	
4910	14°49.0'N 83°44.0'E	28.5	33.29	14.8±1.6	9.6±0.3	1.55±0.16	
4911	15°29.0'N 83°31.0'E	29.2	33.13	12.4±0.7	8.4±0.4	1.48±0.05	

Appendix 3.1. Concentrations of Ra isotopes, temperature and salinity of the surface waters of the Bay of Bengal.
4912	17°19.0'N 83°39.0'E	29.7	33.14	12.8±1.5	10.2±0.5	1.25±0.14				
VISAKHA PATNAM	17°72'N 83°48'E	-	-	37.3±2.8	41.9±2.8	0.89±0.03				
SK-63 (Ma	SK-63 (March-April 1991)									
H-2	20°49'N 88°12.2'E	27.65	31.143	24.5±1.4	9.9±0.4	2.48±0.17				
H-3	20°37.3'N 88°14.9'E	28.05	31.367	25.7±1.2	9.8±0.3	2.63±0.14				
H-4	20°28'N 88°18.1'E	27.89	31.421	18.5±1.3	8.9±0.3	2.09±0.17				
H-7	20°08.4'N 88°23.5'E	27.51	32.044	13.2±0.9	6.6±0.2	1.98±0.15				
H-13	17°59.8'N 88°59.9'E	28.22	32.213	12.5±1.2	6.2±0.2	2.01±0.20				
G-1	19°50.8'N 86°26.2'E	27.98	32.518	17.1±1.0	8.1±0.3	2.11±0.14				
G-2	19°45.5'N 86°27'E	27.69	32.054	17.7±1.0	9.6±0.3	1.85±0.13				
G-5	19°33.1'N 86°36.9'E	27.73	31.655	18.5±1.2	8.8±0.3	2.09±0.15				
G-8	19°03.1'N 86°59.6'E	28.66	32.204	15.2±0.8	7.9±0.2	1.93±0.12				
G-10	18°N 87°47.3'E	28.20	32.913	14.4±1.1	7.9±0.3	1.83±0.16				
G-11	17°15.6'N 88°17.3'E	28.43	32.08	13.7±1.1	8.6±0.3	1.59±0.14				
F-1	18°50.6'N 84°43.4'E	28.35	33.638	11.9±0.8	7.6±0.2	1.55±0.12				
F-2	18º41.1'N 84º51.7'E	28.44	32.736	12.5±1.0	6.7±0.4	1.87±0.19				
F-5	18°27.7'N 85°06.5'E	28.14	34.093	13.7±0.9	6.8±0.2	2.03±0.15				
F-7	18°13.1'N 85°18.7'E	28.71	32.493	13.7±1.2	8.8±0.3	1.56±0.14				

F-9	17°42.5'N 85°45.1'E	28.46	32.461	12.7±0.8	7.1±0.2	1.80±0.12
F-11	16°27.1'N 86°56.9'E	28.68	32.139	14.5±1.1	7.9±0.3	1.84±0.15
E-1	17°24.7'N 83°14.8'E	28.73	32.312	22.8±1.0	11.2±0.3	2.04±0.10
E-2	17°17.6'N 83°19.9'E	28.75	32.213	16.1±0.9	8.5±0.3	1.90±0.12
E-4	17°11'N 83°24.6'E	28.78	32.300	16.5±1.0	8.6±0.3	1.91±0.13
E-6	17°02.6'N 83°31.5'E	29.07	32.664	18.3±1.1	9.5±0.3	1.93±0.13
E-8	16°50.8'N 83°44.3'E	28.88	32.523	17.3±1.0	9.1±0.3	1.89±0.12
E-13	14°47.9'N 85°12.6'E	29.07	32.275	19.2±1.0	9.6±0.2	2.00±0.11
D-2	16°06.9'N 81°55.4'E	28.90	32.637	21.7±0.9	11.7±0.3	1.85±0.08
D-7	15°31.7'N 82°12.5'E	29.02	33.179	19.4±1.0	10.1±0.3	1.92±0.11
C-8	14°N 81°3.8'E	29.03	32.169	23.1±0.8	11.5±0.2	2.00±0.08
C-2	14°00.2'N 80°20.6'E	28.02	34.364	12.1±0.6	9.2±0.2	1.32±0.07
C-12	14 <sup>°</sup> N 83°1.6'E	29.78	33.447	16.0±1.2	9.8±0.3	1.62±0.12
B-4	12°40.5'N 80°39.4'E	28.99	32.932	21.1±1.0	10.2±0.3	2.07±0.11
B-10	12°30.4'N 81°59.5'E	29.33	32.969	16.6±0.9	9.7±0.3	1.71±0.10
A-2	10°42.8'N 80°6.2'E	29.43	33.611	13.2±0.9	6.0±0.3	2.19±0.18
A-5	10°47.9'N 80°20.8'E	29.88	32.885	12.2±1.0	6.4±0.3	1.90±0.18

A-10	10°59.6'N 81°59.5'E	29.81	32.682	15.4±1.2	8.2±0.4	1.88±0.17
SK-70 (De	cember 199	1)				
D-1	16°14.3'N 81°53.3'E	26.14	28.530	28.0±1.0	8.3±0.3	3.38±0.16
D-2	16°07.0'N 81°54.9'E	26.04	30.536	17.4±0.9	6.0±0.3	2.92±0.22
D-4	15°55.3'N 82°01.2'E	27.06	33.316	13.5±0.8	6.3±0.2	2.13±0.16
D-6	15°42.3'N 82°05.4'E	26.97	33.281	10.7±0.7	6.1±0.2	1.76±0.13
D-9	14°55.9'N 82°33.8'E	27.21	33.154	11.8±1.1	6.0±0.3	1.97±0.20
C-3	14°N 80°25.7'E	26.55	28.939	27.2±1.2	8.5±0.3	3.21±0.18
C-5	14°00.2'N 80°37.3'E	27.01	29.827	35.9±1.1	14.3±0.3	2.52±0.09
C-9	13°59.9'N 89°19.7'E	27.3	33.686	12.1±0.8	7.4±0.4	1.64±0.13
C-12	13°56.1'N 83°04.8'E	27.36	33.839	12.5±0.5	8.7±0.2	1.44±0.07
B-1	12°42.5'N 80°18.9'E	26.64	28.536	33.8±1.1	13.6±0.4	2.48±0.11
B-4	12°39.5'N 80°39.7'E	26.94	31.980	22.8±0.8	11.3±0.2	2.02±0.08
A-1	10°40.4'N 80°01.5'E	26.94	27.190	42.1±1.1	14.2±0.3	2.96±0.10
A-3	10°44.9'N 80°12.0'E	26.96	28.566	35.3±1.0	14.0±0.3	2.52±0.08
A-12	10°57.2'N 84°02.0'E	28.18	33.543	15.1±0.8	8.8±0.2	1.73±0.09
SS-152 (F	ebruary 199	97)				
3829	8°31.0'N 86°2.0'E	28.27	33.813	9.3±0.5	7.4±0.2	1.26±0.08

3831	11º27.3'N 79º58.2'E	27.87	33.003	17.3±0.6	9.9±0.3	1.74±0.08
3833	11º29.5'N 79º54.8'E	27.28	32.912	21.0±0.7	10.1±0.3	2.09±0.09
3838	14°46.0'N 80°21.0'E	26.47	33.725	12.6±0.5	8.0±0.2	1.57±0.08
3844	12°31.0'N 84°30.0'E	27.30	33.592	12.5±0.6	8.4±0.2	1.49±0.09
SS-172 (F	ebruary 199	99)				
4028	17°30.0'N 85°59.8'E	26.95	32.615	19.2±0.9	10.2±0.4	1.87±0.11
4030	18°56.0'N	26 17	30 307	04 4 10 7	40 5:00	0.00.000
	89°32.3'E	20.17	52.521	21.1±0.7	10.5±0.3	2.00±0.09
4031	89°32.3'E 16°55.0'N 91°08.4'E	26.10	32.588	21.1±0.7 17.8±0.6	10.5±0.3 8.8±0.2	2.00±0.09 2.04±0.09

Error represents  $1\sigma$  for the analysis of each sample.

Appendix 3.2. Concentrations of Ra isotopes, temperature and salinity in the water column profiles (between surface and 500 m depth) collected from the Bay of Bengal and the Arabian Sea.

Depth (m)	Temp °C	Salinity	<sup>228</sup> Ra (dpm/100 kg)	<sup>226</sup> Ra (dpm/100 kg)	<sup>228</sup> Ra/ <sup>226</sup> Ra (A.R.)
		A	rabian Sea – Feb	ruary 1992	
SS-98 #	¢2489 (18°	41.41'N 71°	18.42'E)		
5	26.3	35.9	3.1±0.7	6.1±0.2	0.52±0.12
SS-98 #	<sup>‡</sup> 2494 (18°	0.49'N 70°0.	.6'E)		
5	26.304	35.878	4.1±0.5	5.3±0.2	0.77±0.11
SS-98 #	<sup>‡</sup> 2496 (17°	30.0'N 67°3	0.0'E)		
5	26.696	35.988	5.5±0.8	5.8±0.3	0.94±0.14
100	23.690	35.875	3.7±0.8	6.7±0.3	0.55±0.12
200	18.406	35.700	2.9±0.8	9.0±0.3	0.32±0.09

500	12.223	35.611	1.4±0.9	10.8±0.3	0.13±0.08
SS-98	#2498 (16	°58.64'N 64°59	.4'E)		
5	25.658	36.394	2.9±0.7	8.3±0.2	0.35±0.08
100	21.954	36.019	2.0±1.0	7.9±0.4	0.26±0.13
200	17.017	35.805	2.8±1.2	8.7±0.3	0.32±0.14
500	12.018	35.565	-	11.7±0.4	-
SS-98	#2499 (19	°45.0'N 64°30.0	)'E)		
5	24.903	36.396	0.9±0.4	5.5±0.2	0.17±0.07
100	21.924	36.070	2.2±0.9	7.5±0.3	0.29±0.12
300	14.778	35.884	1.8±1.3	11.7±0.4	0.15±0.11
500	12.586	35.704	1.9±1.5	7.6±0.3	0.25±0.20
SS-98	#2500 (20	°58.6'N 66°55.0	6'E)		
5	24.807	36.425	4.3±0.5	5.8±0.2	0.74±0.09
SS-98	#2502 (21	°51.86'N 67°59	.31'E)		
5	24.482	36.437	6.7±0.6	8.9±0.2	0.76±0.07
100	23.978	36.440	7.1±0.9	7.7±0.3	0.92±0.12
SS-98	#2507 (15	°2.16'N 72°24.	5'E)		
5	27.217	35.387	5.2±0.8	8.8±0.2	0.59±0.10
100	24.751	36.313	3.7±1.1	4.6±0.3	0.80±0.25
200	16.614	35.653	-	6.3±0.4	-
400	12.347	35.496	-	6.9±0.4	-
		Ara	bian Sea – Feb	ruary 1995	
SS-117	7 #3101 (8'	°2.15'N 73°0.17	'E)		
5	28.83	2 33.270	, 11.7±0.6	8.9±0.3	1.31±0.08
150	21.49	6 35.605	2.4±0.6	8.1±0.3	0.30±0.08
300	12.96	8 35.199	1.2±0.7	6.9±0.2	0.18±0.10
SS-117	7 #3102 (6	°11.0'N 64°25.0	'E)		
5	28.463	34.181	7.7±0.5	7.0±0.2	1.10±0.08
150	20.211	35.340	3.0±0.6	7.2±0.2	0.41±0.09
300	13.290	35.201	1.5±0.5	7.5±0.2	0.20±0.06
SS-117	7 #3103 (12	2°58.0'N 64°49.	1'E)		
5	27.19	5 36.545	2.0±0.4	7.0±0.2	0.29±0.06
150	17.27	9 35.649	2.3±0.5	6.8±0.2	0.33±0.07
300	13.80	5 35.688	1.5±0.5	7.6±0.4	0.20±0.07
SS-117	7 #3104 (12	2°49.1'N 71°37.	01'E)		
5	28.25	1 34.269	9.4±0.5	8.6±0.2	1.09±0.06
150	19.23	8 35.583	2.1±0.5	7.0±0.2	0.30±0.07
300	13.30	7 35.413	0.8±0.7	9.1±0.2	0.09±0.08

SS-11	7 #3111 (12°1	2.76'N 74°46.4	4'E)		
5	-	-	6.2±0.2	8.8±0.6	1.42±0.11
40	-	-	4.8±0.6	5.8±0.3	0.82±0.12
		Aral	bian Sea – Marc	h 1995	
SS-11	8 #B8 (8°31.0	1'N 74°0.63'E	)		
5	19.96	35.377	5.4±0.7	4.3±0.2	1.26±0.17
150	19.96	35.376	1.1±0.8	1.9±0.1	0.58±0.42
300	12.21	35.194	1.4±0.9	6.5±0.2	0.22±0.14
SS-11	8 #B1 (9°34.7	'N 75°59.99'E			
5	29.93	34.031	9.6±0.7	8.4±0.2	1.14±0.08
40	28.69	34.407	10.5±0.6	7.2±0.2	1.46±0.10
SS-11	8 #E1 (16°34.	0'N 72°59.57'E	Ξ)		
5	28.17	35.330	8.0±0.7	6.4±0.2	1.25±0.11
40	27.40	35.278	6.3±0.6	6.9±0.2	0.92±0.09
SS-11	8 #F9 (17°17.	84'N 69°24.7'E	E)		
15	26.96	35.925	5.1±0.6	7.3±0.2	0.69±0.08
150	19.86	35.689	4.4±0.7	8.6±0.2	0.51±0.09
300	14.56	35.636	2.4±0.8	9.6±0.2	0.26±0.09
SS-11	8 #H1 (22°28.	92'N 68°15.0'I	Ξ)		
5	24.875	36.244	5.9±0.8	7.2±0.2	0.82±0.11
40	24.150	36.274	3.1±0.7	4.0±0.2	0.78±0.17
SS-11	8 #H12 (19°45	5.9'N 64°36.6'I	Ξ)		
5	25.290	36.610	3.4±0.6	6.1±0.2	0.57±0.11
150	17.810	35.806	2.3±0.6	8.4±0.2	0.27±0.07
300	15.799	36.186	3.0±0.7	10.4±0.2	0.29±0.06
		Arabi	an Sea – Februa	ary 1996	
SS-13	2 #3269 (12°4	8.3'N 71°37.3	Έ)		
5	30.328	34.979	6.9±0.5	7.7±0.2	0.90±0.07
150	18.645	35.576	2.8±0.5	7.1±0.2	0.39±0.06
300	13.370	35.472	0.80±0.	65 10.3±0.2	0.08±0.06
SS-13	2 #3271 (12°5	7.7'N 64°28.9	Έ)		
5	29.176	35.519	3.4±0.5	8.7±0.2	0.39±0.06
150	19.838	35.675	3.1±0.7	8.0±0.2	0.39±0.09
300	14.028	35.702	1.4±0.5	9.5±0.2	0.15±0.06
SS-13	2 #3272 (13°1	5'N 58°20.9'E	)		
5	29.001	36.479	2.0±0.5	7.5±0.2	0.27±0.06
150	20.743	35.863	2.1±0.5	8.2±0.2	0.25±0.06
300	13.945	35.592	1.2±0.7	9.4±0.2	0.13±0.07

SS-13	32 #3273 (5°43	3.4'N 56°11.5'E)			
5	30.332	35.075	5.0±0.5	7.4±0.2	0.68±0.07
150	19.334	35.417	2.0±0.5	8.4±0.2	0.24±0.06
300	12.362	35.196	1.2±0.6	9.5±0.2	0.13±0.06
SS-13	82 #3274 (6°10	).9'N 64°25.1'E)			
5	29.994	34.884	-	-	-
80	25.047	35.983	1.7±0.5	8.4±0.21	0.20±0.06
300	12.215	35.182	-	10.0±0.2	-
SS-13	2 #3275 (8°2.	15'N 74°0.17'E)			
5	29.734	34.404	9.7±0.6	8.8±0.2	1.09±0.07
150	15.195	35.135	2.8±0.6	7.3±0.2	0.38±0.08
300	11.901	35.160	2.0±0.5	9.5±0.2	0.22±0.14
		Arabia	n Sea - March 19	98	
SS-16	64 #4016 (19°4	I5.5'N 64°37.2'E)			
10	26.03	36.560	3.0±0.4	9.5±0.2	0.32±0.04
75	24.14	36.586	4.0±0.4	7.7±0.2	0.52±0.06
150	19.91	36.033	2.5±0.5	6.0±0.2	0.41±0.08
250	17.07	36.132	1.4±0.4	9.1±0.2	0.16±0.04
402	14.18	35.960	1.4±0.4	8.3±0.2	0.17±0.05
SS-16	64 #4017 (17°4	I5.5'N 60°40.9'E)			
5	27.56	36.227	1.6±0.4	7.3±0.2	0.21±0.05
101	21.87	36.085	2.0±0.4	8.9±0.2	0.23±0.04
204	16.78	35.887	2.6±0.4	7.9±0.2	0.33±0.05
301	14.64	35.881	2.3±0.6	12.3±0.2	0.19±0.05
SS-16	64 #4018 (13°2	21.8'N 53°15.4'E)			
4	28.91	35.400	2.6±0.4	7.6±0.2	0.34±0.05
75	26.70	36.041	2.5±0.4	6.7±0.2	0.37±0.06
135	23.78	35.803	1.9±0.6	5.0±0.2	0.37±0.11
328	14.39	35.679	-	9.8±0.2	-
500	12.75	35.719	-	12.5±0.2	-
SS-16	64 #4019 (3°57	′'N 56°47.9'E)			
7	30.00	34.418	5.9±0.5	5.9±0.2	1.01±0.09
80	28.38	36.036	2.0±0.4	5.8±0.2	0.34±0.06
152	16.29	35.318	1.5±0.5	9.6±0.3	0.16±0.05
283	12.42	35.172	-	9.2±0.3	-
402	-	-	-	9.4±0.3	-
SS-16	6°8. #4020	7'N 64°21.2'E)			
6	30.41	34.227	8.8±0.5	8.6±0.2	1.02±0.07
81	26.28	35,902	1.5±0.4	5.6±0.2	0.27±0.08

150	16.42	35.279	1.1±0.7	6.4±0.2	0.16±0.11
306	11.57	35.141	1.6±1.2	8.9±0.4	0.18±0.13
SS-16	4 #4021 (12°57	.9'N 64°29'E)			
6	29.10	35.572	3.1±0.4	6.4±0.2	0.48±0.07
76	25.40	36.458	1.1±0.7	3.1±0.2	0.36±0.22
152	18.66	35.698	4.0±0.9	9.5±0.3	0.42±0.09
310	13.28	35.570	-	8.4±0.3	-
429	11.95	35.498	-	7.9±0.2	-
		Bay of Be	ngal - February	1997	
SS-15	2 #3827 (3°42.0	)'N 75°54.5'E)			
5	28.45	34.555	6.6±0.5	8.0±0.4	0.82±0.07
100	26.64	35.146	4.9±0.4	7.0±0.4	0.70±0.07
300	11.38	35.065	-	8.5±0.4	-
500	9.85	35.031	1.4±0.7	12.0±0.4	0.12±0.05
SS-15	2 #3829 (8°31.0	)'N 86°2.0'E)			
5	28.40	33.800	9.7±0.5	7.9±0.3	1.23±0.08
70	27.27	34.440	12.6±1.4	11.6±0.8	1.09±0.14
150	20.12	34.888	5.6±0.5	11.9±0.3	0.47±0.04
300	11.93	35.025	1.7±0.6	10.1±0.5	0.17±0.06
500	9.53	35.001	1.1±0.6	12.6±0.2	0.09±0.05
SS-15	2 #3831 (11°27	.3'N 79°58.2'E)			
5	27.87	33.003	17.3±0.6	9.9±0.3	1.74±0.08
18	26.99	33.358	14.8±0.5	8.2±0.2	1.80±0.08
45	25.28	34.095	11.1±0.5	8.4±0.2	1.32±0.07
SS-15	2 #3833 (11°29	.5'N 79°54.8'E)			
5	27.28	32.912	21.0±0.7	10.1±0.3	2.09±0.09
14	26.83	33.553	12.4±0.8	6.5±0.2	1.90±0.14
SS-15	2 #3838 (14°46	.0'N 80°21.0'E)			
5	26.47	33.725	12.6±0.5	8.0±0.2	1.57±0.08
75	23.46	34.526	9.4±0.5	7.3±0.2	1.29±0.07
SS152	2 #3839 (15°29.	9'N 80°44.8'E)			
14	26.87	33.251	10.5±0.5	5.4±0.2	1.95±0.12
49	25.83	33.938	10.6±0.5	7.3±0.2	1.44±0.08
SS-15	2 #3844 (12°31	'N 84°30'E)			
5	27.30	33.592	12.5±0.6	8.4±0.2	1.49±0.09
70	26.81	34.011	7.2±0.4	6.5±0.3	1.10±0.09
150	20.35	34.897	4.7±0.5	8.9±0.3	0.53±0.06

300	13.47	35.038	2.2±0.4	9.5±0.2	0.23±0.05
SS-152 #	\$3846 (0°01'N 8	0°3'E)			
5	28.85	34.867	4.5±0.5	7.7±0.2	0.59±0.07
70	24.73	35.201	3.2±0.5	7.0±0.2	0.45±0.07
150	14.44	35.123	1.1±0.4	7.5±0.5	0.14±0.06
300	11.76	35.052	-	10.6±0.2	-
500	9.85	34.999	-	11.3±0.2	-
		Bay of Ber	ngal - February	/ 1999	
SS-172 #	4028 (17°28.5'N	N 85°57.6'E)			
1	26.95	32.615	19.2±0.9	10.2±0.4	1.87±0.11
100	22.23	34.690	5.7±0.5	7.7±0.2	0.74±0.07
300	11.95	35.001	1.8±0.4	10.9±0.3	0.17±0.04
400	10.79	35.004	1.7±0.5	10.5±0.3	0.16±0.04
SS-172 #	4030 (18°51'N 8	89°31.8'E)			
6	26.17	32.327	21.1±0.7	10.5±0.3	2.01±0.09
100	23.16	34.599	6.1±0.5	8.6±0.2	0.70±0.06
196	15.10	34.913	2.5±0.4	10.4±0.2	0.24±0.04
301	11.91	34.989	1.3±0.7	10.2±0.3	0.13±0.07
398	10.82	34.999	1.4±0.8	11.9±0.3	0.12±0.07
SS-172 #	4031 (17°0.16'N	N 91°8.0'E)			
5	26.10	32.588	17.8±0.6	8.8±0.2	2.04±0.09
70	26.55	33.491	13.8±0.5	9.3±0.2	1.48±0.06
151	17.69	34.805	3.4±0.4	8.6±0.2	0.40±0.05
250	12.36	34.905	1.5±0.4	11.6±0.3	0.13±0.03
400	10.51	35.004	0.79±0.58	9.1±0.2	0.09±0.06
SS-172 #	4034 (13°16.5'N	N 93°16.8'E)			
5	28.30	33.338	20.7±0.7	10.8±0.3	1.91±0.08
80	26.55	34.070	9.2±0.5	7.2±0.2	1.26±0.07
151	16.965	34.836	3.9±0.5	11.2±0.2	0.35±0.04
248	12.307	34.934	1.2±0.4	11.4±0.2	0.11±0.03
350	10.268	35.005	-	11.8±0.3	-
SS-172 #	4036 (13°3.89'N	N 94°5.62'E)			
6	28.29	33.450	15.4±0.6	8.1±0.2	1.90±0.09
100	25.73	34.383	7.1±0.5	7.2±0.2	0.98±0.07
202	14.27	34.936	2.6±0.4	10.2±0.2	0.25±0.04
300	11.45	35.011	1.8±0.4	9.7±0.3	0.18±0.05
405	10.23	35.009	0.87±0.54	11.3±0.2	0.08±0.05
SS-172 #	4037 (10°48.05	'N 94°46'E)			

6	28.47	33.094	16.2±0.6	6.5±0.2	2.48±0.12
100	25.14	34.500	4.1±0.4	4.6±0.2	0.88±0.10
201	12.98	34.930	1.9±0.4	7.5±0.2	0.26±0.05
301	11.32	34.999	1.4±0.5	11.0±0.2	0.13±0.04
399	10.63	35.022	1.1±0.7	13.0±0.3	0.09±0.06
SS-172 #40	39 (6°30.26'N 9	2°0.1'E)			
5	28.89	34.165	7.3±0.5	9.2±0.3	0.80±0.06
71	28.35	34.836	6.2±0.5	7.9±0.3	0.79±0.07
150	17.25	34.900	3.0±0.5	8.9±0.2	0.33±0.06
226	12.42	35.060	2.3±0.7	11.4±0.3	0.20±0.06
300	11.31	35.045	-	9.1±0.2	-
SS-172 #40	41 (5°°0.1'N 86	°E)			
5	28.76	34.500	6.8±0.5	8.7±0.2	0.78±0.06
73	26.80	35.217	0.78±0.47	2.5±0.2	0.31±0.19
130	19.00	35.119	2.5±0.4	8.5±0.2	0.29±0.05
221	12.69	35.030	-	10.1±0.2	-
331	11.06	35.067	1.3±0.5	10.3±0.2	0.12±0.05

- not measured.

Error represents  $1\sigma$  for the analysis of each sample.

# Part B. Rare Earth Elements and Uranium in the Yamuna and the Chambal rivers

**Chapter 4** 

Introduction

#### 4.1. Introduction

The suspended matter and dissolved constituents of the rivers are the products of physical and chemical erosion of rocks, soils and alluvial material that are present in their drainage basin (Garrels and Mackenzie, 1971). These erosion products provide insight into the weathering processes on a basin-wide scale. Over the past three decades considerable efforts have been made to study the erosion processes and to place constraints on the material fluxes to oceans via rivers. Detailed geochemical studies involving major and trace elemental analyses of water and sediments have provided important information on the global biogeochemical cycles of elements in the continent-ocean-atmosphere system (Stallard and Edmond, 1983; Sarin et al., 1989; Krishnaswami et al., 1992; Dupre et al., 1996; Canfield, 1997; Chen et al., 2002; Dalai et al., 2002).

Extensive erosion of bedrock by rivers occurs predominantly in regions of steep gradients, large water flow and tectonic activity in their catchments. These eroded sediments are transported to the coastal zone. The study of geochemistry of elements and isotopes in the weathered products (bed sediments, dissolved and suspended matter) helps to understand various earth system processes such as weathering and transportation acting at present and in the past. In this study, two aspects of weathering and transport are investigated. These are (i) the major ion chemistry of the Chambal river system to elucidate the mineral weathering processes in its catchment and (ii) REE and U geochemistry of the Yamuna and the Chambal rivers.

### 4.2 Geochemistry of uranium

Large ion lithophile (LIL) elements include K, Rb, Cs, Sr, Ba, REE, Th and U. All these elements are concentrated in the continental crust. Among the actinides and REE, U is relatively mobile during weathering of silicates. It is the most abundant of the naturally occurring actinides (Ac, Th, Pa and U) with concentrations ranging from ~1  $\mu$ g g<sup>-1</sup> in sedimentary rocks to 120  $\mu$ g g<sup>-1</sup> in phosphates (Langmuir, 1997). <sup>238</sup>U is the chief constituent of natural U (Table 4.1). Knowledge of uranium content and <sup>234</sup>U/<sup>238</sup>U isotopic ratio in river waters is not only useful to study mobilization of uranium during weathering, but also for providing information on the uranium isotope mass balances of the oceans. The average concentration of U in seawater is 3 µg L<sup>-1</sup> (Krishnaswami, 2001) and continental surface waters contain 0.1 to 500  $\mu$ g L<sup>-1</sup> (Osmond, 1980; Scott, 1982; Krishnaswami, 2001). This is due to its varied chemical behaviour in response to redox conditions. Under reducing conditions U has a 4<sup>+</sup> valency and is less soluble; under oxidizing conditions it exhibits a  $6^+$  valency and forms readily soluble anionic complexes such as  $U(CO_3)_2^{2^+}$ . Most surface waters are oxidizing and once U enters such oxic surface drainage system, it behaves as a conservative constituent. The <sup>234</sup>U/<sup>238</sup>U activity ratio in rocks is generally close to the secular equilibrium value of 1. However, 234U/238U activity ratio in river waters exceeds the equilibrium value because of preferential release of <sup>234</sup>U due to  $\alpha$ -recoil effects (Scott, 1982; Hussain and Lal, 1986; Andersson et al., 1995). Riverine <sup>234</sup>U/<sup>238</sup>U activity ratio is thought to be increased by physical weathering (Kronfeld and Vogel, 1991) because the grinding of rocks increases the surface area from which <sup>234</sup>U can be directly recoiled and released to river water. Where intensive weathering prevails, the <sup>234</sup>U/<sup>238</sup>U activity ratio of the leached U tends to be close to the equilibrium value of unity (Moore, 1967; Bhat and Krishnaswami, 1969; Sarin et al., 1990). Where leaching is less intense, as in semi-arid regions, this ratio can become guite high (Scott, 1982). U content combined with the variability of its isotope ratio is used to infer mixing proportion of various waters. Despite wide variation in the U content of rivers, the global average value is  $0.25 - 0.30 \ \mu g \ L^{-1}$  (Sarin et al., 1990; Klinkhammer and Palmer, 1991; Palmer and Edmond, 1993).

Nuclide	Abundance (%)	Half-life	α-Energy (MeV)	α-Yield (%)
<sup>232</sup> U		68.9 y	5.320	68.2
			5.264	31.6
<sup>234</sup> U	0.0055	2.455x10⁵ y	4.775	71.4
			4.722	28.4
<sup>235</sup> U	0.7200	7.038x10 <sup>8</sup> y	4.398	55.0
			4.366	17.0
			4.215	5.7
<sup>238</sup> U	99.2745	4.468x10 <sup>9</sup> y	4.198	79.0
			4.151	20.9

Table 4.1. Nuclear data for U isotopes (Firestone, 1998)

# 4.3 Geochemistry of Rare earth elements

The REE comprise of La to Lu, occupying the IIIA group of the Periodic Table. Although rare earths have different numbers of total electrons, the variation occurs not in the outermost shells, as is generally the case, but in one of the inner shells - the 4f shell (Table 4.2). The various rare earths are generally identified with the number of electrons they have in the 4f shell. The 4f shell has room for 14 electrons; lanthanum has no electrons in the 4f shell and lutetium has 14.

Element	Symbol	Z	Atomic Weight <sup>1</sup>	Ground State Configuration	lonic Radius (Å) <sup>2</sup>	
					CN6	CN8
Lanthanum	La	57	138.9055	[Xe]5d <sup>1</sup> 6s <sup>2</sup>	1.032	1.160
Cerium	Ce	58	140.115	[Xe]4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	1.01	1.143
Praseodymium	Pr	59	140.9077	[Xe]4f <sup>3</sup> 6s <sup>2</sup>	0.99	1.126
Neodymium	Nd	60	144.24	[Xe]4f <sup>4</sup> 6s <sup>2</sup>	0.983	1.109
Samarium	Sm	62	150.36	[Xe]4f <sup>6</sup> 6s <sup>2</sup>	0.958	1.079
Europium	Eu	63	151.96	[Xe]4f <sup>7</sup> 6s <sup>2</sup>	0.947	1.066
Gadolinium	Gd	64	157.25	[Xe]4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	0.938	1.053
Terbium	Tb	65	158.9254	[Xe]4f <sup>10</sup> 6s <sup>2</sup>	0.923	1.040
Dysprosium	Dy	66	162.50	[Xe]4f <sup>11</sup> 6s <sup>2</sup>	0.912	1.027
Holmium	Ho	67	164.3033	[Xe]4f <sup>12</sup> 6s <sup>2</sup>	0.901	1.015
Erbium	Er	68	167.26	[Xe]4f <sup>13</sup> 6s <sup>2</sup>	0.890	1.4
Thulium	Tm	69	168.9342	[Xe]4f <sup>13</sup> 6s <sup>2</sup>	0.880	0.994
Ytterbium	Yb	70	173.04	[Xe]4f <sup>14</sup> 6s <sup>2</sup>	0.868	0.985
Lutetium	Lu	71	174.967	[Xe]4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	0.861	0.977
Scandium	Sc	21	44.95591	[Ar]3d <sup>1</sup> 4s <sup>2</sup>	0.745	0.870
Yttrium	Y	39	88.9059	[Kr]4d <sup>1</sup> 5s <sup>2</sup>	0.9	1.019
	Eu <sup>2+</sup>				1.17	1.25
	Ce <sup>4+</sup>				0.87	0.97

# Table 4.2. Some basic REE data.

<sup>1</sup> From De Bievre et al. 1984.

<sup>2</sup> Trivalent Ionic Radii unless otherwise stated; (Shannon, 1976).

This electronic structure has a major consequence on the geochemical behaviour. As the outermost electrons primarily determine an element's chemical behaviour and rare earths all have three outer electrons, so they are chemically very similar.

From La to Lu, the nuclear charge and the number of 4f electrons increases by one at each step. The shielding of one 4f electron by another is quite imperfect owing to the shapes of the orbital, so that at each increase in the number of electrons, the effective nuclear charge experienced by each 4f electron increases, thus causing a reduction in size of the entire 4f shell. The accumulation of these successive contractions from La to Lu due to the imperfect shielding of one electron by another in the same sub-shell is known as the lanthanide contraction.

When discussing dependence of REE concentration on atomic number Z, it is convenient to remove the large odd/even Z variation in their abundances associated with nucleosynthesis, by normalizing observed concentrations to those of reference material such as Chondrite or PAAS (Post-Archean Australian Shale, McLennan, 1989). There is a progressive change in chemical properties of the trivalent REE associated with contraction of ionic radii as the 4f shell fills between La (Z=57) and Lu (Z=71). Marked deviations from such uniform behaviour may occur if quadrivalent Ce or divalent Eu are involved. An anomaly is commonly defined as the ratio of the shale-normalized concentration of a particular REE to that interpolated form those of its neighbours. Any anomaly less than unity are considered as negative and more than one is designated as positive.

Henderson (1984), Brookins (1989) and McLennan (1989) provided general reviews of REE geochemistry in aqueous and sedimentary systems. The subtle, but well understood, variations in the properties of the REE make them sensitive to mineral/melt equilibria, leading to their special utility in geochemical studies of igneous systems (Lupin and McKay, 1989). For sedimentary rocks, these characteristics are equally important but are less direct. Because REE are not easily fractionated during sedimentation, sedimentary REE patterns may provide an index to average provenance compositions (McLennan, 1989; Moorey and Setterholm, 1997; Chandrajith et al., 2000; Hoskin and Ireland, 2000; Singh and Rajamani, 2001). The REE as a group are of particular interest for studying oceanic chemistry (Elderfield, 1988). For example, Liu et al. (1988) have related variations in the REE patterns in marine carbonates to changes in circulation as the Atlantic basin opened.

## 4.4 Distribution of REE in river water

Apart from substitution on rock forming minerals, REE occur in a wide variety of REE-rich accessory minerals, such as apatite, titanite, monazite and allanite (Clark, 1984; Mason and Moore, 1982). The mobility and fractionation of the REE during weathering is highly dependent on their distribution among these minerals, since these different minerals are more or less resistant to weathering (Humpris, 1984). Once in solution, pH seems to be a key factor in controlling the fate of the REE. The solubility of these elements tends to increase with decreasing pH. Johannesson et al. (1995) reviewed the solubility control of REE and the significance of  $CO_3^{2-}$  and  $PO_4^{3-}$  as complexing ions in terrestrial waters. High concentrations of  $CO_3^{2-}$  can enhance the solubility of REE, whereas high concentrations of PO<sub>4</sub><sup>3-</sup> seem to reduce the REE solubility due to precipitation of REE phosphates. From seawater, REE may be removed through formation of rare earth phosphate co-precipitates (Byrne and Kim, 1993) or by incorporating onto Fe-Mn oxyhydroxides. Data on the importance of REE complexes with organic ligands are scarce, but existing stability constants indicate that humic complexes might be important for the REE mobility in natural waters (Wood, 1990 and 1993). In addition to precipitation of phosphates, REE may also be retained in soils through precipitation of aluminum-phosphate-sulphate minerals (APS minerals), such as gorceixite, which are isostructural with alunite. Furthermore, secondary Fe and Mn weathering products and clay minerals may act as traps for the REE (Land et al., 1999).

# 4.5 Distribution of REE in river sediments

Uniformity in the distribution of REE in sediments from different sources is generally interpreted as being due to mixing of different lanthanide patterns in the upper crust during weathering, erosion, transportation and deposition. There is also evidence of fractionation and mobilization during weathering, especially in geochemical reactions that involve changes in pH in soils and river waters (Nesbitt, 1979).

For example, under reducing conditions, Eu is reduced from the trivalent to the divalent state, it increases in ionic radius, and this effect leads to distinctive geochemical behaviour as compared to the other lanthanides, producing enrichment or depletion of this element relative to the other REE. Under reducing conditions,  $Eu^{2+}$  is almost identical to  $Sr^{2+}$  and camouflage of  $Eu^{2+}$  and  $Sr^{2+}$  in  $Ca^{2+}$  sites during rock genesis is well documented. On the other hand, in the oxidising environment Ce may lose an electron to become quadrivalent making its properties different from other trivalent REE. In both cases, abundances relative to the other trivalent REE are used to assess the redox behavour in geochemical systems.

The REE have traditionally been divided into two groups, the light rare earths (LREE, elements from La to Sm) and the heavy rare earths (HREE, from Gd to Lu). This differentiation is related to the inflection in the REE patterns that occurs around Eu due to the difference in the ionic radius produced by lanthanide contraction. The LREE/HREE fractionation is evaluated by means of the La/Yb ratio. This ratio is particularly useful for studying sediment origin and REE mobility in the crust. Goldstein and Jacobsen (1988) have examined the chemical composition of suspended particulate matter in some major world rivers and observed a positive correlation between the La/Yb ratio and the Sm-Nd depleted mantle model age in these river sediments. These sediments have LREE enriched patterns relative to the North American Shale Composite (NASC) and their normalized ratios (La/Yb)<sub>N</sub> are between 1.6-2.7.

The distribution of REE generally shows an almost uniform pattern due to factors such as river transportation processes and high level of terrigenous mixing in the bed sediments. Martin and Meybeck (1979), Goldstein and Jacobson (1988) and Condie (1991) observed that although the REE in a weathering profile may get fractionated, by the time REE enter the suspended load of major rivers, they show uniform shale like REE pattern, not unlike their average source rocks. However, Sholkovitz (1988) showed that river-bourne sediments commonly have REE patterns that are strongly depleted in HREE relative to shale. Therefore, the processes responsible for the REE chemistry of different deposits laid down by the fluvial system are not well understood. Cullers et al. (1987, 1988) studied the chemistry of riverbed sediments produced in different climatic conditions and observed that silt and clay size fractions most closely resemble their source REE patterns but with higher abundance. These authors also observed that in sediments

derived from an intensely weathered source, all the size fractions have negative Eu anomaly, whereas in moderately weathered sediments, only the sand fraction shows a positive Eu anomaly. It is important to understand the Eu systematics as the major distinction between Archean and Post-Archean sediments and therefore the nature of their sources is based on their Eu anomaly (McLennan et al., 1979, McLennan and Taylor, 1984; Taylor and McLennan, 1985). The relative importance of the nature of source rocks vs. the prevalent surface weathering conditions in the chemistry of clastic sediments needs to be clarified. This calls for more databases on modern clastic sediments derived from diverse lithologies and from different climatic conditions.

# 4.6 Motivation for this study

The river Yamuna, draining the western part of the Ganga catchment in the southern slopes of the Himalaya, is the largest tributary of the Ganga (Negi, 1991). In its course the Yamuna drains a variety of lithologies in the Lesser Himalaya thereby providing an opportunity to examine the influence of lithology on water chemistry. Yamuna river is a glacier fed, river with high relief and has a number of tributaries in the Himalaya, prominent of which are the Tons, Giri, Aglar, Asan and Bata. The strong altitudinal gradients in mountain regions combined with the pristine condition of the area provide unique opportunity to study the geochemical weathering processes. In contrast, the Chambal, a major tributary of Yamuna, drains the Vindhyan, the Indo-Gangetic plain which is undergoing major land-use changes, with large areas of intensely farmed agricultural land, urbanized and industrial regions and open uplands. The Vindhyan is composed of crystalline igneous and metamorphic rocks (Valdiya et al., 1982). Based on their texture and composition, several types of granites have been recognized in Bundelkhand plateau. The headwaters of the Chambal and a part of their drainage area are in the Deccan traps. The Chambal river water is of variable quality, influenced at places by effluents from industries and urban metropolitan areas and sediments, nutrients and agrochemicals from the land surfaces. However, the present knowledge on the chemical composition of sediments, bedrocks and waters of the Yamuna and the Chambal river catchments is very limited and there are no studies accomplished on their REE composition. This study for the first time, attempts to give the dissolved REE composition of the Yamuna river along with that in the bed sediments. Spatial variations in the REE content of fluvial bed sediments within the two contrasting large catchments of the Yamuna and the Chambal rivers are studied. Furthermore, analysis of U concentration and <sup>234</sup>U/<sup>238</sup>U activity ratio in the dissolved load of the Yamuna and the Chambal rivers was undertaken in this study to determine the extent of mobility of U and its isotopic disequilibrium in these rivers and their relative contribution to the dissolved U concentration of the Ganga river. U concentration and its isotopic composition are constrained by the dominant lithologies in weathering these catchment regions: igneous rocks vs. sedimentaries.

# **Chapter 5**

# **Methods and Approaches**

# 5.1 Introduction

Chemical weathering plays a major role in the geochemical cycle of elements (Lerman and Meybeck, 1988). Many common rock-forming minerals weather at significantly different rates. Differential weathering of minerals give rise to a range of geochemical and isotopic signatures in the weathered sediments. These signatures remain largely intact when they are ultimately displaced from the catchment source and transported as suspended matter and bed sediments in riverine systems. Many studies concentrate on a particular aspect of natural river water chemistry such as the role of elevation (Drever and Zobrist, 1992), lithology (Sarin et al., 1989 and 1992a; Pandey et al., 1999), climate (Bluth and Kump, 1994), seasonal variations (Devol et al., 1995), individual cyclonic discharge events (Alexander et al., 2001) or anthropogenic inputs (Douglas et al., 2002) in controlling chemical variability and transport of major and trace elements. The Yamuna and the Chambal watersheds (Fig. 5.1) were studied for the geochemistry of REE and U that are less documented in the Indian rivers.

This chapter discusses geology and climate of the Yamuna and the Chambal river catchments and describes sample collection, viz., river water, sediments and source rocks and analytical methods employed to carry out various chemical measurements.

# 5.2 The Yamuna river catchment

# 5.2.1 Geologic setting of the Yamuna river catchment

The Himalaya is divided into four distinct physiographic divisions from south to north.

 Siwalik Hills: These form a series of low hills aligned more or less parallel to the main Himalayan arc. The Siwalik Hills are very well developed in the western and central Himalaya, east of which they gradually merge with the lower Himalaya foothills. Longitudinal valleys separate the Siwalik Hills in the south from the lower Himalaya in the north. These are made up of sediments deposited by the ancient Himalayan rivers in their channels and flood plains. There are flat stretches within the otherwise rugged Siwalik terrane called the duns consisting of gravelly deposits in depression of now vanished lakes that were formed in the synclinal valleys (Valdiya, 1998).

- 2. Lesser Himalaya: This consists of the foothills of the main Himalayan range that lies further towards north. In many areas the lower Himalaya rise abruptly above the valleys. The Lesser Himalaya, covering a zone of 60 to 100 km wide in between the Siwalik and the higher Himalaya, represents a relatively gentle and mature topography with gentle slopes and deeply dissected valleys, which bear evidences of recent rejuvenation. On an average, the elevation ranges from 1500 m in the valley beds to 2700 m along the crest of the ridges (Devi, 1992). The lesser Himalaya comprise of Precambrian Paleozoic sedimentary strata with minor occurrences of displaced Crystallines (Valdiya, 1980). The sedimentaries are divided into two NW-SE elongated sequences by the crystalline klippe lying in between. The northern sequence of Precambrian sedimentaries is known as the inner belt whereas the southern part known as the outer belt contains sediments of possible Paleozoic age. The secondary succession of the outer belt is known as Krol Belt.
- Higher Himalaya: This consists of the main Himalayan mountains that extend in arc shape along the periphery of the Indian sub-continent. The higher Himalaya is characterized by tectonically active topography, comprising of very thick piles of Precambrian high-grade metamorphic and granitic gneisses, known as Higher Himalayan Crystallines (HHC) (Valdiya, 1998).
- 4. Trans Himalaya: Across the snow-clad peaks of the main Himalaya lies a vast table at an elevation of 3000 m. This is primarily a rain deficient area

as the SW monsoon is unable to cross the main Himalayan barrier that lies to the south of this tract. These conditions resemble of a desert and the Trans Himalaya has often been described as a cold desert.

The Yamuna originates the Higher Himalaya near its source region and through Lesser Himalaya (Fig. 5.2) where a significant part of the study area is contained. The Main Central Thrust (MCT) demarcates the boundary between the Lesser and the Higher Himalaya in the north whereas the Main Boundary Thrust (MBT) defines the boundary between the Lesser Himalaya and Siwaliks in the south. The drainage basins of the Yamuna and its tributaries in their upper reaches in Himalaya cover the northwestern part of the Uttaranchal State (Fig. 5.1). The Yamuna and its tributaries flow through various formations in the lesser Himalaya comprising diverse lithology set in complex stratigraphic position due to the faulting and thrusting activities. The following section provides a compilation of available information on the lithology of this region drained by the Yamuna and its tributaries (Valdiya, 1980).

#### 5.2.2 Major rivers of the Yamuna river catchment

The Yamuna originates from the Yamunotri Glacier at the base of the Bandapunch peak in the Higher Himalaya (Negi, 1991, Dalai et al., 2002). The glacial lake of Saptarishi Kund, near the Kalind Mountain, at an altitude of 4421 m, is the source of the Yamuna. The Yamuna has a number of tributaries in Himalaya, prominent among them are the Tons, Giri, Aglar, Asan and Bata (Table 5.1). Also it receives a number of southern tributaries, the largest of which are the Chambal, the Sindh, the Betwa, and the Ken. The Yamuna runs almost parallel to the Ganga till it joins the latter at Allahabad after a course of about 1,376 km (Fig. 5.1). Among all the tributaries of the Ganga, the Yamuna has the largest drainage area and stands second in terms of water discharge. It receives waters from glacier/snow melt in the source region, from monsoon rains and from springs and various tributaries along its course down stream. Near its source in the Higher Himalaya, the Yamuna drains mainly the crystallines of Ramgarh and

Almora groups (Gansser, 1964). Occurrences of calc-schists and marble with sulphide mineralization have been reported in the areas upstream of Hanuman Chatti (Jaireth et al., 1982). From the Higher Himalaya, the Yamuna flows in the southwest direction and enters the Lesser Himalaya where it drains a variety of lithologies. It flows through a large stretch of quartzite of Berinag Formation. Downstream, it passes through the massive dolomitic limestone and marble of Mandhali and Deoban formations. The Yamuna then enters a large stretch of the sedimentaries of the Chakrata Formation, Chandpur Formation and Nagthat formation. Barites occur in the silisiclastic sediments of Nagthat Formations in the Tons river section (Sachan and Sharma, 1993) and in the lower horizons of Krol limestones at Maldeota and Shahashradhara, where they occur as veins (Anantharaman and Bahukhandi, 1984). Southwest of Kalsi, the Yamuna enters the Siwaliks comprising the channel and floodplain deposits by the Himalayan rivers in the past.

In the Lesser Himalaya, occurrences of shales are reported into the Infra Krol, the Lower Tal, the Deoban and the Mandhali formations (Gansser, 1964: Valdiya 1980). These are exposed at a number of locations in the Yamuna and the Tons catchments, the largest being at Maldeota and Durmala, around Dehradun, where phosphorite is mined economically. Gypsum occurs in Krol formation in the form of pockets and bands (Ananatharaman and Bahukhandi, 1984: Valdiya, 1980). Near Shahashradhara, gypsum is found as replacement deposits in the upper Krol dolomitic limestone. Geothermal springs occur mainly in and around the source region, in Yamunotri and Janaki Chatti.

The Yamuna has been dammed at Dakpathar, 6 km downstream of Kalsi. The main human settlements along the river are at Yamunotri, Hanuman Chatti, Barkot, Naugaon, Kalsi, Vikasnagar and Paonta. Brief description on other smaller streams is given in Table 5.1.

#### 5.2.3 Climate of the Yamuna river catchment

The drainage basins of the Yamuna and its tributaries, covering the northwestern part of the Uttaranchal state experience tropical monsoon climate with much variability introduced by the altitude, mountain barriers, air masses and their movement (Devi, 1992). January is the coldest month while the maximum temperature is in the month of June. After June, the temperature decreases with the onset of southwest monsoon with a secondary maximum of temperature in September when there is a sharp drop in cloudiness in the region. Alpine, sub-alpine, temperate and sub-tropical vegetation covers the Yamuna catchment.

Both diurnal and annual ranges of temperatures decrease from the plains up to the elevations ranging from 2100 to 2400 m, beyond which, they again increase. The amount of insolation received along the mountain slopes differs according to the gradient and direction of slopes. South and southwest facing slopes are expected to receive maximum insolation than those facing north and northeast as the sun remains south of the area throughout the year. Fig. 5.3 shows the monthly temperature variations in some of the places in the Yamuna catchment. The driest month of April and May have the largest diurnal range and the most humid months July and August have the least. The amount of rainfall varies with elevation as well as with the location. Heavy orographic rainfall occurs on the windward side of the ranges with a rapid decrease on the leeward side.

The tropical storms and depressions largely influence the local rainfall. Heavy rains are associated with slowly moving tropical cyclone clouds due to an increase in the duration of rainfall. The southwest monsoon hits the region around the last week of June and withdraws around the last week of September. The annual rainfall at Dehradun and Kalsi, situated at the foothills of the Himalayas, is ~210 cm whereas in Mussoorie, lying on the windward side of the mountain slope, receives an annual rainfall of ~270 cm. About 80% of this is contributed by southwest monsoon during July-September (Fig. 5.3). During

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monsoon, heavy flood in the Yamuna causes serious damage in the region. Potential evaporation (P.E.), which represents the water loss in the hydrological cycle, shows large monthly variations in the Yamuna catchment (Dalai, 2001).



Fig. 5.1. Map of India showing the Yamuna and the Chambal rivers and their confluence with the Ganga.



Fig. 5.2. Simplified, geological lithologies of the Yamuna river catchment in the Himalaya. Only some of the tributaries samples are shown.

Table 5.1. Small streams and tribuataries of the Yamuna catchment (Negi,1991; Dalai et al., 2002).

Stream	Description
Tons	The Tons drains similar types of lithology as described for the Yamuna. In its catchment, black shales occur in areas around Tiuni
	and Likhandi area on the Chakrata-Tiuni road. It joins the Yamuna
	at Kalsi. Its catchment bears some of the densest forests in the
	Tiuni and Minus.
Aglar	The river Aglar originates as a number of small streams fed by
Agiai	drainage of the Yamuna and the Bhagirathi, thereafter it flows in
	western direction to join the Yamuna at the Yamuna Bridge.
Ciri	Originates near Shimla as a spring fed by ground water and flows
GIII	ioins the Yamuna near Paonta Sahib, it drains condomerates.
	sandstones, siltstones, quartzites, phyllites, carbonaceous and
	pyritiferous shales and slates interbeded with limestones (Srikantia
	and Bhargava, 1998). Two spring fed streams emanating from the limestone caves of the
Asan	Mussoorie ridge merge to form the Asan river that flows southwest
	to join the Yamuna near Herbettpur. In its lower reaches it drains
	predominantly the Siwaliks. Broad river terraces developed along
	tropical forests occur in the upper catchment of the river.
	Originates in the boulder below the Nahan ridge in Himachal
Bata	Pradesh fed by rainwater and joins the Yamuna downstream of
	Paonta Sahib. It drains predominantly the sandstones of the Siwaliks with minor condomerates and claystone
	Originates in the Higher Himalaya and drains the Almora
Didar Gad	Crystallines before joining the Yamuna.
Barni Gad	Drains dolomitic limestone before joining the Yamuna near Kuwa. It
	It rises from the Dhauladhar Range and is fed by the Chandra
Pabar	Nahan glacier and springs emanating from underground water. It
	joins the Tons near Tiuni. In its upper reaches it drains the Almora
	Crystallines. Downstream it flows through quartzite, phyllites, slates
Godu Gad	Originates in the Higher Himalava where it drains the Almora
	Crystallines. It flows through massive coarse-grains quartzite
	before it joins the Tons near Mori (Valdiya, 1980).
Shei Khad	A tributary of the Tons. Shej Khad drains predominantly dolomites



Fig. 5.3. Mean monthly (a) temperature and (b) rainfall variations at some stations in the Yamuna catchment in the Himalaya (Devi, 1992).



Fig. 5.4. Mean monthly variation of the water discharge in the Yamuna at New Delhi bridge. More than 80% of the discharge occurs during July, August and September (Data from Dalai, 2001).

Soil formation is governed by the climate (precipitation and temperature), parent lithology, vegetation and gradient in the catchment. The soils in these regions have been grouped as brown-hill soils (Devi, 1992), which form from weathering of granite, gneiss and garnetiferrous and biotitic schist. Soils on the slope (15-40%) are shallow due to erosion and mass wasting processes and usually have very thin surface horizons. Soil loss in the region varies with the extent of vegetation. Intensive cultivation is observed on terraced hill slopes. The proportion of the area under forest in the Yamuna catchment is above 40%, higher than that in the foothills and the plains.

The total length of the Yamuna from its origin till its confluence with Ganga at Allahabad is 1376 km. The Yamuna emerges from the hills near Tajewala where the water is taken off by the western and eastern Yamuna canals. The Yamuna river drains an area of about 9600 km<sup>2</sup> in the Himalaya with an annual water flow of  $10.8 \times 10^{12}$  L at Tajewala (Rao, 1975; Jha et al., 1988). About 80% of water discharge occurs in the month of July to September. Fig. 5.4 shows the monthly variations in water discharge at New Delhi Bridge (Dalai, 2001). The maximum monthly discharge occurs in August and is 40 times that of the

minimum in January, reflecting substantial water input from precipitation in the monsoon season.

#### 5.3 Chambal river catchment

#### 5.3.1 Geologic setting of the Chambal river catchment

The Vindhyan range is formed with the scraps of the ancient Aravalli ranges. It traverses nearly the whole width of peninsular India with length of about 1050 km and an average elevation of ~300 meters. The Archaeans occupy large areas in southeastern and northern part of the Madhya Pradesh state (Fig. 5.1) and a minor part at the west. Deccan Trap lava flows cover the major areas in the western and central parts of the state. Large inliers of old rocks belonging to the Archaeans, Vindhyan and Gondwanas project through the Deccan Trap in various parts of the state. The Quaternary deposits comprising mainly older and newer alluvium are restricted to the major river valleys. The Chambal is the chief tributary of the Yamuna and rises in the Vindhyan Range just south of Mhow, western Madhya Pradesh state at an elevation of 354 m. The Chambal Basin lies between 22° 27' to 27° N and 73° 20' to 84° E. The total area occupied by the Vindhyan basin is of the order of 100,000 km<sup>2</sup>. Vindhyan mountain forms the prominent plateau-like range of sandstones to the north of the Narmada valley, particularly Bundelkhand and Malwa (Krishnan, 1982). A map of simplified geological lithologies of the area from where samples are collected is shown in Fig. 5.5.

The great Boundary Fault, through which the River Chambal has carved its course, passes through southeastern parts of Rajasthan (Fig. 5.1). This fault is visible in Begun (Chittaurgarh district) and northern parts of Kota. It reappears again in Sawai Madhopur and Dhaulpur districts. Besides this, several mega lineaments also traverse in the state. Southern and southeastern Rajasthan is mostly a plateau. The Hadauti plateau, having intrusions of black volcanic rocks into the Vindhyan, extends to a great part in Jhalawar, Baran and Kota districts. The Malwa plateau also extends into the southern part of Chittaurgarh and Banswara districts having an average altitude of 500 m above MSL and is dotted with isolated low ranges at few places. This plateau in Rajasthan occurs in the upper catchment of the Chambal river to the south-east of the Mewar plains. The greater part of this area is drained by the river Chambal and its right bank tributaries like Kali Sindh, Parwan and Parvati. This plateau has two defined units of Vindhyan scrapland and Deccan lava plateau.

A large part of the soils in the alluvial plains of the Chambal river system (where the annual rainfall is <100 cm) is impregnated with alkaline and saline soils (Sarin et al., 1989). The Chambal catchment exhibits a wide range of landuse types, with large areas of intensely farmed agricultural land, urbanized and industrial regions and open uplands (CBPCWP, 1982). River water is of variable quality, containing effluent from industries and urban conurbations and sediments, nutrients and agrochemicals from the land surfaces.

# 5.3.2 Major rivers of the Chambal river catchment

# The Chambal

The Chambal river has its origin south of Mhow, near Manpura from the northern parts of the Vindhyan. The Chambal River is denuding its beds over long geological periods developing to flat valleys with low gradients. From its source it flows north into southeastern Rajasthan state (Fig. 5.1). Turning northeast, it flows past Kota and along the Rajasthan-Madhya Pradesh border; shifting east-southeast, it forms a portion of the Uttar Pradesh-Madhya Pradesh border and flows through Uttar Pradesh to empty into the Yamuna after a 900-km course. The Banas, Kalisindh, Sipra, and Parbati are its chief tributaries. These rivers are entirely rain fed with the result that many of them shrink into rivulets during the summer season. The lower course of the Chambal river is lined by a 16 km belt of badland gullies resulting from accelerated soil erosion and is the site of a major project in soil conservation.

# The Kalisindh

River Kalisindh originates in the northern slopes of the Vindhyan hills. Its basin lies between 23°53' and 25°34'N and 75°39' and 76°30'E with a catchment area of 7944 km<sup>2</sup>. It flows in Madhya Pradesh, enters Rajasthan near Binda village in Jhalawar District and flows for about 145 km north in Rajasthan before joining river Chambal near Nonera village in Kota District. The catchment in Rajasthan extends over parts of Jhalawar and Kota Districts.

#### The Parwati

Parwati river originates in the northern slopes of the Vindhyan hills in Madya Pradesh. Its basin lies between 24°19' and 25°51' N and 75°22' and 77°12'E with a catchment area of 5001 km<sup>2</sup>. It enters Rajasthan near Chatarpura village in Baran District, where it forms the boundary between Madhya Pradesh and Rajasthan for about 18 km, then flows for about 83 km in Rajasthan before again forming the boundary between Madhya Pradesh and Rajasthan for a length of about 58 km up to Pali village in Kota District, where it joins the Chambal. The river catchment in Rajasthan is situated in Kota and Jhalawar Districts.

# 5.3.3 Major valley projects in the Chambal river basin

# Gandhi Sagar Dam

This is the first of the four Chambal Valley Projects, located on the Rajasthan-Madhya Pradesh border. It is a 64 m high masonry gravity dam, with a storage capacity of  $6,920 \times 10^6 \text{ m}^3$  and a catchment area of 22,584 km<sup>2</sup>, of which only 1,537 km<sup>2</sup> are in Rajasthan. The hydropower station is located at the dam site and comprises five generating units, four of 23 MW each and one 27 MW capacity. The water released after power generation is utilized for irrigation through Kota Barrage.



Fig. 5.5. Simplified, geological lithologies of the Chambal river catchment.

### Rana Pratap Sagar Dam

Rana Pratap Sagar dam is the second in the series of Chambal Valley Projects, located 52 km downstream of Gandhi Sagar dam across the river Chambal in Rajasthan. It is a straight masonry gravity structure, 54 m high. The powerhouse consists of 4 units of 43 MW each, with firm power generation of 90 MW at 60% load factor. The total catchment area of this dam is 24,864 km<sup>2</sup>, of which only 956 km<sup>2</sup> are in Rajasthan. The free catchment area below Gandhi Sagar dam is 2,280 km<sup>2</sup>. The storage capacity is 1,566 x  $10^6$  m<sup>3</sup>.

## Jawahar Sagar Dam

Jawahar Sagar dam is the third dam in the series of Chambal Valley Projects, located 29 km upstream of Kota city and 26 km downstream of Rana Pratap Sagar dam, across the river Chambal. It is a concrete gravity dam, 45 meter high and 393 m long, generating 60 MW of power with an installed capacity of 3 units of 33 MW. The total catchment area of the dam is 27,195 Km<sup>2</sup>, of which only 1,496 km<sup>2</sup> are in Rajasthan. The free catchment area below Rana Pratap Sagar dam is 2,331 km<sup>2</sup>.

#### Kota Barrage

Kota Barrage is the fourth in the series of Chambal Valley Projects, located about 0.8 km upstream of Kota City in Rajasthan. Water released after power generation at Gandhi Sagar, Rana Pratap Sagar and Jawahar Sagar Dams, is diverted by Kota Barrage for irrigation in Rajasthan and in Madhya Pradesh through canals on the left and the right sides of the river. The total catchment area of Kota Barrage is 27,332 km<sup>2</sup>, of which the free catchment area below Jawahar Sagar Dam is just 137 km<sup>2</sup>. The storage capacity is 99 x 10<sup>6</sup> m<sup>3</sup>. It is an earthfill dam with a concrete spillway. The right and left main canals have a headwork discharge capacity of 188 and 42 m<sup>3</sup> sec<sup>-1</sup> respectively. The total length of the main canals, branches and distribution system is about 2,342 km, serving an area of 229 kha of CCA.



Fig 5.6. Mean monthly variations of (a) maximum temperature (b) minimum temperature and (c) rainfall in the Chambal catchment in the Vindhyan region.


Fig. 5.7. Mean seasonal variation of the water discharge in the Chambal at Kota and Udi (CBPCWP, 1982).

### 5.3.4 Climate of the Chambal river catchment

Temperature data from the meteorological stations, Kota (257 m above mean sea level), Guna (478 m), Ratlam (486 m), Indore (567 m), Mimach (496 m) and Khandwa (318 m), which fall in the Chambal river catchment are plotted in Fig. 5.6. The climate of the area is warm and humid, with a mean annual minimum and maximum temperatures of 32.2° C and 18.9° C respectively. Maximum temperature displays a bimodal distribution, with peaks in summer (May) and spring (October) (Fig. 5.6). The average rainfall is 991 mm in this region with nearly 90% of this rainfall is received during the five monsoon months from June to October about 60% is received in the two months of July & August (Fig. 5.7). The rainfall is heavy in the upper hilly and upper plains areas of the basin. It gradually decreases towards the lower plains and the lower hilly areas and again increases towards the coast and southwestern portions of the basin.

Main crops of the Chambal basin are Wheat, Soya bean, Cotton, Rice and gram. Large-scale urbanization and industrial development brought in its wake the problem of pollution of river water. Length of the Chambal river is 965 km and the area of the catchment is  $1.4 \times 10^5$  km<sup>2</sup>. The mean annual runoff at Udi is 31.4 x  $10^{12}$  L (Rao, 1975; CBPCWP, 1981).

### 5.4 Sample sites, collection and Analytical Methods

# 5.4.1 Sampling of the Chambal and the Yamuna river water and bed sediments

Water and bed sediment samples from Chambal River and its tributaries were collected during September 1998 from 22 locations (Fig. 5.8, Appendix 5.1) and from Yamuna River and its tributaries (Dalai et al., 2002) during October 1998 (post-monsoon) from 33 locations (Fig. 5.9, Appendices 5.2 and 5.3). During subsequent field trips to the Yamuna catchment in June 1999 (summer) and September 1999 (monsoon), mainstream samples were taken above tributary confluences. The sampling was done along the entire stretch of the catchments. A few samples were also collected from the Ganga at Rishikesh (at the foothill of the Himalaya) to compare the results with those for the Yamuna and those reported earlier from this location (Sarin et al., 1989). In addition, water samples were collected from two springs, the Kempti fall, near Mussoorie and the Shahashradhara, near Dehradun (Fig. 5.9). The altitudes of the sampling locations range from ~500 to 2400 m.

Temperature and pH were measured at the sampling sites during summer (June) and monsoon (September) field campaigns. Temperature was measured with a temperature probe (MA Line) with a precision of  $\pm 0.1^{\circ}$ C. A microprocessor based pH meter (Eutech Cybernetics, Model pH Scan2) was used to measure pH with a precision of  $\pm 0.1$  unit. Prior to measurements, the meter was calibrated with freshly prepared buffer solutions using buffer Merck<sup>®</sup> capsules of pH 4, 7, 9.2. For REE, water samples, collected generally from the mid-stream, were filtered through Gelman<sup>®</sup> 0.4 µm filters and collected in acid-washed polyethylene

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bottles that were rinsed several times with distilled, deionized water followed by ambient sample water. These are acidified with  $Ultrex^{\ensuremath{\mathbb{R}}}$  HNO<sub>3</sub> to give pH of 2. For the U isotopes, 10 – 20 L samples were collected in plastic containers and was filtered through 1 µm Gelman<sup>®</sup> cartridge filters. River waters were titrated for alkalinity measurement in the field immediately after collection using 0.005M HCl with Merck<sup>®</sup> mixed indicator.

Bed sediments were collected from water sample sites that were used for the major (AI, Fe, Mn, Mg, Ca, Na and K) and REE analysis of the bulk samples.

### 5.4.2 Analysis of bed sediments

The strategy employed for the analytical methods of sediment and water samples is shown schematically in Fig. 5.10. Sediment samples were placed in a drying oven at 110° C for 24 hours. After drying they were kept in a desiccator until cool, crushed to <60 mesh in the agate martar, mixed well to avoid selective crushing and stored in an airtight vial until analysed. Major elements along with Mn were determined with ICP-AES (Jobin Yvon, JY38S) except Na and K, which were measured with Flame AAS (Perkin Elmer, 4000). The analytical precision  $(1\sigma, n=4)$  was generally better than 5% for all the above elements.

CaCO<sub>3</sub> estimation was done using coulometer (UIC CO<sub>2</sub> coulometer, Model CM5012). CO<sub>2</sub> was evolved from samples through the extraction unit supplied along with the UIC Coulometer by treating nearly 10-60 mg of the sample with 5 ml of 30% H<sub>3</sub>PO<sub>4</sub> at 70° C. CO<sub>2</sub> free air (stripped by passing it through a 50% KOH solution) was used as carrier gas at a rate of 70 mL min<sup>-1</sup> for flushing CO<sub>2</sub> from the system. The liberated CO<sub>2</sub> was flushed by the carrier gas and dried by passing it through a column of activated silica gel and anhydrous MgClO<sub>4</sub> and passed through the coulometer titration cell (with Pt cathode and Ag anode) containing monoethanol amine solution and an indicator. Pure and dried Na<sub>2</sub>CO<sub>3</sub> was used as a standard for calibration. The precision of CaCO<sub>3</sub> measurement by coulometric analysis is better than 1%.



Fig. 5.8. Sampling locations of Chambal river basin.



Fig. 5.9. Sampling locations of the Yamuna river basin. The location numbers are only for the October 1998 collection. The corresponding sample numbers for the other sampling periods are given in Appendix 5.2. and 5.3.

Organic carbon ( $C_{org}$ ) and nitrogen (N) concentrations were measured using an automatic CN analyzer (Fisons Carlo Erba, Model ANA 1400). For the estimation of total carbon and nitrogen, the sediment samples were introduced in small aliquots of 10-30 mg in tin cups through an auto sampler into the combustion tube of the analyzer. The calibration was done using Deer River Black Shale as standard reference material containing 2.53% C and 0.12% N. The average blank concentration measured over a period of the measurement of these samples is  $1.31\pm0.12 \ \mu g$  C. The measurement precision for total carbon is 2.5% estimated by repeat analysis of Deer River Black Shale for several weeks (Sarin et al., 1997). The measurement precision is 8% in the case of total nitrogen concentration greater than 0.1%. The total C content was determined directly in the dried samples. The organic carbon was obtained by difference between the total and inorganic carbon.

REE determination in sediments was done by fusing the sample, dissolving the melt and extracting the REE by using ion exchange chromatography (Cook et al., 1986; Govindaraju and Mevelle, 1987; Djingova and Ivanova, 2002), Towards this, 1 g sample was mixed with 2 g lithium metaborate in a platinum crucible and heated to 850° C overnight. The glassy melt was taken in a 150 mL FPA beaker with 100 mL complexing solution (prepared by mixing 50 g of oxalic acid, 500 mL of 14.5N HCl, 25 mL of  $H_2O_2$  and distilled water to make up the volume to 5 L) and stirred on a magnetic stirrer at 80° C for 5 hours. It should be noted that HF was not used in the dissolution process due to the possible formation of insoluble REE fluorides even in acidic solutions (Cotton and Wilkinson, 1980). The dissolved solution was directly loaded onto Bio-Rad<sup>®</sup> AG50-X8 cation exchange resin column previously conditioned with 1N HCI. After the solution was completely passed, the column was washed with 2N HCl, 30 mL three times, 10 ml H<sub>2</sub>O followed by 15 mL 4N HNO<sub>3</sub>. The REE fraction was eluted with 30 mL 7N HNO<sub>3</sub> four times and the solution is combined and evaporated to almost dryness. The residue was

dissolved with 25 mL of 1N HNO<sub>3</sub> and the solution was stored in 30 mL polypropylene bottles. This solution was directly used for REE assay in the ICP AES (Jobin Yvon, Model JY38S). The REE fraction separation from the sediment for the ICPAES measurement is schematically shown in the Fig. 5.11. The argon plasma was operated with a RF frequency of 40.68 MHz at a forward power of 1200 W. The operating conditions are given in the Table 5.2. The analytical wavelengths selected are the characteristic lines of the elements, which are free of spectral interference. This eliminates the need for corrections of the concentration level of interest. Table 5.3 indicates the relative accuracy of the rare earth element data for the USGS standards by comparison of our values to those reported (Potts et al., 1992). Except Er, other REE in these standards compared well with the reported values. The precision is expressed as a coefficient of variation [(Std. Deviation /mean)\*100]. To obtain these data, 6 separate aliquots of the samples/standards were analyzed. The analytical precision (1 $\sigma$ , n=6) in all samples for all REE was better than 5%. Total procedural blanks for the REE in the solution were below 5% (typically <1%) of measured values in the solution. In many cases the REE concentrations in the blank solution were below detection limit (5 ng  $L^{-1}$ , corresponding to 0.15-0.55 ng g<sup>-1</sup> in the sediment depending on the volume of the solution after ion exchange column purification). Pure REE standards obtained from Johnson-Matthey were used for analytical calibration. Repeat measurements of measured REE of G-2 are plotted against each other (Fig. 5.12a). Dashed line represents 1:1 line, whereas solid lines are best-fit lines of data points. The two lines overlap with each other indicating excellent agreement between duplicates over the entire range of concentrations. Fig. 5.12b shows the comparison of measured and reported (Potts et al., 1992) rare earth elemental concentrations in the reference standards MAG-1, W-2 and G-2. There is an excellent agreement between the measured and reported values within the concentration range of REE.

ICP Spectrometer:	Jobin-Yvon 38S (Sequential mode)
Focal length:	1 m
Halographic grating:	3600 grooves mm <sup>-1</sup>
Resolution:	0.006 nm for Co line at 228.616 nm
Coolant flow:	13 mL min <sup>-1</sup>
Sheath gas flow:	0.3 mL min <sup>-1</sup>
Observation height:	Optimized
Signal integration:	0.75 s
PMT Voltage	700-800 volts
Nebulizer:	V groove
Sample uptake rate:	1 mL min <sup>-1</sup>

 Table 5.2. ICP-AES specification and operating conditions.

Table 5.3. Comparison of the reported and measured values of REEanalysis by ICP AES after column separation in rock standards.

		Wave	Concentration (ppm)						
Element	Ζ	length,	G	-2	MA	G-1	W-2		
		λ	Reported*	Measured	Reported*	Measured	Reported*	Measured	
La	57	398.852	86	86.3	43.9	42.7	11.4	10.5	
Ce	58	418.660	159	155.4	88	85.4	24	21.2	
Nd	60	430.358	53	51.9	38	34.2	14	10.3	
Sm	62	359.260	7.2	8.8	7.5	7.8	3.3	2.9	
Eu	63	381.967	1.4	1.4	1.6	1.5	1.1	1.0	
Gd	64	335.047	4.1	3.5	5.8	5.5	3.6	2.9	
Dy	66	353.170	2.5	2.1	5.2	4.8	3.8	3.2	
Но	67	345.600	0.37	0.44	1.0	0.92	0.76	0.66	
Er	68	390.631	1.2	0.83	3	2.4	2.5	1.8	
Yb	70	328.937	0.78	0.63	2.6	2.5	2.1	1.8	
Lu	71	261.542	0.11	0.11	0.4	0.37	0.33	0.24	

\* Reported values are from Potts et al., 1992.



Fig. 5.10. Analytical scheme for chemical analysis of (a) sediment and (b) water samples



Fig 5.11. Analytical scheme for separation of REE using cation exchange resin from sediments for ICPAES technique.



Fig. 5.12. (a) Repeat measurements of measured REE ( $\mu g g^{-1}$ ) of G-2 are plotted against each other. Dashed line represents 1:1 line, whereas solid lines are best-fit lines of data points. The two lines overlap with each other indicating excellent agreement between duplicates over the entire range of concentrations. (b) Comparison of measured and reported (Potts et al., 1992) rare earth elemental concentrations ( $\mu g g^{-1}$ ) in the reference standards MAG-1, W-2 and G-2.

Further to monitor the accuracy of the analysis independently, a few samples were analyzed for REE by Instrumental neutron activation analysis (INAA). For this, sediment samples were crushed and dried (at 110°C) and sealed in containers suitable for irradiation at CIRUS reactor of the Bhabha Atomic Research Centre, Bombay. The samples were irradiated to a flux of ~10<sup>13</sup> n cm<sup>-2</sup> s<sup>-1</sup> for ~4 days together with USGS standard MAG-1 (Bhandari et al., 1993a and 1993b). The gamma rays subsequently emitted were counted with a 100 cm<sup>3</sup> coaxial high purity germanium (HPGe) detector coupled to an MCA. Prof. N. Bhandari, PRL, provided the above counting facilities. Gamma ray spectra of the irradiated samples and standards were obtained by repeatedly counting at regular intervals of time (up to about 6 weeks after irradiation) and concentrations of REE were determined from the counting data. Typical errors of counting (1 $\sigma$ ) are <3% except for Nd, Gd and Tb for which it is ~12%. The values between the two techniques agreed well (Table 5.4, Fig. 5.13).

In addition to REE, several transition metals (Zn, Pb, Cr, Cd, Cu, Ni and Mn) as well as major constituents of the mineralogical matrix (Fe, Al, Na, K, Ca and Mg) were determined after HCI-HNO<sub>3</sub>-HF acid digestion by ICPAES (Jobin Yvon, Model 38S) and Na and K by FAAS (Perkin Elmer, Model 4000). All results of the analysis of the sediments are quoted as dry weight of the sediment.

### 5.4.3 Analysis of river water

Na and K concentrations in the river waters were measured by flame AAS (Perkin Elmer, Model 4000). Calibration was done using standard solutions prepared in the laboratory by dissolving analytical grade NaCl and KCl salts. The concentrated stock solutions were suitably diluted to bring the concentrations in the linear analytical range. Based on duplicate analysis of a number of samples, the coefficients of variation for various measurements were calculated using the formula:

$$CV(\%) = \left[\frac{1}{2N}\sum\left(\frac{d_i}{x_i}\right)^2\right]^{\frac{1}{2}} \times 100$$

where d<sub>i</sub> is the difference between the duplicates with mean x<sub>i</sub> and N is the total sets of duplicates analyzed. These are 2.2 and 3.1 % for Na and K respectively. Si, Ca and Mg concentrations were measured by ICPAES (Jobin Yvon, Model 38S) in the unacidified and filtered water samples by sequential scanning of emission lines at wavelengths 251.611, 279.806 and 422.673 nm respectively. A few samples of acidified water samples were also measured for Ca and Mg and it was found that there is no measurable difference in the concentration with respect to unacidified samples, implying that no calcite precipitation had taken place after the collection of samples. The laboratory standards for Ca, Mg and Si were prepared by dissolving analytical grade CaCO<sub>3</sub>, pure Mg metal and Na<sub>2</sub>SiF<sub>6</sub> respectively. ICP standards from Merck<sup>®</sup> are also used for checking the calibration curves. Cl, NO<sub>3</sub> and SO<sub>4</sub> in the water samples were measured by Ion Chromatograph (Dionex, Model 2000i/SP). The instrument was calibrated with respect to standard solutions prepared in the laboratory from the respective salts (NaCl, KNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>). Cl, NO<sub>3</sub> and SO<sub>4</sub> were separated on an AS4A column using a mixture of 1.8 mM Na<sub>2</sub>CO<sub>3</sub> and 1.7 mM NaHCO<sub>3</sub> as an eluent. River water samples were analysed at 10 and 30  $\mu$ S scale. The reproducibility of Cl, NO<sub>3</sub> and SO<sub>4</sub> based on repeat runs of samples is  $\sim \pm 5\%$ .

REE in river water samples are measured at SARM Facility, Centre de Recherches Petrographiques et Geochimiques-CNRS, FRANCE by Carignan using SCIEX PE ELAN 6000 ICP-MS coupled with on-line liquid chromatography as the sample introduction system. EI CHROM THRU Spec resin was used for REE preconcentration (Carignan et al., 2000). The total extraction yields (close to 100%) is reproducible within 2-5%. Matrix extraction prior to analysis removes possible isobaric interference, eliminates signal suppression in the plasma and makes preconcentration of elements possible.

Sample code	Technique	Sc	La	Ce	Nd	Sm	Eu	Gd	Tb	Yb	Lu	Ва	Zr
Mag-1	А	-	42.7	85.4	34.2	7.8	1.46	5.5	-	2.53	0.37	-	-
	В	17.5	41.7	88.7	37.0	7.7	1.59	5.3	0.97	2.48	0.37	460	108
RS98-25	А	-	31.2	62.0	23.9	5.3	0.79	3.9	-	2.31	0.28	-	-
	В	9.4	32.1	65.9	26.0	5.4	0.90	5.0	0.79	2.64	0.37	295	99
RS98-26	А	-	67.7	134.5	49.0	11.3	1.13	7.7	-	5.33	0.82	-	-
	В	7.5	59.4	127.4	50.6	9.6	1.16	9.3	1.30	5.58	0.82	210	193
RS98-27	А	-	37.8	75.8	29.3	6.2	0.85	4.5	-	2.90	0.36	-	-
	В	7.5	40.1	82.4	29.4	6.6	0.91	5.0	0.90	2.71	0.39	346	134
RS98-28	A	-	-	-	-	-	-	-	-	-	-	-	-
	В	7.1	34.3	67.6	22.5	5.6	0.80	4.7	0.77	1.94	0.33	285	111
RS98-29	А	-	52.4	105.4	28.9	7.9	0.88	5.5	-	6.20	0.94	-	-
	В	10.2	55.0	106.2	32.6	7.3	0.93	6.2	1.22	6.54	0.74	229	148
RS98-30	Α	-	49.1	94.4	36.2	8.0	1.07	5.3	-	5.10	0.76	-	-
	В	11.4	50.1	99.9	35.5	7.6	1.18	5.2	1.20	5.03	0.78	345	138
RS98-31	A	-	33.9	65.5	27.6	5.9	1.02	4.0	-	2.31	0.34	-	-
	В	10.1	34.2	69.1	24.0	6.0	1.20	4.9	0.81	1.82	0.32	416	135
RS98-32	A	-	41.8	85.2	33.1	6.7	1.01	4.6	-	2.94	0.42	-	-
	В	7.5	51.8	102.4	37.4	8.5	1.29	4.6	1.07	2.65	0.41	321	173
RS98-33	A	-	32.0	63.2	27.3	5.2	0.87	3.6	-	2.24	0.34	-	-
	В	8.1	35.9	72.6	26.9	8.8	1.02	5.7	0.89	3.86	0.52	386	225
RS98-34	A	-	54.8	111.2	41.5	8.7	1.23	6.0	-	4.03	0.60	-	-
	В	9.5	72.5	136.0	51.2	11.7	1.63	6.2	1.47	4.15	0.66	349	365

Table 5.4. Comparison of concentrations (ppm) of REE in the Yamuna riverbed sediment samples measured by ICPAES (A) and INAA (B).



Fig. 5.13. Comparison of concentrations of REE in the Yamuna bed sediment samples measured by ICPAES and INAA techniques.

To measure dissolved U and  $^{234}$ U/ $^{238}$ U activity ratio of the river water samples, ~10 L of river water sample was filtered soon after collection into clean polypropylene containers and acidified with conc. HNO<sub>3</sub> to pH of ~2. This was followed by addition of ~100 mg of Fe carrier (as FeCl<sub>3</sub>) and  $^{232}$ U tracer (1 mL of 9.0±0.16 dpm mL<sup>-1</sup>). The solution was continuously stirred and purged with compressed air to break the uranyl carbonate complex and also to establish tracer equilibrium with river water uranium. After a few hours, the pH was adjusted to 8 by adding concentrated NH<sub>4</sub>OH and U was co-precipitated with Fe(OH)<sub>3</sub>. The U from ferric hydroxide precipitate was separated, purified and assayed by alpha spectrometry following procedures of Krishnaswami and Sarin (1976) and Sarin et al. (1992).

Sample Code	River	рН	Conductivity [10 <sup>2</sup> µmhos]
CH-1	Chamla	8.2	4.8
CH-2	Chambal	9.2	3.4
CH-3	Ghambir	8.15	3.0
CH-4	Shipra	8.4	7.4
CH-5	Kalisindh	8.7	4.4
CH-6	Lakimdar	8.5	4.9
CH-7	Chota Kalisindh	8.4	2.3
CH-8	Newaj	8.2	4.3
CH-9	Dhudhi	8.3	4.1
CH-10	Newaj at Kisangar	8.4	3.95
CH-11	Gherganga	8.5	3.5
CH-12	Chappi	8.4	3.55
CH-13	Ujar	8.6	2.9
CH-14	Kalisindh at Jalawar	8.6	3.9
CH-15	Aav	8.7	3.7
CH-16	Aamjar	8.4	5.4
CH-17	Kalisindh at Kota-Kisankanj Rd.	8.7	3.5
CH-18	Parbati	8.7	3.25
CH-19	Talera	8.2	3.1
CH-20	Gudapachod	8.7	3.5
CH-21	Mangli	8.6	4.6
CH-22	Chambal at Jawahar Sagar Dam	8.4	2.75

Appendix 5.1. Sampling details along with pH and conductivity values of the Chambal river catchment.

Appendix 5.2. Bed sediment and dissolved U sampling details of the Yamuna river catchment. River water. pH of the water samples are also shown.

River	Location	Code	Collection Date	PH <sup>@</sup>
<u>Yamuna n</u>	nainstream			
Yamuna	Hanuman Chatti	RW98-16	10/1998	8.3
		RW99-13	6/1999	8.7
Yamuna	Downstream of Pali Gad Bridge	RW98-20	10/1998	8.4
Yamuna	Barkot	RW98-25	10/1998	8.7
		RW99-19	6/1999	8.9
Yamuna	Kuthnaur village	RW99-17	6/1999	8.5
Yamuna	Upstream of Naugaon	RW98-22	10/1998	8.7
Yamuna	Near Lakhmandal	RW99-18	6/1999	9.2
Yamuna	Downstream of Barni Gad's confluence	RW98-14	10/1998	8.9
		RW99-11	6/1999	9.1
Yamuna	Downstream of Nainbag	RW98-12	10/1998	8.6
Yamuna	Downstream of Aglar's confluence	RW98-9	10/1998	8.7
Yamuna	Upstream of Ton's confluence	RW98-6	10/1998	8.7
		RW99-30	6/1999	
Yamuna	Downstream of Ton's confluence	RW99-31	6/1999	8.4
Yamuna	Rampur Mandi, Paonta sahib	RW98-1	10/1998	8.6
		RW99-2	6/1999	8.6
		RW99-58	9/1999	8.4
Yamuna	Downstream of Bata's confluence	RW98-4	10/1998	8.4
		RW99-5	6/1999	8.9

Yamuna	Yamuna Nagar, Sabarappur	RW98-33	10/1998	8.4
	Ganaranpar	RW99-7	6/1999	8.7
Yamuna	<u> Fributaries</u>			
Didar Gad	Hanuman Chatti- Barkot Road	RW98-18	10/1998	8.0
Pali Gad	Pali Gad Bridge	RW98-19	10/1998	8.4
Barni Gad	Kuwa	RW98-13	10/1998	9.2
Purola	Between Naugaon and Purola	RW98-21	10/1998	8.7
Godu Gad	Purola-Mori Road	RW98-26	10/1998	8.3
Pabar	Upstream of confluence with Tons	RW99-27	6/1999	7.9
Tons	Mori	RW98-27	10/1998	8.1
		RW99-22	6/1999	8.4
Tons	Downstream of Mori	RW98-28	10/1998	7.9
Tons	Before Pabar joins	RW99-26	6/1999	8.0
Tons	Tiuni	RW98-29	10/1998	8.0
Shej Khad	Minas	RW98-31	10/1998	8.6
Tons	Minas, after confluence	RW98-30	10/1998	8.4
		RW99-24	6/1999	8.7
Amlawa	Kalsi-Chakrata Road	RW98-5	10/1998	8.6
Tons	Kalsi, Upstream of confluence	RW98-32	10/1998	8.7
		RW99-29	6/1999	9.0
Aglar	Upstream of Yamuna Bridge	RW98-8	10/1998	8.8
	5	RW99-10	6/1999	
Giri	Rampur Mandi	RW98-2	10/1998	8.4
		RW99-3	6/1999	8.5
Bata	Bata Mandi	RW98-3	10/1998	8.5

		RW99-4	6/1999	8.9
Tons	Tons Pol, Dehradun	RW98-10	10/1998	8.6
Asan	Simla Road Bridge	RW98-11	10/1998	8.3
<u>Ganga</u>				
Ganga	Rishikesh	RW98-34	10/1998	8.6
		RW99-6	6/1999	8.4

—: not measured

# Appendix 5.3. Sampling details along with temperature and pH of the river water samples for REE.

River	Location	Sample code*	Collection Date	Temp. <sup>@</sup> ℃	pH <sup>@</sup>
Yamuna	Rampur Mandi	RW99-2 (RW98-1)	6/1999	21.9	8.6
Giri	Rampur Mandi	RW99-3 (RW98-2)	6/1999	27.8	8.5
Ganga	Rishikesh	RW99-6 (RW98-34)	6/1999	15.7	8.4
Yamuna	Yamunanagar, Saharanpur	RW99-7 (RW98-33)	6/1999	8.2	8.7
Yamuna	Downstream of Barni Gad's confluence	RW99-11 (RW98-14)	6/1999	21.1	9.1
Yamuna	Hanuman Chatti	RW99-13 (RW98-16)	6/1999	10.2	8.7
Yamuna	Kuthanur Village	RW99-17 (RW98-21)	6/1999	15.7	8.5
Yamuna	Rampur Mandi	RW99-58 (RW98-1)	9/1999	20.6	8.4
Ganga	Rishikesh	RW99-59 (RW98-34)	9/1999	18.6	8.4
Spring	Shahashradhara	RW99-60	9/1999	7.1	7.1
Asan	Simla Road Bridge	RW99-61 (RW98-11)	9/1999	27.4	7.9
Tons	Kalsi, Upstream of confluence	RW99-63 (RW98-32)	9/1999	21.3	8.5
Yamuna	Upstream of Ton's confluence	RW99-64 (RW98-6)	9/1999	22.1	8.4

Yamuna	Downstream of Ton's confluence	RW99-31	6/1999	26.9	8.4
Yamuna	Downstream of Aglar's confluence	RW99-51 (RW98-9)	9/1999	18.1	8.6
Aglar	Upstream of Yamuna Bridge	RW99-52 (RW98-8)	9/1999	22.4	8.5
Yamuna	Yamunanagar, Saharanpur	RW99-54 (RW98-33)	9/1999	24.1	8.2
Yamuna	Downstream of Bata's confluence	RW99-55 (RW98-4)	9/1999	27.5	7.7
Giri	Rampur Mandi	RW99-57 (RW98-2)	9/1999	26.6	8.3
Chambal	Upstream of Jawahar Sagar	CH-22	9/1998	-	-

-: not measured.

\* Sample codes given in brackets are the corresponding sediment samples collected during non-monsoon period (October 1998, appendix 5.2).

<sup>@</sup> Temperature and pH data from Dalai (2001).

## **Chapter 6**

REE in the Yamuna and the Chambal rivers

### 6.1 Introduction

Systematic geochemical studies of the river basins provide information on the sources of various chemical elements to the rivers, their fluxes to the oceans, silicate vis-à-vis carbonate weathering rates in the basins and associated atmospheric CO<sub>2</sub> drawdown. There are several studies on the dissolved load of the Ganga-Brahmaputra river system draining the Himalaya (Sarin and Krishnaswami, 1984; Sarin et al., 1989; Krishnaswami et al. 1992; Sarin et al., 1992a; Pande et al., 1994; Ahmad et al., 1998; Galy and France-Lanord, 1999 and 2001; Galy et al., 1999; Dalai et al., 2002; Di-Giovanni et al., 2002). These rivers contribute significantly to the global sediment and water discharge (Milliman and Syvitski, 1992).

In this study, concentrations of REE have been measured in the dissolved and particulate phases of the Chambal and the Yamuna rivers in order to understand the geochemical mobility of REE. Water discharge in the upper reaches of the Yamuna river is influenced by glacier melt waters and weathering and erosion are rapid due to steep gradients. Furthermore, the Yamuna basin near its source is, in general, free from any major anthropogenic sources. In contrast, headwaters of the Chambal river lie in the arid region (precipitation < 100 cm) and the catchment area is characterized by a wide range of land-use activities (intensely farmed agricultural land, urbanized and industrial regions). Major ions in the Chambal river have been measured in this study to characterize its water chemistry. The baseline water quality data helps to understand the weathering of different rock types and the processes responsible for the input and transport of minor elements in the dissolved phase, such as REE and U. The second motive to study major ion chemistry of the Chambal river is to obtain an overview of the weathering regime and to compare it with the Himalayan rivers, viz., Yamuna for which major ion data are available (Dalai, 2001; Dalai et al., 2002).

This chapter is organized in the following manner: data on the dissolved constituents of the rivers viz., major ions and REE are discussed first followed by the corresponding elements in bed sediments.

### 6.2 Major ions and REE in the dissolved phase

### 6.2.1 Major ions in the Chambal river

Concentrations of major cations and anions in the Chambal headwaters have been measured to assess the weathering processes occurring in the Vindhyan region. The Chambal and its tributaries were sampled during post-monsoon (September 1998) season for a synoptic geochemical study when the sub-surface flow is expected to be minimal. Water samples from the Chambal mainstream and its tributaries are alkaline in nature with pH values ranging from 8.15 to 9.2 (Table 6.1). The average temperature of the sampled waters in the basin was ~ 25° C.



Fig. 6.1. Distribution of total dissolved solids (TDS) in rivers and streams of the Chambal river catchment. The TDS range from 181 to 547 mg  $L^{-1}$  with a mean of 322 mg  $L^{-1}$ .

The total dissolved solids (TDS) in the Chambal river range from 181 to 547 mg L<sup>-1</sup> (Table 6.1, Fig. 6.1) corresponding to conductance of these samples are range from 230 to 740  $\mu$ S cm<sup>-1</sup>. Among the major downstream tributaries of the Chambal river, the Chota Kalisindh has the lowest TDS, ~181 mg L<sup>-1</sup>, while the Shipra river has the highest, ~547 mg L<sup>-1</sup>. A large part of the soils in the alluvial plains of the Chambal river system (where the annual rainfall is <100 cm) is impregnated with alkaline and

salinesalts (Bhumbla, 1975; Sarin et al., 1989). Contribution of these salts could be significant to the TDS in the Chambal river. The relationship between the TDS and the conductance of these samples (Fig. 6.2) can be expressed as:

Conductance ( $\mu$ S cm<sup>-1</sup>) = (1.26± 0.02) x TDS (mg L<sup>-1</sup>) – (12.89 ± 5.03) ...(6.1)

(r =0.9715, P < 0.005)

The slope of the regression line in equation [6.1] overlaps with that reported (1.44  $\pm$  0.1) by Sarin et al. (1989) for the Chambal, Betwa, Ken and Son (classified as lowland rivers of the Ganga river); thus indicating that abundance ratios of the dominant ions in the waters draining the Bundelkhand Plateau of the Vindhyan Basin has remained nearly same over 2-3 decades. The mean TDS concentration of ~322 mg L<sup>-1</sup> is ~5 times the global mean of 65 mg L<sup>-1</sup> (Meybeck and Helmer, 1989). For comparison, the average TDS of the Betwa, Ken, Son and Ganga (at Patna) rivers are 388, 241, 116 and 178 mg L<sup>-1</sup> respectively (Sarin et al., 1989). TDS values of the rivers draining the Deccan Traps range from 46 to 136 mg L<sup>-1</sup> (Dessert et al., 2001). The Yamuna river system in the upper reaches has a wide range of TDS, 32 to 620 mg L<sup>-1</sup> (Dalai et al., 2002) with more than 85% of the samples having TDS <300 mg L<sup>-1</sup>.



Fig. 6.2. Plot of conductance against TDS in the Chambal river water samples.

Sample	River	рΗ	Conductivity	Na	Κ	Mg	Ca	HCO <sub>3</sub>	CI	NO <sub>3</sub>	SO <sub>4</sub>	Si	NICB	TDS
Code			[10 <sup>2</sup> µmhos]					μM					%	mg L <sup>-1</sup>
CH-1	Chamla	8.2	4.8	1965	188	518	876	3221	935	138	108	279	9	366
CH-2	Chambal	9.2	3.4	1247	176	424	604	2279	600	-	122	225	10	256
CH-3	Ghambir	8.15	3.0	925	140	366	716	2527	316	14.3	66.6	189	7	248
CH-4	Shipra	8.4	7.4	2455	247	938	1539	4212	1967	281	301	386	8	547
CH-5	Kalisindh	8.7	4.4	892	110	864	1135	3716	436	86.4	97.6	450	11	375
CH-6	Lakimdar	8.5	4.9	1172	94.5	1033	1068	4162	453	83.1	114	550	10	418
CH-7	Chota Kalisindh	8.4	2.3	554	87.5	313	574	1784	239	20.9	61.0	157	10	181
CH-8	Newaj	8.2	4.3	1032	130	757	1008	3766	491	69.4	99.3	343	4	369
CH-9	Dhudhi	8.3	4.1	1164	109	782	749	3171	571	51.4	87.8	479	8	334
CH-10	Newaj at Kisangar	8.4	3.95	999	103	749	863	3270	480	46.8	94.7	418	8	333
CH-11	Gherganga	8.5	3.5	587	46.5	601	1090	3171	271	42.0	53.6	607	11	321
CH-12	Chappi	8.4	3.55	678	57.1	650	1043	3122	294	37.3	57.3	521	13	315
CH-13	Ujar	8.6	2.9	480	75.8	490	896	2725	234	-	41.7	393	9	264
CH-14	Kalisindh at Jalawar	8.6	3.9	859	91	774	951	3072	401	71.3	95.8	454	15	323
CH-15	Aav	8.7	3.7	974	67.6	741	828	3171	332	38.6	80.1	432	11	318
CH-16	Aamjar	8.4	5.4	2398	161	580	973	4063	746	101.0	259	214	4	433
CH-17	Kalisindh at Kota- Kisanganj Rd.	8.7	3.5	735	74.6	630	906	3072	312	55.7	82.4	411	7	306
CH-18	Parbati	8.7	3.25	727	73.4	576	828	2973	267	50.4	60.8	354	5	288
CH-19	Talera	8.2	3.1	719	59.4	473	878	2478	269	63.4	79.5	171	15	248
CH-20	Gudapachod	8.7	3.5	1007	58.2	453	913	2924	387	31.3	92.4	168	7	286
CH-21	Mangli	8.6	4.6	1749	71.1	605	826	3072	802	53.2	187	171	8	338
CH-22	Chambal at Jawahar Sagar Dam	8.4	2.75	785	73.4	399	611	2230	378	-	117	168	1	226

 Table 6.1. Major ion composition of the headwaters of the Chambal river.

- Below detection limit.

	Ν	MINIMUM	MAXIMUM	MEAN
рН	22	8.15	9.2	8.5±0.2
Conductivty	22	2.3	7.4	3.9±1.1
(10 <sup>2</sup> µmhos)				
TDS (mg L <sup>-1</sup> )	22	181	547	322±79
Na (µM)	22	480	2455	1096±558
Κ (μΜ)	22	46.5	247	104±51
Mg (µM)	22	313	1033	624±190
Ca (µM)	22	574	1539	903±209
HCO <sub>3</sub> (μM)	22	1784	4212	3099±627
CI (µM)	22	234	1967	508±377
NO <sub>3</sub> (μM)	19	14.3	281	70±59
SO <sub>4</sub> (μM)	22	41.7	301	107±64
Si (µM)	22	157	607	343±142

Table 6.2. Range and mean concentrations of major ions in samples from headwaters of the Chambal river.

The data on the major ion composition of the Chambal river catchment are given in Table 6.1 and the range and mean concentrations of major ions are given in Table 6.2. Total dissolved cation charge ( $TZ^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$ ) and anion charge ( $TZ^- = CI^- + NO_3^- + HCO_3^- + 2SO_4^{2-}$ ) in the Chambal waters varied from 2416 to 7656 µEq and 2166 to 7062 µEq respectively. For comparison, the world river water average has an estimated  $TZ^+$  of 1200 µEq (Meybeck, 1979). The normalized inorganic charge balance, NICB, defined as ( $TZ^+ - TZ^-$ )/ $TZ^+$ , is reported in Table 6.1. The NICB values range between 1-15% with a mean value of 8.8±3.4%. In majority of the samples, the NICB is within the analytical uncertainties of measurements. The significant deficit of negative charges observed in a few samples (10-15%) can be interpreted in terms of contribution from organic anions such as acetates, oxalates and humic components. The importance of such organic anions in the charge balance of river waters has been reported for tropical rivers such as the Nyong (Viers et al., 2000) and those flowing in the Guayana shield (Edmond et al., 1995). This speculation, however, need to be confirmed through DOC and humic acid measurements. The charge balance between cations  $(TZ^{+})$  and anions  $(TZ^{-})$  in the Chambal basin is:

 $TZ^{+}$  (µEq)= (1.059±0.032) x  $TZ^{-}$  (µEq)+ (140.4±128) ....[6.2]

with a correlation coefficient of 0.991 for 22 data points (Fig. 6.3). Among cations, Na is by far the most abundant (in molar units) and constitutes 35-54% of the total cations. The order of cation abundance in these streams is Na  $\approx$  Ca > Mg > K. This is unlike in the Himalayan rivers, where the cation abundance is Ca > Mg > Na > K. This difference, as discussed later, probably arises from contribution of Na to the Chambal waters from alkaline and saline soils (Sarin et al., 1989). Scatter plots showing relation between major ions in the Chambal waters are shown in Fig. 6.4. K against Na\* (Na corrected for cyclic salt and halite contributions,  $Na^* = Na - CI$ , is plotted in Fig. 6.4d. The halite correction ranged between 31-49% of the Na abundance. In one sample from the Shipra (CH-4), the correction amounts to as high as 80%. These high chloride corrections for Na, as will be discussed in Section 6.2.2, are an indication of its contribution from sources such as saline soils, evaporated precipitation and anthropogenic inputs. K/Na<sup>\*</sup> molar ratios in the Chambal river water range from 0.1 to 0.5 with an average of 0.19 (Fig. 6.4d). The K/Na\* ratios in the Betwa, Ken and Son rivers are 0.003, 0.06 and 0.24 respectively (Sarin et al., 1989). The headwaters of these rivers are in the Deccan Trap basalts, which have K/Na molar ratio of 0.16. Both Na\* and K are high in the upper reaches of the Chambal river and decrease along its course. This could be either due to the presence of Deccan Trap basalts in the headwaters that weather easily compared to other silicate rocks downstream (Chapter 5, Fig. 5.5) or by the effect of adsorption onto clays.

In the Chambal river samples, Ca/(Na+K) equivalent ratio ranges from 1.5 to 3.2. However, in some samples (e.g., CH-1), contribution of Na exceeds that of Ca and Mg (all in equivalent concentrations) and it accounts for as much as 45% of the total cations, due to the weathering of alkaline/saline soils. Among the anions, the abundance decreases as  $HCO_3 > CI > SO_4 > NO_3$ , in the Chambal waters, with  $HCO_3$  constituting 60-90% of the total anions (Fig. 6.5). The largest contribution of dissolved ions to the Chambal river comes from following tributaries: Shipra (CH-4), Kali Sindh (CH-5), Lakimdar (CH-6) and Aamjar (CH-16) (Chapter 5, Fig. 5.7).

On a ternary cation diagram (Mg, Ca, Na+K) the data fall in the central part suggesting that all these ions play similar roles in contributing to cation budget of the rivers sampled (Fig. 6.6a). Anions plot on the mixing line of Alkalinity and Cl+SO<sub>4</sub>, suggesting their contributions from silicate and carbonate weathering and alkaline/saline soil dissolution. (Fig. 6.6b).



Fig. 6. 3. Plot of  $TZ^{\dagger}$  against  $TZ^{-}$ . Most of the points fall on a straight line.



Fig. 6.4. Scatter plots showing relationships between major ions in the Chambal river water samples.



Fig. 6.5. Plot of HCO<sub>3</sub> against total anions ( $\mu$ Eq L<sup>-1</sup>) in the Chambal river samples. The

In majority of the streams,  $(Ca+Mg)/HCO_3$  equivalent ratio ranges between 0.8 and 1.2 suggesting that significant part of the alkalinity can be balanced by Ca and Mg (Fig. 6.4c). This interpretation requires that Na and K abundances in water to be balanced largely by other anions such as Cl, SO<sub>4</sub> and NO<sub>3</sub>. Mg shows an overall positive trend with Ca (Fig. 6.8a). Variations of HCO<sub>3</sub> and Ca/Mg molar ratios in the Chambal river and its various tributaries are shown in Fig. 6.7. One interpretation for this observation is that a significant fraction of Mg and Ca in the rivers are from a common source, weathering of basalts and dolomites/carbonates. The Ca/Mg molar ratio in the Chambal river ranges between 1 and 2 and shows no discernible trend with Ca concentration (Fig. 6.7b). The Betwa, Ken, Son, Ganga and Yamuna river waters have molar ratios in the range of 1.1 to 7.7 (Sarin et al., 1989 and 1992; Dalai et al., 2002). For comparison, reported Ca/Mg molar ratios for the world rivers span a wide range, Yangtze (3.0, Chen et al., 2002), Huanghe (~1.0, Zhang et al., 1995), Mackenzie (1.5 – 7.1, Millot et al., 2003). Factors which can determine Ca/Mg ratios in

the Chambal river are (i) its supply and (ii) behaviour of Ca and Mg in rivers. The sources of Ca and Mg are Deccan Trap basalts and dolomites. Deccan Trap basalts in the catchment region have Ca/Mg molar ratio of ~1.2 (Deshmukh et al., 1996) and their weathering could determine the Ca/Mg molar ratio in the headwaters of the Chambal. The other likely cause for the observed Ca/Mg molar ratios in the Chambal river can be their supply via dissolution of dolomites that constitute a significant portion of the Precambrian carbonates (Ray et al., 2003) in the drainage basin of Chambal. Preferential removal of Ca with respect to Mg from the rivers by precipitation as calcite can also decrease Ca/Mg molar ratio in waters. This mechanism has been proposed by Sarin et al. (1989) for the Ganga water in the plains to account for decreasing Ca/Mg molar ratio along the course and by Jacobson et al. (2002) for the Himalayan rivers in general.

To check on the role of calcite precipitation, the calcite saturation index (CSI), defined as log ([Ca<sup>2+</sup>][HCO<sub>3</sub>-] / K<sub>calcite</sub>), where [] denotes activities, was calculated for the Chambal waters following the procedures of Drever (1988). The calculation shows that the CSI of all samples are > 0, indicating supersaturation with respect to calcite (Fig. 6.8c). This is an indication that part of Ca in these rivers can be removed by calcite precipitation. Most of the bed sediments of the Chambal river have CaCO<sub>3</sub> in the range of 5.1 to 18%; two of the samples, CH-12 and CH-21, however, have much higher CaCO<sub>3</sub>, 44 and 24% respectively (Table 6.11). The origin of these carbonates in the Chambal bed sediments is uncertain but could in part be due to precipitation of calcite from river water. However, the observation that measured Ca and Mg concentrations in unacidified river water samples are nearly identical to those measured in acidified samples (Chapter 5, section 5.4.3) suggests that there is no detectable loss of Ca via precipitation in the laboratory during storage. The lack of nucleation processes and/or presence of precipitation inhibitors (eg. dissolved organic carbon or phosphate) can retard precipitation of calcite (Huh et al., 1998; Dalai et al., 2002). Other reason for lack of precipitation during storage could be the differences in biogeochemical conditions with respect to rivers. Thus based on presently available data, it is not possible to conclusively arrive at the cause(s) for variations in Mg/Ca

molar ratio; it can either be because of input from multiple sources, calcite precipitation or both.



Fig. 6.6. Ternary plots of major cations and anion compositions ( $\mu$ Eq) for the river waters of the Chambal catchment. (a) Cations for most of the samples plot near centre suggesting that all these ions contribute nearly equally to the cation budget. (b) Anions plot on the mixing line of Alkalinity and Cl+SO<sub>4</sub>, suggesting contributions from weathering of basalts and carbonates as well as alkaline/saline soils.



Fig. 6.7. River flow diagram showing  $HCO_3$  ( $\mu$ M) and Ca/Mg molar ratio variations (in parenthesis) downstream of the Chambal river. Only tributaries that are sampled for major ions are shown.



Fig. 6.8. Scatter plot of (a) Mg concentration and (b) Ca/Mg molar ratio against Ca concentration in the Chambal river waters. There is a positive correlation between Ca and Mg. The Ca/Mg ratio shows significant scatter with increasing Ca. (c) Frequency plot of calcite saturation index (CSI). All samples have CSI > 0, suggesting that the river water samples are supersaturated with respect to calcite.

Among anions, the contribution of CI dominates in samples with relatively low  $HCO_3$  content. This increase in CI content is paralleled by a corresponding increase in Na (Fig. 6.9). The concentrations of NO<sub>3</sub> and SO<sub>4</sub> in the upland and lowland streams show large variations with concentrations ranging from 14-281  $\mu$ M and 42–301  $\mu$ M, respectively. Significant inputs of NO<sub>3</sub> in river water can originate from leaching of soils as important soil sources of NO<sub>3</sub> are the oxidation of organic matter and from fertilizer

applications (Meybeck, 1982; Probst, 1985) The waters with relatively high concentrations of NO<sub>3</sub> and SO<sub>4</sub> are also chloride rich. All these anions also correlate positively with concentrations of Na indicative of a common source for them such as saline or alkaline soils (Fig. 6.10) or anthropogenic input. In the Deccan plateau, the Vertisols (deep and medium deep black soils) occur extensively (Bhargava and Bhattacharjee, 1980). They are developed mainly from basalts under semi-arid climate, in which minerals such as NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub> precipitate as noticed in parts of the Chambal command area. This sodification of soils is a characteristic of areas exposed to repeated cycles of wetting and drying where the Na ions and the alkalinity are supplied by silicate weathering and transported by rivers or shallow ground water (Gaillerdet et al., 1999).



Fig. 6.9. Cross-plot of CI and Na. The line indicates relative proportions in marine aerosols.

A plot of  $HCO_3$  against (Na\*+K) shows the data points fall significantly above the 1:1 line (Fig. 6.11a), indicating that other cations (Ca and Mg) are needed to balance  $HCO_3$ . A plot of Mg/Na vs Ca/Na, reveals a linear relationship (Fig. 6.11b) between high Ca/Na, Mg/Na end member being Deccan Trap basalts and the low Ca/Na, Mg/Na
end member being atmospheric deposits, alkaline/saline soils etc. The intensity of weathering of silicates can be gauged from Si/(Na\*+K) ratio, where Na\* = (Na – Cl, halite correction). Si/(Na\*+K) ratios depend on the initial mineral or final weathering product. For example it is 1.7 for weathering of average shield to kaolinite and 3.5 to gibbsite; 1.0 for average shale to kaolinite (Huh et al., 1998). The dissolved Si concentration in the Chambal streams ranges from 157 to 607  $\mu$ M and are similar to those from rivers flowing through the Deccan Traps and Reunion Island rivers (200 to 800  $\mu$ M, Louvat and Allegre, 1997; Dessert et al., 2001). Si/(Na\*+K) molar ratio < 1.2 (Fig. 6.11c) indicates that silicate weathering is only moderate in the Chambal basin. As (Na\*+K) increases, Si shows a decreasing trend. Heterogeneity of lithologies, supply of Na and K from saline and alkaline soils and non-conservative behaviour of Si (loss to diatoms) all can contribute to the lower ratio found in the samples.



Fig. 6.10. Correlation Plots of (a) NO<sub>3</sub> against SO<sub>4</sub> and (b) CI against SO<sub>4</sub> in the Chambal river water samples.



Fig. 6.11. (a)  $HCO_3$  vs (Na\*+K) shows the samples fall above 1:1 line. (b) Mg/Na vs Ca/Na, showing a linear relationship with high Ca/Na, Mg/Na end member being Deccan Trap basalts and the low Ca/Na, Mg/Na end member being atmospheric deposits, saline soils etc. (c) Si vs (Na\*+K), Na\*=Na – Cl. Lines indicate ratios expected for average shield weathering to gibbsite (3.5) and average shale weathering to kaolinite (1.0) assuming no quartz dissolution (Stallard and Edmond, 1983).

#### 6.2.2 Sources of major ions in the Chambal river

Major ions are supplied to rivers via atmospheric deposition, chemical weathering of various lithologies in the basin and anthropogenic sources. The dissolved concentrations of major ions and their ratios in the Chambal river are used to constrain contributions from various sources and to derive silicate and carbonate weathering rates. The impact of atmospheric deposition on dissolved load can be calculated from the chemical composition of rain in the region. Available rainwater data in this region is shown in the Table 6.3. Generally sea-salt aerosols and atmospheric dust are the dominant sources of major ions to rain. Na has another important source in addition to seawater viz. continental dust, which is responsible for the lower Na/CI molar ratio of rain of the interior part of India compared with that in the seawater (0.86). The average CI concentration in rainwater is 79  $\mu$ M compared to 508  $\mu$ M in rivers (Table 6.2). Rainwater contribution of CI to the Chambal river on average is < 15%; the contribution, however, would vary from the mean for individual rivers depending on local rain and river water CI. The contribution of Na to river waters from atmospheric deposition can be estimated from Na/CI ratios in rain which is ~0.5 (Table 6.3). Using this value, the Na contribution from atmospheric deposition is <5% of its river concentration. K concentration in rains is  $\sim 20 \ \mu$ M and this is  $\sim 15\%$  of its abundance in the river waters. Ca and Mg in rainwater are negligibly small ( $\sim$ 5%) to be of any significance to their river water budget. It is seen from the above, that most of it in the Chambal has to be derived from sources other than precipitation. Potential sources are (i) alkaline/saline soils and halites (ii) anthropogenic inputs (iii) evaporated precipitation and groundwater. As the samples were collected during peak monsoon (September), the river stage is high and hence groundwater input and evaporated precipitation are less likely to contribute to major ion budget. Alkaline/saline soils are reported in the basin and their dissolution and/or anthropogenic inputs are the additional sources of CI to the drainage basin. Major ion compositions at two locations (CH-20 and CH-22) of the present study are compared with the reported average major ion concentrations for the water samples collected during 1973-76 at the same locations (Rawal, 1978). They are same within the analytical uncertainties of measurements and hence anthropogenic input and

land use change have not altered the river water composition for the past few decades. As will be discussed later, deriving cation contribution from silicate weathering is based on Si concentration in the river and its contribution from anthropogenic sources is small. Sarin et al. (1989) reported Si concentration at Dholpur of 296  $\mu$ M (during September 1982) and a sample close to this location has Si content of 411  $\mu$ M (September 1998). Considering that these two samples are not from the same location and the differences in monsoon intensity and seasonal changes in rainfall during the years sampled, there is no significant anthropogenic input of Si to the Chambal river system over the past two decades.

Components	Agra <sup>a</sup>	Kalyan <sup>♭</sup>	Delhi <sup>c</sup>	Karba <sup>d</sup>
PH	7.01	5.7	5.4	4.8
CI	31.8	112	140	31.8
SO4	18.2	54.2	45	107
Na	18.4	103	81.7	20.7
Κ	7.6	26.1	44.3	3.7
Са	28.1	46.5	67	91.5
Mg	22.8	19.5	34.8	21.4

Table 6.3. Average concentration of major ions in rainwater ( $\mu$ M).

<sup>a</sup> Kumar et al., 2002

<sup>b</sup> Khemani et al., 1989

<sup>c</sup> Ravichandran and Padmanabhamurthy, 1994 <sup>d</sup> Chandrawanshi et al., 1997

# 6.2.2.1 Silicate weathering

Silicate weathering in river basins is generally estimated using suitable proxies. Na\*, (Na\* = Na - Cl), is a commonly used proxy in rivers. Rivers receive Na from precipitation and rock weathering in the river basin. The contribution of Na to rivers from atmospheric deposition, as shown in section 6.2.2, is < 5%. The balance, therefore, has to be derived from the drainage basin from weathering of halites/saline soils and silicates. The contribution from halites and NaCl component of saline soils can be estimated from Cl content of rivers in excess of that in precipitation. The relevant relations are:

Na<sub>atm</sub> = Cl<sub>atm</sub> x (Na/Cl)<sub>rain</sub> Na<sub>halite/ss</sub> = Cl<sub>r</sub>-Cl<sub>atm</sub> where subscripts atm, halite/ss refer atmosphere and halites and saline soil respectively. As  $CI_r$  is >>  $CI_{atm}$ , as an approximation, correction for  $Na_{atm}$  and  $Na_{halite/ss}$  have been made assuming it be equivalent to measured CI in river. Thus,

 $Na_s = Na_r - CI_r$  and  $K_s = K_r$ 

where the subscripts s and r refer to silicate and river respectively. Rivers derive their Mg from carbonates and silicates whereas Ca from carbonates, evaporites and silicates. The silicate component of Ca and Mg can be derived as:

 $Ca_s = Na_s \times (Ca/Na)_{sol}$  $Mg_s = Na_s \times (Mg/Na)_{sol}$ 

where (Ca/Na)<sub>sol</sub> and (Mg/Na)<sub>sol</sub> denotes ratios with which these elements are released to rivers from silicates. These ratios are taken to be in the same ratios as in the Deccan Trap basalts. For the Chambal river, a significant correlation exists between Ca/Na and Mg/Na ratios (Fig. 6. 11.b), indicating a mixing between two end members one with high Ca/Na and Mg/Na and the other with low Ca/Na and Mg/Na. The high Ca/Na, Mg/Na end member may be Deccan Trap basalts and carbonates and the low Ca/Na, Mg/Na end member may possibly be atmospheric precipitation, saline soils etc.

Assigning values for  $(Ca/Na)_{sol}$  and  $(Mg/Na)_{sol}$  are crucial for the correct estimation of Ca<sub>s</sub> and Mg<sub>s</sub>. The parent rocks in the Chambal drainage area are basalts and their Ca/Na and Mg/Na molar ratios of 2.26 and 1.90 respectively (Subbarao et al., 2000). Assuming that Ca, Mg and Na are released to water in the same ratio as in basalts, the Ca<sub>s</sub> and Mg<sub>s</sub> are calculated. The results show that Ca<sub>s</sub> and Mg<sub>s</sub> in many samples far exceed the Ca and Mg measured in water. This may be due to several reasons or the combination of them: (i) the calculated Na<sub>s</sub> is not entirely from silicate weathering. There can be other sources such as Na<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub> from alkaline/saline soils. (ii) The assumption that these ions are released in the ratio same as that in basalt may not be valid. Ca, Mg and Na may be released to water incongruently (iii) removal of Ca from water by calcite precipitation. It is difficult to isolate the impact of these causes in attributing to the discrepancy between calculated and observed Ca. The results of Mg also show similar trend as Ca. If calcite precipitation is a significant factor, it would affect Ca more significantly than Mg, as the partition coefficient for Mg in calcite precipitation is 0.03 (Huang and Fairchild, 2001). These constraints make it difficult to calculate the silicate cation fraction in the Chambal basin reliably by this approach. Of the 22 samples analyzed, five samples (CH-4, 5, 11, 12 and 13) have  $Ca_s < Ca_r$ . However in these samples Mg<sub>s</sub> are always greater than Mg<sub>r</sub>.

The above calculation also prompts to think in terms of fractionation of Ca, Mg and Na during weathering; the (Ca/Na)<sub>sol</sub> and (Mg/Na)<sub>sol</sub> ratios being less than the corresponding abundance ratio in basalts. Louvat and Allegre (1997) had used such an approach to derive solute components of major ions in rivers of Reunion. The problem in such an approach is in fixing the appropriate (Ca/Na)<sub>sol</sub> and (Mg/Na)<sub>sol</sub> ratios. It is equally possible that the use of Na<sub>s</sub> for normalizing may be incorrect; as the calculated Na<sub>s</sub> (Na<sub>s</sub>=Na<sub>r</sub>-Cl<sub>r</sub>) may have contributions from the dissolution of evaporites (Na<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>) in the Chambal catchment area. Thus the resolution of measured major ion concentration with its various components based on Na<sub>s</sub> as index is not promising in this basin. Use of Ca and Mg also are fraught with similar problems because of the multiple sources and their potential non-conservative behaviour in the rivers.

Mineral	Formula Wt.	Na	κ	Mg	Са	SiO <sub>2</sub>	HCO₃
Albite NaAlSi <sub>3</sub> O <sub>8</sub>	262.2	1	0	0	0	2	1
Anorthite CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	278.1	0	0	0	1	0	2
Pyroxene CaMgFeAl <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	450.3	0	0	1	1	1	4
Diopside CaMg(SiO <sub>3</sub> ) <sub>2</sub>	216.5	0	0	1	1	2	4

Table 6.4. Number of moles of ions released into solution per mole of mineral in the presence of  $CO_2$  (Faure, 1991).

The uncertainties discussed above in deriving the cation fraction from silicate weathering prompted to explore the use of Si to derive silicate-weathering rates in the Chambal basin. The problem in the case is to know the cation/Si ratios being

weathered. Based on abundances of these elements in various minerals, the following working values are used for calculating silicate weathering using Si as an index.

Assuming Deccan Trap basalts have on an average 30% albite, ~5% orthoclase, <5% olivine, 30% anorthite, 25% pyroxene and 15% diopsode (Deshmukh et al., 1996; Sen, 2001) and by taking the number of moles released into solution per mole of mineral (Faure, 1991; Table 6.4), the following (major ions)/SiO<sub>2</sub> molar ratios of can be obtained:  $HCO_3/SiO_2 = 2.24$ ,  $Ca/SiO_2=0.55$ ,  $Mg/SiO_2 = 0.30$  and  $Na/SiO_2=0.27$ . Using these molar ratios and the dissolved Si concentration in the Chambal river water samples, fraction of cation contribution from the Deccan Trap basalts can be estimated.

$$(X_{i})_{s} = \left[ \left( \frac{X_{i}}{Si} \right)_{sol} \right] \times Si$$
  

$$f cat_{s} = \frac{\sum(X_{i})_{s}}{\sum(X_{i})_{r}} = \frac{Na_{s} + K_{r} + Ca_{s} + Mg_{s}}{Na_{r} + K_{r} + Mg_{r} + Ca_{r}}$$
....6.3

where  $\left(\frac{X_i}{Si}\right)_{sol}$  is the ratio of major cations/Si released to the rivers from silicates (basalts). The estimated fraction of cation contribution from Deccan Basalts is 10.7 – 35.4% with a mean of (22.3±6.4) % (Table 6.5). This calculation assumes that cation/Si ratio released to waters is the same as that are in basalts and that Si behaves conservatively in water. The validity of these assumptions is currently uncertain. If Si is removed from water and/or if cations are released preferentially over Si from silicates, then the estimated cation contributions from silicate weathering are lower limits.

#### 6.2.2.2 Carbonate weathering

Precambrian carbonates, which are widely exposed in the Chambal drainage basin, are composed of both calcites and dolomites (Ghosh, 1976; Ray et al., 2003; Subbarao, Personal communication, 2003). Considering that carbonates can be weathered more easily than silicates, they are also expected to contribute significantly to the major ion budget of the Chambal river. Carbonate contribution of Ca and Mg to the cations of the Chambal river can be derived as:

$$fcat_{c} = \frac{\sum(X_{i})_{c}}{\sum(X_{i})_{r}} = \frac{Ca_{r} - (Ca_{s} + Ca_{e}) + (Mg_{r} - Mg_{s})}{Na_{r} + K_{r} + Mg_{r} + Ca_{r}} \qquad \dots 6.4$$

where e denotes evaporite. The reliability of calculated  $fcat_c$  depends initially on how well Ca<sub>s</sub> and Ca<sub>e</sub> can be constrained. Assuming all SO<sub>4</sub> to be evaporite origin, the calculated  $fcat_c$  ranges from 9.8 to 64.3% with a mean of (41±16) % (Table 6.5). This is a lower limit of the carbonate contribution. Here Ca<sub>s</sub> and Mg<sub>s</sub> fractions are calculated using the Ca/Na and Mg/Na ratio in the silicate rocks as 0.7 and 0.3. On the other hand, if the Ca<sub>s</sub> and Mg<sub>s</sub> are calculated using the Ca/Si and Mg/Si molar ratios derived for the Deccan Basalts and substituted to the above equation [6.4], then,  $fcat_c$  ranges from 33.0 to 60.5 % with a mean of (51.3±7.1) % (Table 6.5). Knowing the cation fractions from silicate and carbonate weathering, which do not add up to 100%, the remaining fraction is attributed due to the weathering of alkaline/saline soils and evaporites (10 - 55 %). The sample from Aamjar (CH-16) has the highest Na and the corresponding calculated fraction of saline/alkaline soil contribution of cations 55%.

Table 6.5. Silicate and carbonate contributions of total cations to the Chambal river.

Method	f cat <sub>s</sub>	f cat <sub>c</sub>
Using Ca/Si=0.55 and Mg/Si=0.3	10.7-35.4%	33-60.5%
	(22.3±6.4)%	(51.3±7.1)%

In summary, the chemistry of the Chambal river is dictated by several inputs; such as chemical weathering of Deccan Basalts, dissolution of carbonate + evaporite and saline/alkali soils with minor supply from atmospheric deposition. The system is complex to quantitatively discern the contribution from each of these sources, however based on likely assumptions and end member values; constraints have been placed on their contribution.

#### 6.2.2.3 Weathering rates and CO<sub>2</sub> consumption rates

Data on silicate and carbonate components of cations and silica concentrations in rivers coupled with the drainage area and water discharge rates provide silicate and carbonate weathering rates in the basin. The silicate and carbonate weathering rates are calculated using the following equations:

^

$$SWR = (M_{NA} \times Na_{s} + M_{K} \times K_{s} + M_{Ca} \times Ca_{s} + M_{Mg} \times Mg_{s} + M_{SiO_{2}} \times Si) \times \frac{Q}{A}$$
$$CDR = (M_{Ca} \times Ca_{c} + M_{Mg} \times Mg_{c} + M_{CO_{3}} \times (Ca_{c} + Mg_{c}) \times \frac{Q}{A} \qquad \dots \dots 6.5$$

where Na<sub>s</sub>, K<sub>s</sub>, Ca<sub>s</sub>, Mg<sub>s</sub> are the molar concentrations from silicate weathering obtained by multiplying expected (major ion)/Si molar ratio in the Deccan Trap basalt with dissolved Si molar concentration in the river waters. These concentrations and silica (Si) are multiplied by respective atomic/molecular weights  $(M_{\chi_i})$  of the above ions to get the abundance of silicate fraction. This is multiplied by runoff (water discharge, Q/ drainage area, A) to obtain the silicate weathering rate (SWR). A similar procedure is followed to obtain carbonate weathering rate (CWR). The SWR and CWR are calculated to be 1.4 x  $10^3$  and 5.1 x  $10^3$  kg km<sup>-2</sup> y<sup>-1</sup> (Table 6.6) using the annual water discharge value at Kota (Chapter 5, Fig. 5.7) and based on major ion composition of the Chambal river at Jawahar Sagar dam (CH-22). This is a lower limit for the Chambal basin as the water discharge is restricted due to damming. A number of medium and large-scale irrigation projects based on storage and diversion of water withdraw water from the Chambal river (CBPCWP, 1982). On the other hand, Udi (26°42'N, 78°56'E), located after the Ganga Sagar Dam, integrates the catchment area of the Chambal and its tributaries, Kali Sindh, Newaj and Parbati. Using average silicate cations (Nas, Ks, Ca<sub>s</sub>, Mg<sub>s</sub>) and silica (all in mg  $L^{-1}$ ) of the Chambal river, 36.8 mg  $L^{-1}$  and the annual discharge at Udi, the SWR of Chambal basin is 7.9 x 10<sup>3</sup> kg km<sup>-2</sup> y<sup>-1</sup> (Table 6.6). This value is about 4 times less than that of the Yamuna river at Batamandi (Dalai et al., 2002). The difference is mainly due to the high runoff and relief in the Yamuna basin of the Himalaya (Dalai et al., 2002). This is in spite of the fact that the headwaters of the Chambal are at the Deccan Trap, which are more easily weatherable compared to granites of the Yamuna headwaters (Dessert et al., 2001; Das et al., 2003, In

preparation). The CWR calculated at Udi is 22.6 x  $10^3$  kg km<sup>-2</sup> y<sup>-1</sup>. This is lower by a factor of 5 compared to the Yamuna river. This is again due to the difference in the runoff and relief of the two basins.

The flux of CO<sub>2</sub> consumed during silicate weathering ( $\Phi$ CO<sub>2</sub>, in moles km<sup>-2</sup> y<sup>-1</sup>) in the Chambal basin, estimated from the calculated silicate cations, river discharge and the basin area: ( $\Phi$ CO<sub>2</sub>)=( $\Phi$ TZ<sup>+</sup><sub>sil</sub>); gives a value of ( $\Phi$ CO<sub>2</sub>) ~0.30 x10<sup>5</sup> moles km<sup>-2</sup> y<sup>-1</sup> at Kota for the sample CH-22 where TZ<sup>+</sup><sub>sil</sub> = 404 µEq. By taking the average TZ<sup>+</sup><sub>sil</sub> of the Chambal river samples, 780 µEq and the discharge value at Udi, CO<sub>2</sub> consumption rate,  $\Phi$ CO<sub>2</sub> is 1.7 x 10<sup>5</sup> moles km<sup>-2</sup> y<sup>-1</sup>. This is lower by a factor of 3 compared to that measured for the Yamuna river at Batamandi.

River	Water Discharge 10 <sup>12</sup> L y <sup>-1</sup>	Area 10 <sup>3</sup> km <sup>2</sup>	SW	R <sup>a</sup>	CWF	R <sup>a</sup>	CO <sub>2</sub> drawdown <sup>b</sup>
Chambal @Kota	2.2	30	(i) 1.4	(ii) 0.54	(i) 5.1	(ii) 1.9	0.30
Chambal @Udi	30	139	7.9	3.1	22.6	8.4	1.7
Alaknanda <sup>c</sup> @Bhagwan	14.1	11.8	10.2	3.9	63.2	23.4	3.6
Bhagirathi <sup>c</sup> @Devprayag	8.3	7.8	15.2	5.8	41.1	15.2	4.1
Ganga <sup>c</sup> @Rishikesh	22.4	19.6	12.9	4.9	51.7	19.1	2-3
G-B	1002	1555	13.6	5.3	31.7	11.7	3.3
Yamuna <sup>d</sup> @Batamandi	10.8	9.6	25-28	10	115-123	43-46	4-7

Table 6.6. Weathering rates and CO<sub>2</sub> consumption in the Chambal river basin and other river basins in the Himalaya.

<sup>a</sup> Calculated using the mean density 2.6 and 2.7 g cm<sup>3</sup> for silicates and carbonates respectively. (i):  $10^3$  kg km<sup>-2</sup> y<sup>-1</sup>; (ii) : mm ky<sup>-1</sup>.

<sup>b</sup> Drawdown via silicate weathering in 10<sup>5</sup> moles km<sup>-2</sup> y<sup>-1</sup>.

<sup>c</sup> Krishnaswami et al., 1999.

<sup>d</sup> Dalai et al., 2002.

## 6.2.3 REE river water chemistry

The dissolved concentrations of individual REE and total REE ( $\Sigma$ REE), Ce, Eu and Gd anomalies in river water samples are given in Tables 6.7 and 6.8. The concentration ranges along with mean values are presented in Table 6.9. The pH values of these samples varied from 7.1 to 9.1 (Table 5.2). In general, pH controls both the absolute abundance of REE in dissolved phase and their relative REE patterns. Higher pH values in river waters result in lower concentrations and more fractionated composition relative to local rocks in the catchment (Sholkovitz, 1995).

In river water samples analyzed in this study, the concentrations of REE follow the order: Ce > Nd, La > Pr, Sm, Gd, Dy > Eu, Er, Yb > Tb, Ho, Tm, Lu.  $\Sigma$ REE varied from 87 ng L<sup>-1</sup> (Giri river at Rampur Mandi, RW99-3) to 1374 ng L<sup>-1</sup> (Yamuna after the confluence of Bata, RW99-55). REE concentrations vary widely in samples collected in the Yamuna and its tributaries. For example, La concentration ranges from 15 to 267 ng L<sup>-1</sup>. These values are higher than typical REE concentrations reported for temperate rivers (eg. Mississippi river, 10 ng L<sup>-1</sup> of La, Sholkovitz, 1995; Shiller, 2002). The REE abundance in river waters is controlled by weathering of major and accessory minerals, many of the latter containing high concentrations of REE. Further, the solute-particle interaction in rivers such as ion exchange and absorption on surface coatings also control the REE abundances. In felsic rocks, HREE become more leachable with increasing alteration. In basalts with high fractions of glassy components, the leachablility of HREE is lower than in basalts with better crystallinity (Moller et al., 2003).

The individual dissolved REE concentrations in the Yamuna river do not show any discernible relationship with both  $\Sigma$ REE and the TDS (Fig. 6.12). This lack of correlation with TDS seems to indicate that either the dissolved REE concentrations in these waters are not a simple function of chemical weathering of the drainage basin, which dictates TDS content or that they are having multiple end members, viz. aluminosilicate minerals, hydrous oxide phases (acting both as source and sink) and

minerals. Alternately, the REE are released to river water either heavv disproportionately to the major ions from this basin, a likely inference considering REE are more abundant in resistant accessory phases or that they are sequestered onto various particulate phases after their release. Likewise, the weak correlation of individual REE with  $\Sigma$ REE reflects their geochemical behaviour in the aqueous phase. Shale-normalized ratios (shale is Post-Archaean Australian shale, PAAS, REE concentrations from McLennan, 1989) of light-to-heavy REE (LREE/HREE) in the dissolved phase of the Yamuna river can shed light on the fractionation of these elements during weathering and transport. A ratio of 1 indicates similar mobilization of these two groups of elements relative to shale. A ratio less than 1 suggests a lower degree of mobilization of the LREE to dissolved phase. The shale-normalized ratio of LREE/HREE in Yamuna water samples varied from 0.27 to 0.77 with an average value of 0.55 (Table 6.9), suggesting that in these waters, HREE is preferentially mobilized over LREE. The shale-normalized patterns of the Yamuna water samples are plotted in Fig. 6.13.



Fig. 6.12. (a)  $\Sigma REE$  (ng L<sup>-1</sup>) vs. TDS (ng L<sup>-1</sup>) (b) La (ng L<sup>-1</sup>) vs. TDS (ng L<sup>-1</sup>) in the Yamuna water samples. The poor correlation between either  $\Sigma REE$  or the individual dissolved REE concentrations and the TDS indicate that either release and transport of REE and TDS are not a simple function of chemical weathering of major lithologies or that they are having multiple end members viz. aluminosilicate minerals, hydrous oxide phases and heavy minerals.

The average REE pattern normalized to PAAS for the river water samples is compared with that of the bed sediments in Fig. 6.14. It is important to point out here that the REE concentrations in the dissolved phase are 5-6 orders of magnitude lower than those in sediments (Fig. 6.14). Hence even a very minor release of REE from sediments is adequate to account for their measured concentration in river water. The data in Fig. 6.15 show pronounced middle REE enrichment in the river water samples from the Yamuna (RW99-51, RW99-55 and RW99-58), the Tons (RW99-63), the Asan (RW99-61) and the Giri (RW99-57) rivers. This enrichment is seen as a hump in the shale-normalized ratios of REE towards the middle of the REE series (MREE, Nd - Gd). Such MREE enrichment is typical of phosphates (Johannesson et al., 1996; Weber et al., 1998). The behaviour of the REE during weathering and transport of a parent material is a function of many parameters including (1) the abundance and distribution of mineral phases containing REE in the rocks and sediments of the basin, (2) the stability of these REE bearing mineral phases with respect to the aqueous fluids involved in the weathering reactions, (3) the chemistry of the aqueous fluids (eg., pH, eH, concentrations of inorganic and organic complexing ligands and (4) adsorptiondesorption reactions of REE with solid surfaces.

A comparison of the composition of the Yamuna river water and bed sediments (Fig. 6.15) suggests that dissolved composition of REE is strongly fractionated and is enriched in MREE with respect to sediments. Such trends observed in the Amazon, Fly and Sebik rivers have been attributed by Hannigan and Sholkovitz (2001) to preferential dissolution of more soluble mineral phases such as phosphates (which are enriched in MREE) during weathering processes. Phosphate minerals are enriched in bulk REE concentrations as they substitute for Ca in the apatite lattice (Wright et al., 1987). Apatite,  $(Ca_5(PO_4)_3(OH, F, Cl)_2)$ , is a common accessory phase in metamorphic rocks in a wide range of geological settings and is a relatively common component of the heavy mineral assemblages. Banfield and Eggleton (1989) reported REE mobilization and fractionation resulting from the dissolution of apatite on small scale during weathering of granite. The high Himalayan Crystalline Series is an ~100 m wide

belt of leucogranites that extends across the Himalaya (Ayres and Harris, 1997) which contain apatite. While assessing the role of various lithologies in contributing to Sr budget and its isotopic composition of the Yamuna river, Dalai et al. (2003) pointed out the significance of minor phases such as calc-silicates, calcites and apatites of the Yamuna basin in contributing dissolved Sr to rivers. Apatites are enriched in Sr, U and REE and their weathering can provide these elements to the dissolved phase.

The Yamuna water samples show negative Eu anomalies. Chondrite-normalized Eu/Eu\* ratios vary between 0.49 and 0.73 (Table 6.9, Fig. 6.15). Normally Eu depletion in the upper continental crust is due to chemical fractionation within the continental crust, related to production of granites with negative Eu anomalies (Taylor and McLennan, 1985). By and large sedimentary rocks as well as river and seawater (Martin et al., 1976; Elderfield, 1988) are characterized by Eu depletion.

In case of Ce, about 60% of the samples in the Yamuna river system have chondrite-normalized Ce/Ce\* ratios from 0.90 to 1.03 indicating the lack of measurable anomalies in them. Eight of the 19 samples have Ce/Ce\* in the range of 0.25-0.86 (Table 6.8, Fig. 6.15). These samples are from the Yamuna (RW99-13, RW99-17, RW99-51 and RW99-54, RW99-64), the Ganga (RW99-59) and the Aglar (RW99-52) rivers. The Yamuna river sample at Rampur Mandi (RW99-58) shows the positive Ce anomaly value of 1.16 and the spring sample from Shahashradhara (RW99-60) has the negative Ce anomaly value of 0.25. The development of negative Ce anomalies in waters is strongly pH dependent and is observed mainly in alkaline rivers (Elderfield et al., 1990; Nelson et al., 2003). In the Connecticut River waters, Sholkovitz (1992 and 1995) showed that the colloidal pool is preferentially enriched in Ce, leaving the solution phase with a negative Ce anomaly. More work is required to identify the cause(s) for the observed Ce anomaly in the Yamuna river system.

Sample Code	River	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
RW99-2	Yamuna	Rampur Mandi	18.4	40.8	4.8	22.3	5.0	-	4.8	0.9	3.7	0.9	2.4	0.4	1.5	-
RW99-3	Giri	Rampur Mandi	15.0	35.4	2.3	18.3	4.1	-	4.7	-	3.0	0.5	1.3	0.3	1.4	-
RW99-6	Ganga	Rishikesh	61.0	127	17.9	69.2	16.5	3.6	16.9	2.5	12.3	2.4	6.9	1.1	4.1	0.6
RW99-7	Yamuna	Yamunanagar, Saharanpur	45.2	91.7	11.7	50.2	12.3	2.9	14.0	1.9	10.3	2.2	7.5	0.8	5.7	0.7
RW99-11	Yamuna	Downstream of Barni Gad's	43.4	85.7	11.6	44.9	11.9	2.7	12.2	1.5	11.8	2.1	5.2	0.7	4.2	0.8
	Vanaviaa	confluence	40 5	40.0	<b>F C</b>	04.4	0.0		~ ~ ~	10	7.0	4 5	4.0	0.5	2 5	0.7
RVV99-13	ramuna	Hanuman Chatti	16.5	13.8	5.0	24.1	6.3	-	6.9	1.0	0.1	1.5	4.3	0.5	3.5	0.7
RW99-17	Yamuna	Kuthanur Village	39.0	64.0	7.2	39.0	9.1	-	9.5	1.3	8.6	1.6	5.0	0.9	4.8	1.0
RW99-31	Yamuna	Downstream of Ton's confluence	49.1	107	9.2	46.8	11.9	2.6	13.4	2.2	11.3	2.2	5.7	0.8	5.9	1.0
RW99-51	Yamuna	Downstream of Aglar's confluence	98.2	179	19.4	91.5	23.9	4.9	23.0	3.8	20.9	3.9	11.1	1.6	8.8	1.9
RW99-52	Aglar	Upstream of Yamuna Bridge	26.6	39.8	5.6	24.4	6.2	-	6.2	1.2	5.9	1.5	4.0	0.5	3.3	-
RW99-54	Yamuna	Yamunanagar,	60.0	116	13.8	62.2	16.4	3.7	15.3	2.5	14.6	2.5	7.5	0.9	5.7	0.9

Table 6.7. Dissolved REE concentrations (ng L<sup>-1</sup>) of the Yamuna river and its tributaries. Detection limit for the measurement of REE using LC-ICPMS is given in the last row.

		Saharanpur														
		Downstream of														
RW99-55	Yamuna	Bata's	267	558	64.9	253	58.3	9.8	55.9	8.0	43.6	7.9	23.1	3.1	19.1	3.0
		confluence														
RW99-57	Giri	Rampur Mandi	96.6	200	24.2	101	26.3	4.7	27.4	4.0	26.8	5.1	12.3	1.8	9.6	1.6
RW99-58	Yamuna	Rampur Mandi	97.5	250	25.5	103	27.0	5.2	32.0	4.2	28.0	4.7	13.0	2.2	10.8	1.5
RW99-59	Ganga	Rishikesh	30.4	58.9	8.6	34.8	10.9	2.0	14.1	2.3	13.1	2.5	5.8	0.5	4.3	0.7
RW99-60	Spring	Shahashradhara	78.2	38.8	11.0	43.9	6.8	2.0	10.3	1.6	8.9	2.2	6.6	0.5	3.6	0.5
RW99-61	Asan	Simla Road Bridge	179	411	49.7	194	46.1	10.6	54.9	8.4	44.8	9.2	25.5	3.0	21.3	2.8
RW99-63	Tons	Kalsi, Upstream of confluence	244	551	64.8	253	60.6	11.9	61.0	8.6	50.5	9.1	27.9	4.2	21.3	3.0
		Upstream of														
RW99-64	Yamuna	Ton's	22.2	40.1	5.6	22.1	5.0	-	5.2	-	5.1	0.7	2.7	0.3	1.9	-
		confluence														
СН_22	Chambal	Upsream of	55 6	106	1/ 8	58.8	13 /	3.2	115	1 8	111	21	63	٥٥	57	0 0
011-22	Chambai	Jawahar Sagar	55.0	100	14.0	50.0	13.4	5.2	14.5	1.0	14.4	2.4	0.5	0.9	5.7	0.9
Rainwater		Dehradun	18.4	21.4	23.1	23.1	25.4	24.4	23.2	25.5	26.8	29.1	31.9	32.6	33.2	32.4
Detection L	.imit (6σ)		6.65	13.22	2.09	4.77	2.40	1.78	2.09	0.69	0.81	0.27	0.48	0.24	0.98	0.33

- Below detection limit.

Sample code	∑REE ng L <sup>-1</sup>	ΣLREE* ng L <sup>-1</sup>	ΣHREE* ng L <sup>-1</sup>	(La/Yb) <sub>CN</sub>	Ce/Ce* <sup>†</sup>	Eu/Eu* <sup>†</sup>	Gd/Gd* <sup>†</sup>
RW99-2	106	91.3	14.6	8.3	0.97	-	0.96
RW99-3	87.0	75.1	11.9	7.2	1.03	-	1.20
RW99-6	342	291	46.8	10.1	0.92	0.66	1.15
RW99-7	257	211	43.1	5.4	0.91	0.68	1.26
RW99-11	239	198	38.5	7.0	0.90	0.68	1.31
RW99-13	92.3	66.3	26.0	3.2	0.35	-	1.19
RW99-17	191	158	32.7	5.5	0.75	-	1.22
RW99-31	270	224	42.5	5.6	1.01	0.63	1.10
RW99-51	492	412	75.0	7.5	0.84	0.64	1.05
RW99-52	125	103	22.6	5.5	0.70	-	0.95
RW99-54	322	269	49.9	7.1	0.88	0.71	1.05
RW99-55	1374	1201	164	9.4	0.97	0.52	1.15
RW99-57	542	449	88.6	6.8	0.94	0.54	1.17
RW99-58	604	502	96.4	6.1	1.16	0.54	1.31
RW99-59	189	144	43.3	4.8	0.86	0.49	1.15
RW99-60	215	179	34.2	14.7	0.25	0.73	1.24
RW99-61	1061	880	170	5.7	1.03	0.64	1.18
RW99-63	1371	1173	186	7.7	1.02	0.60	1.18
RW99-64	112	95.0	16.6	7.9	0.83	-	1.25
CH-22	299	248	46.9	6.6	0.86	0.70	1.32

Table 6.8. Dissolved  $\Sigma REE$ ,  $\Sigma LREE$ ,  $\Sigma HREE$ , (La/Yb)<sub>CN</sub> and Ce and Eu anomalies of the Yamuna river and its tributaries.

- Not determined due to low concentration of Eu in the samples.

- \* LREE are La to Sm and HREE are Gd to Lu
- <sup>†</sup> The Ce, Eu and Gd anomalies are calculated as follows:  $\begin{array}{l} Ce/Ce^{*} = 3Ce_{CN}/(2La_{CN}+Nd_{CN}) \\ Eu/Eu^{*} &= Eu_{CN}/(Sm_{CN}^{*}Gd_{CN})^{0.5} \\ Gd/Gd^{*} &= Gd_{SN}/(0.33Sm_{SN}+0.67Tb_{SN}) \end{array}$

	Min.	Мах	Geometric Mean	Average
La	15.0	267	54.5	77.1
Ce	13.8	558	98.2	156
Pr	2.3	64.9	12.9	18.9
Nd	18.3	253	56.2	77.8
Sm	4.1	60.6	13.6	18.9
Eu	2.0	11.9	4.2	5.0
Gd	4.7	61.0	14.7	20.1
Tb	0.69	8.6	2.2	3.0
Dy	3.0	50.5	12.8	17.3
Но	0.50	9.2	2.4	3.3
Er	1.3	27.9	6.9	9.2
Tm	0.30	4.2	0.92	1.3
Yb	1.4	21.3	5.4	7.3
Lu	0.50	3.0	1.1	1.4
∑REE	87.0	1374	289	414
∑LREE	66.3	12.6	239	349
∑HREE	11.9	186	46.4	62.4
La <sub>N</sub> /Yb <sub>CN</sub>	3.2	14.7	6.7	7.1
La <sub>N</sub> /Sm <sub>CN</sub>	1.7	7.2	2.5	2.7
Gd <sub>N</sub> /Yb <sub>CN</sub>	1.5	3.3	2.2	2.2
Eu/Eu*	0.49	0.73	0.62	0.63
Ce/Ce*	0.25	1.2	0.82	0.86
Gd/Gd*	0.95	1.3	1.2	1.2

Table 6.9. Range and mean concentrations (ng L<sup>-1</sup>) of dissolved REE and Eu, Ce and Gd anomalies in the Yamuna river and its tributaries.



Fig. 6.13. Dissolved REE concentrations normalized to that of PAAS for the Yamuna river and its tributaries. A large range of REE fractionation is observed among these samples with MREE enrichment.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
La	1.000	0.981	0.962	0.990	0.945	0.251	0.942	0.224	0.899	0.223	0.688	-0.034	0.562	-0.135
Се		1.000	0.966	0.995	0.960	0.274	0.961	0.236	0.919	0.228	0.696	-0.031	0.575	-0.125
Pr			1.000	0.975	0.992	0.504	0.984	0.453	0.966	0.444	0.840	0.196	0.740	0.113
Nd				1.000	0.965	0.285	0.965	0.246	0.925	0.243	0.712	-0.018	0.587	-0.119
Sm					1.000	0.538	0.990	0.488	0.982	0.479	0.861	0.233	0.769	0.151
Eu						1.000	0.494	0.986	0.596	0.978	0.915	0.907	0.967	0.895
Gd							1.000	0.451	0.988	0.447	0.849	0.189	0.751	0.098
Tb								1.000	0.547	0.998	0.861	0.952	0.933	0.945
Dy									1.000	0.543	0.898	0.295	0.816	0.217
Но										1.000	0.846	0.960	0.921	0.958
Er											1.000	0.670	0.982	0.647
Tm												1.000	0.782	0.999
Yb													1.000	0.772
Lu														1.000

Table 6.10. Inter-element correlation matrix for the dissolved REE of the Yamuna river and its tributaries (n=20).



Fig. 6.14. Distribution pattern of REE normalized to PAAS in river waters and sediments of the Yamuna river.



Fig. 6.15. Histogram of the chondrite normalized Eu and Ce anomalies in the Yamuna river water samples.



Figure 6.16. Scatter plot of PAAS normalized concentrations of Yb vs Nd of the Yamuna river water samples. Dashed line indicates seawater ratio. The data shows a linear trend with a correlation coefficient, r=0.9.

Inter-element correlation among the various dissolved REE in the Yamuna river and its tributaries are given in the Table 6.10. A good positive correlation (r>0.9) is seen between any two neighbouring elements except for the Ce and Eu. The correlation becomes weaker as the two elements are separated from each other in terms of their atomic numbers. It would be interesting to know fractionation between LREE and HREE along the Yamuna river. Sholkovitz and Szymczak (2000) have shown that in the Amazon, Fly and Sepik estuarine systems that estuarine reactions can modify the relative abundance of dissolved REE reaching the oceans. They have shown that there are two distinct processes operating on dissolved REE in estuaries, large-scale salt-induced coagulation in the low salinity region and small to extensive release in the mid to high salinity region. Due to the MREE enrichment in the Yamuna river,  $\Sigma LREE/\Sigma HREE$  ratios show variations. In order to find fractionation between LREE and HREE in the Yamuna river, shale-normalized Yb against Nd concentrations of the Yamuna river water samples are plotted in Fig. 6.16. The river water samples have  $(Yb/Nd)_{SN}$  ratio of 1, showing no relative fractionation with respect to shale, whereas  $(Yb/Nd)_{SN}$  ratio in seawater is 4.3 (Elderfield et al., 1990), indicating an enrichment of HREE over LREE is taking place not in the river course and only during estuarine and marine processes.



Fig. 6.17. Histogram of the Shale normalized Gd anomalies (Gd/Gd\*) in the Yamuna river water samples. Most of the samples have very small positive Gd anomalies.

# 6.2.4 Gadolinium anomalies in river waters

Except at the surface, seawater in all oceans shows shale-normalized REE patterns with positive anomalies of La and Gd. These anomalies result primarily from the lower solubility of La and Gd complexes compared to those of their respective neighbours in the REE series. Gd anomaly (Gd/Gd\*) in river water is quantified by:

 $Gd/Gd^* = Gd_{SN}/(0.33Sm_{SN}+0.67Tb_{SN})$  ......[6.6]

where SN refers to shale-normalized values. Although the extent of the Gd anomaly in seawater is small (Gd/Gd\* = 1 - 1.2), it is used as an indicator of the types of ligands that control surface complexation of REE on marine particles. Occasionally natural distribution of REE in river waters is modified with anthropogenic influences and show pronounced positive Gd anomalies (Knappe et al., 1999). This is observed in populated and industrialized regions (Gd/Gd\* >2 and up to 1500, closer to the source of contamination, Bau and Dulski, 1996; Nozaki et al., 2000; Elbaz-Poulichet et al., 2002).

The source of the Gd is most likely gadopentetic acid, Gd(DTPA)<sup>2-</sup>, which is used in magnetic resonance imaging (Kummerer and Helmers, 2000). A significant number of Yamuna river water samples show positive Gd anomalies (shale-normalized Gd/Gd\* values 0.95 to 1.32, Table 6.8, Fig. 6.17). The small positive Gd anomaly is due to low solubility of Gd complexes compared to those of neighbours in the REE series. These Gd anomaly values are less than those reported for rivers in Germany and Japan (Bau and Dulski, 1996; Nozaki et al., 2000; Elbaz-Poulichet et al., 2002), which have catchments in industrialized areas implying the absence major anthropogenic input of REE in the upstream of the Yamuna river. It would be interesting to find out the Gd/Gd\* downstream to know the effect of sewage from urbanized areas along this river.

# 6.3 Major element and REE composition of bed sediments

#### 6.3.1 Major and trace elements

Table 6.11 shows chemical composition of the Chambal bed sediments. These sediments have a wide range of major and minor elemental abundances and are not homogenous in their chemical composition. For comparison, few samples available from the Ganga river along the plains were also analyzed and their results are shown in Table 6.11. The range and mean concentrations of major and trace elements of the Chambal river samples are shown in Table 6.12. Among the major oxides, CaO in samples from the Chambal basin shows a large variation (4.8 to 28.3% in the Chambal basin bed sediments) with a mean of 8.9% due to the presence of variable amount of carbonates. In all but three samples, CaO is within a range of 4.8 - 10%. CaCO<sub>3</sub> in the Chambal bed sediments has a mean of 13.7% and varied from 5.1 to 44.8%. In the Yamuna bed sediments, CaO varied from 0.6 to 14.1% (Mean=2.4%) and CaCO<sub>3</sub> varied from 0.1 to 43.5% (Mean=4.8%) (Dalai, 2001).

Chemical weathering which involves the dissolution of soluble elements and their subsequent removal enriches river suspended matter in the less soluble elements (such as AI and Fe) relative to the parent rock and depleted in soluble elements (Na and Ca). As K is retained more in clay minerals in soils, the variation of Na, Mg and AI in bed sediments will give information on their mobility relative to the source rocks.

Sample	CaCO₃	C <sub>Org</sub>	$AI_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	$P_2O_5$	Mn	Cu	Ni	Со	Cr	Zn	Pb
Code					(%)									ppm			
							Chamb	al Rive	ər								
CH-1	17.8	0.35	8.39	4.78	9.92	1.79	1.09	1.13	0.81	0.65	646	44.0	40.0	23.0	58.5	62.8	18.5
CH-2	8.02	0.27	9.92	5.12	5.76	1.89	1.20	1.30	1.16	0.48	669	51.5	46.9	28.4	66.0	73.7	16.5
CH-3	9.87	0.06	10.6	5.59	4.94	2.17	1.01	1.39	1.14	0.43	697	57.4	49.7	29.2	71.7	79.9	17.0
CH-4	7.92	0.63	12.1	6.12	5.43	2.47	0.81	1.37	0.93	0.56	927	53.3	46.7	27.8	68.3	77.8	16.2
CH-5	8.92	1.10	10.3	6.53	6.80	2.24	1.12	1.02	1.46	0.43	898	71.6	67.3	32.1	88.8	97.5	18.9
CH-6	17.5	0.03	9.11	5.43	8.73	2.11	1.13	0.93	1.35	0.46	980	114	65.8	43.5	88.3	98.5	17.6
CH-7	14.5	1.04	8.92	3.95	9.30	2.09	0.90	1.04	0.88	0.39	752	89.2	54.1	39.3	88.8	83.7	15.0
CH-8	10.6	0.89	9.16	5.62	7.21	1.97	0.85	1.02	1.12	0.48	1004	60.8	49.8	27.4	76.2	72.6	18.8
CH-9	11.2	0.92	9.32	7.02	8.24	2.24	0.65	0.63	1.45	0.26	1264	75.4	59.4	37.4	83.7	80.5	17.7
CH-10	5.06	1.04	12.6	7.92	4.77	2.22	0.66	1.05	1.08	0.34	782	123	68.6	53.2	88.6	90.8	14.5
CH-11	8.78	1.09	11.8	10.7	7.60	2.24	0.65	0.59	1.60	0.26	1524	94.9	69.7	37.9	91.4	92.8	18.3
CH-12	44.8	1.38	6.08	6.68	28.3	2.67	0.81	0.30	0.93	0.29	1715	135	75.2	57.9	100	98.9	17.6
CH-14	10.3	0.75	11.2	9.14	7.75	2.44	0.94	0.84	1.36	0.18	1192	61.2	41.8	36.2	77.4	63.9	9.2
CH-15	14.6	0.86	9.92	7.89	11.3	2.50	0.80	0.83	1.04	0.31	914	115	57.8	43.1	87.3	91.3	14.6
CH-16	9.86	0.69	14.0	5.70	5.93	2.67	0.70	2.00	0.53	0.23	605	81.4	61.3	36.5	119	78.5	13.2
CH-17	9.86	1.21	9.49	6.71	6.73	2.17	1.08	1.19	1.14	0.13	762	38.5	65.5	23.7	90.5	83.4	25.6
CH-18	11.0	0.53	12.0	6.33	6.41	2.45	0.86	1.71	0.75	0.12	609	39.5	61.9	23.3	88.2	84.8	21.0
CH-19	16.4	1.77	7.43	2.83	9.77	1.58	0.92	1.33	0.39	0.15	353	76.5	54.6	35.1	84.9	87.5	16.3
CH-20	12.2	0.86	4.63	1.73	7.68	0.91	0.63	0.82	0.30	0.14	290	51.9	64.7	26.1	91.0	91.2	15.7
CH-21	24.0	0.09	8.05	3.29	15.8	1.61	0.89	1.35	0.39	0.09	391	32.8	24.6	11.6	40.0	80.0	22.4
							Ganga	River <sup>•</sup>	**								
G-1	2.37	0.15	8.20	2.66	1.53	1.23	1.32	1.84	0.31	0.27	268	15.2	16.1	15.8	32.7	74.7	18.1
G-2	2.59	0.12	10.6	6.09	3.29	1.61	1.56	1.55	0.46	0.29	1271	21.0	14.4	16.8	92.7	64.8	15.0
G-3	2.66	0.58	10.3	3.49	2.18	1.84	1.86	1.75	0.38	0.22	222	15.1	18.1	15.7	38.0	69.5	18.3
G-4	7.60	0.32	6.33	2.00	3.81	1.41	1.24	2.04	0.28	0.30	372	6.2	9.3	11.7	21.4	44.0	14.4
G-5	12.4	0.70	7.82	2.24	7.70	0.80	1.29	2.79	0.32	0.16	425	14.1	17.8	14.2	33.8	49.5	16.7
G-6	3.86	0.18	8.37	2.87	3.19	1.16	1.70	2.82	0.65	0.31	458	14.9	19.0	17.9	39.0	59.4	16.1
G-7	1.19	0.16	9.09	2.60	1.37	1.13	1.60	2.47	0.37	0.26	822	13.8	16.4	14.8	34.5	52.1	14.4

Table 6.11. CaCO<sub>3</sub>, C<sub>Org</sub>, major elements and trace elements in bed sediment samples from the Chambal watershed and Ganga River.

\*\* Sampled during March 1982 and November 1983 (Sarin et al., 1992). Sample locations are given in Appendix 6.1.

	Min.	Max.	Mean
C <sub>org.</sub> (%)	0.03	1.77	0.78
Al <sub>2</sub> O <sub>3</sub> (%)	4.6	14.0	9.8
Fe <sub>2</sub> O <sub>3</sub> (%)	1.7	10.7	6.0
CaO (%)	4.8	28.3	8.9
MgO (%)	0.91	2.7	2.1
Na <sub>2</sub> O (%)	0.63	1.2	0.89
K <sub>2</sub> O (%)	0.3	2.0	1.1
TiO <sub>2</sub> (%)	0.3	1.6	0.99
P <sub>2</sub> O <sub>5</sub> (%)	0.09	0.65	0.32
Mn (ppm)	290	1715	849
Cu (ppm)	33	135	73.4
Ni (ppm)	25	75	56.3
Co (ppm)	12	58	33.6
Cr (ppm)	40	119	82.5
Zn (ppm)	63	99	83.5
Pb (ppm)	9.2	26	17.2

Table 6.12. Range and mean concentrations of major and trace elements of the Chambal river sediment samples (n=20).

The average Na/K, Mg/K and Al/K weight ratios of the Chambal sediments are 0.73, 1.4 and 5.7 respectively. For comparison, the corresponding ratios for Deccan Basalts are 0.76, 0.16 and 2.2 respectively (Wilson, 1989; Subbarao et al., 2000). To quantify the extent of chemical weathering undergone by rocks, Nesbitt and Young (1984) introduced a parameter called the chemical index of alteration (CIA). This is calculated from the molecular proportions of oxides (Al, Ca, Na and K) of sediments as:

$$CIA = (AI_2O_3)/(AI_2O_3 + CaO^* + Na_2O + K_2O) \times 100 \qquad \dots [6.7]$$

where CaO<sup>\*</sup> is Ca in silicate fraction and is calculated after correcting for carbonates by assuming that all carbonates in the bed sediments are CaCO<sub>3</sub>. During weathering, most of the aluminum from primary minerals is transformed to clay minerals whereas alkalis and alkaline earths are removed in solution from parent materials. CaO and Na<sub>2</sub>O are generally removed more quickly during weathering than K<sub>2</sub>O. The loss of CaO, Na<sub>2</sub>O and K<sub>2</sub>O from primary rocks causes secondary phases to exhibit higher CIA than parent rock. Sediments derived from intensely weathered rocks and containing residual clay minerals such as kaolinite and/or gibbsite have CIA values approaching 100, and unweathered upper crustal rocks has a CIA value of 50 (Fedo et al., 1995). Average shale has a CIA value of about 70 to 75. The Chambal and the Ganga river sediments have CIA values of 58.6 to 81.8 (74.1±1.4) and 60.1 to 70.9 (66.1±1.6) respectively. For comparison, the corresponding value for the Yamuna sediments calculated using the major ion data of bed sediments (Dalai, 2001) ranged from 60.7 to 75.9 (Mean=68.1±1.0, Dalai, 2001). The Yamuna and Ganga sediments have CIA values lower than those of shale. The CIA values of bed sediments of the Chambal river are higher than that of Yamuna as the river drains the Deccan basalts; which are known to be susceptible for more rapid weathering compared to granites and gneisses (Amiotte-Suchet and Probst, 1995; Dessert et al. 2001). The crystalline and metamorphic rocks of the Himalayan and Aravalli Ranges of the Yamuna catchment are more resistant to chemical weathering than the sedimentary and basaltic rocks of the Chambal catchment.

The molecular proportions of  $Al_2O_3$ , (CaO+Na<sub>2</sub>O) and K<sub>2</sub>O and  $Al_2O_3$ , (CaO+Na<sub>2</sub>O+K<sub>2</sub>O) and (FeO+MgO) are plotted on triangular plots (Nesbitt and Young, 1984 and 1989; Tripathi and Rajamani, 1999, Fig. 6.18 and 6.19). The major element concentrations of the Chambal, the Ganga (Table 6.11) and the Yamuna river sediments (Dalai, 2001) plot on the triangular diagrams in the relatively less weathered region. Weathering has proceeded to a stage at which significant amounts of the alkali and alkaline earth elements were removed from the sediments. These chemical characteristics of the sediments indicate that the Yamuna, the Chambal and the Ganga

sediments were derived from a source, which had suffered relatively moderate weathering.



Fig. 6.18.  $Al_2O_3 - (CaO+Na_2O) - K_2O$  plot of sediment samples from Yamuna, Chambal and Ganga rivers compared to PAAS (triangle) and Upper crust (square) (Taylor and McLennan, 1985). Major ion data for the Yamuna river are from Dalai (2001).



Fig. 6.19. Triangular  $AI_2O_3 - CaO+Na_2O+K_2O) - (Fe_2O_3+MgO)$  plot of sediment samples in comparison with PAAS (triangle) and Upper Crust (square) values (Taylor and McLennan, 1985). Major ion data for the Yamuna sediments are from Dalai, 2001.



Fig. 6.20. Variation of CaO, MgO,  $P_2O_5$ ,  $Fe_2O_3$ , Ti and Mn with  $AI_2O_3$  in bed sediments of the Chambal river. There is a positive trend between  $AI_2O_3$  and MgO and  $AI_2O_3$  and  $Fe_2O_3$ . Inverse trend between CaO and  $AI_2O_3$  implies CaO is derived mostly from carbonates.

Bulk chemical variations in the major elements in sediments from the Chambal river are shown in Fig. 6.20. There is a positive trend between Al<sub>2</sub>O<sub>3</sub> and MgO and as well as  $Fe_2O_3$  of the sediments implying that these are derived mostly from the clays. Inverse trend between CaO and Al<sub>2</sub>O<sub>3</sub> of the sediments indicates that CaO is derived from carbonates. It is known that chemical composition is dependent on grain size, with Al<sub>2</sub>O<sub>3</sub> increasing towards finer sediments. Al<sub>2</sub>O<sub>3</sub> vs. TiO<sub>2</sub> shows a scatter with some samples showing high TiO<sub>2</sub> content compared to the upper crust value of 0.41% (McLennan, 2001). This is attributed to enrichment by heavy minerals (ilmenite) in them. For the bed sediments of the Yamuna river, measured Fe/Al ratios range between 0.11 and 0.86 (Mean=0.50) showing an enrichment of Fe relative to the continental crust (Fe/Al≈0.3) on average. By comparison, the Chambal bed sediments display Fe/Al ratios higher and ranges between 0.49 and 1.45 (Mean=0.81). The higher Fe/AI ratios is observed in the Chambal bed sediments relative to that of the Yamuna bed sediments because these sediments are derived from the weathering of Deccan Trap basalts that have the high Fe/Al ratio of ~1.2 (Mahoney, 1988).  $P_2O_5$  in these sediment samples varies from 0.1 to 0.7% and does not show any correlation with  $AI_2O_3$ .

## 6.3.2 REE transport in stream sediments

One of the effects of chemical weathering processes is that they distort the chemical composition of the parent rock. For example, granite contains about equal proportions of quartz, plagioclase-feldspar and alkali-feldspar. Chemical weathering affects them in the order: plagioclase-feldspar > K-feldspar > quartz. The weathered residues of the feldspars are clay minerals. Thus feldspars progressively gets depleted and the resulting sediments become less representative of the source rock. Thus, the chemistry of bed sediments often does not accurately reflect their source rocks after weathering (Nesbitt et al., 1996). However, the abundance and patterns of REE are reasonably well preserved during weathering, as they are far less mobile during sedimentary processes. The results of REE composition of the bed sediments from the Yamuna, the Chambal and the Ganga rivers along with those of granite samples from Hanuman Chatti are summarized in Appendix 6.1. The normalized REE patterns for

these bed sediment samples and of source rocks from the Yamuna and the Chambal river catchments are shown in Figs. 6.22 – 6.25. Data normalization was done with PAAS REE concentrations (Taylor and McLennan, 1985). In general, variation in normalized REE patterns reduces when data are plotted separately for the major rivers, suggesting that tributaries draining diverse lithology contribute to significant variations.

In the Yamuna and the Chambal river basins, due to their dissected topography and the small size, intense mixing phenomena are not favoured and in the case of the Yamuna river system, the fast-flowing streams inhibit the weathering reactions. These physicochemical conditions and mildly alkaline pH values of the river water have an important influence on the REE patterns of the sediments of these rivers. A conspicuous characteristic in the shale-normalized REE patterns of the Yamuna bed sediments is the strong HREE enrichment with respect to granites at Hanuman Chatti, source rocks for the Yamuna river sediments. The shale normalized REE patterns of Chambal river sediments are similar to Deccan Trap basalts, the primary sediment source of the Chambal river. In general, similarity in the shale-normalized REE patterns for the Yamuna mainstream samples is observed and the tributaries draining diverse lithology exhibit significant variations (Fig. 6.24).

Bed sediments in the Yamuna and the Chambal river basins are characterized by  $\Sigma$ REE concentrations in the range of 78 to 291 µg g<sup>-1</sup> (mean = 165 µg g<sup>-1</sup>) and 96 to 157 µg g<sup>-1</sup> (mean = 134 µg g<sup>-1</sup>), respectively (Table 6.13).  $\Sigma$ REE concentrations of the Yamuna river sediments by and large fall in the range of that in the source rock (granite) in the Hanuman Chatti (Table 6.13). The variation in REE content of sediments from different locations is very small. Comparing the results of this study with available data from the Himalayan river system (Ramesh et al., 2000; Stummeyer et al., 2002), the Yangtze river system, the lower reaches of the Yellow river (Zhang et al, 1998), world average (Bowen, 1979; Martin and Meybeck, 1979) and PAAS (Taylor and McLennan, 1985), it is observed that these data overlap considerably (Table 6.14). In the Chambal river sediments,  $\Sigma$ REE are marginally lower than that of Yamuna sediments and are similar to that in Deccan basalts (Table 6.15, Mahoney et al., 2000).

In sediments, the contents of REE follow the order: Ce > La > Nd > Sm > Eu, Yb, Tb, Lu. The average values of LREE and HREE in bed sediments of both rivers are 151 and 17.5 µg g<sup>-1</sup> respectively (Table 6.13). Ratios of LREE/HREE in sediments vary from 7.2 to 11.8 in the Yamuna (geometric mean = 9.0) and from 4.8 to 9.9 in the Chambal (geometric mean = 7.3) respectively. Four granite samples from Hanuman Chatti at the Yamuna river have LREE/HREE in the range from 9.7 to 22.4 with a mean of 16.9. The relatively low LREE/HREE ratios in the Yamuna river sediments reveal that HREE are enriched in them with respect to the source rock, viz. granites. The dissolved REE concentrations are lower by a factor of 10<sup>6</sup> compared to that in the sediments (Section 6.2.3). A comparison of the shale normalized REE composition of the Yamuna river water and bed sediments (Section 6.2.3; Fig. 6.14) suggests that dissolved composition of REE is strongly fractionated and is enriched in MREE with respect to sediments. Ratios of LREE/HREE for the Yamuna water samples vary from 2.6 to 7.3. This difference can be explained, as discussed in the Section 6.2.3, by the MREE enrichment in the dissolved phase relative to the bed sediments probably resulting from apatite weathering.

Chondrite normalized (La/Yb) ratio is another measure of fractionation between LREE and HREE. The (La/Yb)<sub>CN</sub> ratios of the Yamuna and the Chambal bed sediments are given in Table 6.15. The average (La/Yb)<sub>CN</sub> ratio of the Deccan Trap basalts is 5.2 and that of PAAS is 9.2 (Table 6.16). 17 out of 20 sediment samples from the Chambal river system have (La/Yb)<sub>CN</sub> ratios between 5.9 and 9.8. Samples CH-19, CH-20 and CH-21 have slightly higher (La/Yb)<sub>CN</sub> ratios as these samples are not derived from the Deccan Trap basalts (Chapter 5, Fig. 5.5).

The average  $(La/Yb)_{CN}$  ratio of four granite samples from Hanuman Chatti is 28.7±13.1. The Yamuna mainstream samples integrates the sediments from various tributaries and have  $(La/Yb)_{CN}$  ratios between 8.6 and 9.6 except for the uppermost sample of the Yamuna (RW98-20) which has a value of 11.8. The bed sediments of the tributaries of the Yamuna river have a wider range of  $(La/Yb)_{CN}$  ratios from 5.7 to 13.7 due to diverse lithologies of these tributaries.

Goldstein and Jacobson (1988) reported PAAS normalized (La/Yb) ratios for suspended load material, 1.6 - 2.7, as world average. The PAAS normalized values for the Chambal and the Yamuna sediment samples vary between 0.6 and 1.5 with a mean of 1.0, lower than the values reported by them.

Range and mean concentrations of chondrite normalized Eu and Ce anomalies of the sediments from the Yamuna and the Chambal river catchments are given in Table 6.16. In general, Ce/Ce\* anomaly ranged between 0.83-1.03 for the bed sediments except in CH-12, which has Ce/Ce\* ratio of 0.55 (Fig. 6.21). This sample has 44.8% CaCO<sub>3</sub>. This may be due to mixing of detrital clay and marine limestone present in that sample location. It is likely that the minor variation in the Ce/Ce\* anomaly reflects the process of preferential scavenging of Ce by Fe oxyhydroxides which is a common process during transport (Braun et al., 1990). The presence of Fe-Mn oxyhydroxides as coatings on suspended and bed sediments and their ability to scavenge trace metals, particularly REE, in freshwater environments is well known (Sholkovitz, 1995; Douglas et al., 1999). Leucogranites, granites at Hanuman Chatti and average Deccan basalts have an average Ce/Ce\* value of ~1. As discussed before, the Yamuna river waters also have similar Ce/Ce\* anomaly values except a few samples. Complexation of REE to Fe-Mn oxyhydroxides has only a minor influence on overall REE geochemistry of bed sediments (Fig. 6.27).

Eu anomaly values do not vary significantly in the Yamuna river sediments. The average Eu/Eu\* anomaly values in the Yamuna sediments and waters are 0.55 and 0.63 respectively. These are within the range of Eu/Eu\* values of granites and average upper crust, 0.42 and 0.65 respectively. Any Eu<sup>2+</sup> released during weathering will be oxidized to Eu<sup>3+</sup>, and hence behave like the other trivalent REE. The presence of Eu anomaly in the Yamuna sediments is thus the signature of earlier events in a more reducing igneous environment than that exists at present in the upper crust. There are minor variations in Eu/Eu\* ratios in the bed sediments, implying the contribution of tributaries joining the main stream and also due to changes in the lithology along the course of the river (Fig. 6.21, Allegre, 1996).

	La	Ce	Nd	Sm	Eu	Gd	Dy	Но	Er	Yb	Lu	ΣREE	ΣLREE	ΣHREE
							μg	<b>g</b> <sup>-1</sup>						
Yamuna ma	ain strea	m (n=10)	)											
Min.	29.5	57.7	21.9	5.0	0.72	3.6	3.4	0.73	2.1	1.8	0.26	129.4	115.7	11.8
Max.	43.7	86.6	32.9	6.9	1.01	4.7	5.2	1.17	3.5	3.5	0.53	189.5	170.1	18.5
Geometric Mean	34.0	67.3	26.6	5.7	0.85	4.1	4.2	0.90	2.5	2.4	0.34	149.1	133.7	14.5
Average	34.3	67.9	26.8	5.8	0.85	4.1	4.3	0.91	2.6	2.5	0.35	150.3	134.8	14.6
Yamuna tril	butaries	(n=13)												
Min.	17.8	33.0	14.8	3.3	0.58	2.1	2.6	0.51	1.6	1.4	0.20	77.9	68.8	8.5
Max.	67.7	134.5	52.9	11.3	1.25	7.7	8.1	1.88	6.0	6.2	0.94	291.4	262.5	28.4
Geometric Mean	37.4	74.8	29.6	6.4	0.96	4.5	4.9	1.05	3.1	3.0	0.43	166.4	148.3	16.9
Average	39.6	79.6	31.2	6.8	0.99	4.8	5.2	1.13	3.3	3.2	0.48	176.3	157.2	18.1
Chambal riv	ver (n=20	))												
Min.	22.2	27.0	21.5	5.6	0.88	3.6	3.6	0.77	2.0	1.9	0.26	95.9	78.0	12.6
Max.	34.4	69.5	30.5	7.2	1.65	5.5	5.9	1.16	3.3	2.9	0.46	156.7	136.9	18.5
Geometric Mean	28.4	55.2	25.7	6.2	1.28	4.4	4.9	1.00	2.8	2.5	0.37	133.3	115.8	16.0
Average	28.6	56.2	25.8	6.2	1.29	4.4	4.9	1.00	2.8	2.5	0.38	134.2	116.8	16.0
Ganga river	r* (n=7)													
Min.	27.2	52.6	21.0	4.5	0.81	3.3	3.1	0.76	1.9	2.0	0.24	117.4	105.3	11.2

 Table 6.13. Range and mean concentrations of REE in the Yamuna and the Chambal river bed sediments.

Max.	203	375.1	132.3	29.2	3.7	20.0	18.1	3.9	10.6	11.2	1.6	808.5	739.5	65.3
Geometric Mean	54.9	104.6	39.6	9.0	1.4	6.2	5.7	1.3	3.3	3.6	0.47	230.0	208.2	20.4
Average	68.5	129.8	48.0	10.9	1.5	7.4	6.8	1.5	3.9	4.2	0.57	283.0	257.1	24.4
All bed sediments (n=50)														
Min.	17.8	27.0	14.8	3.3	0.58	2.1	2.6	0.51	1.6	1.4	0.20	77.9	68.8	8.5
Max.	203.0	375.1	132.3	29.2	3.7	20.0	18.1	3.9	10.6	11.2	1.6	808.5	739.5	65.3
Geometric Mean	34.7	68.0	28.5	6.5	1.1	4.6	4.8	1.0	2.9	2.7	0.39	155.9	138.0	16.5
Average	38.2	74.9	30.5	6.9	1.2	4.9	5.1	1.1	3.1	2.9	0.43	169.2	150.6	17.5
Granites (n=4)														
Min.	37.7	69.3	26.3	5.6	0.66	3.0	1.7	0.42	0.72	0.65	0.08	147.5	139.2	6.5
Max.	65.0	127.9	50.1	10.5	0.76	7.1	7.5	1.6	5.0	4.5	0.58	280.2	253.4	26.2
Geometric Mean	45.7	88.8	32.4	6.9	0.70	4.0	2.8	0.60	1.28	1.2	0.15	185.4	173.8	10.3
Average	46.9	91.3	33.6	7.2	0.70	4.3	3.4	0.73	1.85	1.7	0.22	191.9	178.9	12.2

\* Sampled during March 1982 and November 1983 (Sarin et al., 1992)
River*	La	Се	Nd	Sm	Eu	Gd	Dy	Но	Er	Yb	Lu
(1)	34.3	67.9	26.8	5.8	0.85	4.1	4.3	.91	2.6	2.5	0.35
(2)	28.6	56.2	25.8	6.2	1.3	4.4	4.9	1.0	2.8	2.5	0.38
(3)	46.9	91.3	33.6	7.2	0.70	4.3	3.4	.73	1.9	1.7	0.22
(4)	18.5	27	20.6	6.25	1.09	3.9	-	-	-	2.9	0.46
(5)	16.7	35.9	22.2	5.2	1.68	5.9	5.05	1.01	2.46	2.2	0.32
(6)	47	91	42	6.4	1.07	-	-	-	-	2.3	0.39
(7)	45	88	43	6.2	1.38	-	-	-	-	2.5	0.40
(8)	51	103	47.4	9.1	1.9	-	0.98	-	-	3.7	-
(9)	33.8	73.6	35.4	6.4	1.2	-	-	-	-	2.8	0.45
(10)	41	83	32	6.4	1.2					3.6	0.70
(11)	45	95	35	7	1.5	5	-	1	3	3.5	0.5
(12)	38.2	79.6	33.9	5.55	1.08	4.66	4.68	0.99	2.85	2.82	0.43
(13)	30	64	26	4.5	0.88	3.8	3.5	0.80	2.3	2.2	0.32

Table 6.14. Comparison of REE contents in sediments and source rocks for various rivers ( $\mu g g^{-1}$ ).

\*(1) Average concentration of sediments from mainstream of the Yamuna river (This study).

- (2) Average concentration of sediments from mainstream of the Chambal river (This study).
- (3) Granites from Yamuna catchment near Hanuman Chatti (This study).
- (4) Basalts from the Chambal catchment (Sengupta and Deshmukh, 1996).
- (5) Deccan Basalts from Toranmal (21°53'N, 74°28'E) (Mahoney et al., 2000)
- (6) Sediments in mainstream of the Yangtze river (Zhang et al, 1998).
- (7) Suspended matter in mainstream of the Yangtze river (Zhang et al, 1998).
- (8) Sediments in the Amazon river (Gaillardet et al., 1997)
- (9) Sediments from lower reaches of the Yellow river (Zhang et al., 1998).
- (10) Sediments, world average (Bowen, 1979).
- (11) Suspended matter, world average (Martin and Meybeck, 1979).
- (12) Post Archean average Australian Shale (Taylor and McLennan, 1985).
- (13) Continental upper crust (Taylor and McLennan, 1985).

Table 6.15.  $\Sigma$ REE,  $\Sigma$ LREE,  $\Sigma$ HREE, (La/Yb)<sub>CN</sub> and Ce and Eu anomalies of the Yamuna and Chambal river bed sediments.

Sample	∑REE	ΣLREE	ΣHREE	(  a/Vh)		Eu/Eu*
code	µg g⁻¹	µg g⁻¹	µg g⁻¹		Ce/Ce	Eu/Eu
Yamuna river	and tributar	ies				
RW98-20	136.2	123.7	11.8	11.8	0.97	0.52
RW98-25	136.8	122.4	13.5	9.1	0.96	0.53
RW98-22	130.4	116.2	13.3	9.1	0.93	0.60
RW98-14	129.4	115.7	13.0	9.6	0.91	0.50
RW98-12	163.9	147.4	15.7	9.6	0.97	0.51
RW98-9	171.6	153.5	17.2	9.1	0.97	0.49
RW98-6	140.5	125.5	14.1	9.6	0.91	0.55
RW98-1	189.5	170.1	18.5	8.6	0.95	0.51
RW98-4	162.7	145.5	16.2	9.1	0.97	0.57
RW98-33	141.7	127.7	13.2	9.6	0.93	0.61
RW98-18	276.2	248.4	26.5	10.8	0.99	0.41
RW98-19	126.5	111.9	13.6	7.3	0.94	0.73
RW98-13	144.8	127.3	16.3	7.6	0.98	0.68
RW98-21	123.2	113.0	9.6	13.7	0.95	0.49
RW98-26	291.4	262.5	27.8	8.6	0.96	0.37
RW98-27	163.8	147.1	15.9	8.8	0.97	0.49
RW98-29	233.9	204.6	28.4	5.7	0.97	0.41
RW98-31	148.2	132.9	14.4	9.9	0.92	0.64
RW98-30	213.8	187.8	25.0	6.5	0.93	0.50
RW98-32	184.6	166.7	16.9	9.6	0.97	0.56
RW98-8	77.9	68.8	8.5	8.2	0.88	0.67
RW98-2	151.0	133.2	16.7	8.1	0.95	0.65
RW98-11	156.6	139.8	15.7	8.8	1.03	0.63
Chambal rive	r and tributa	ries				
CH1	126.0	110.6	14.3	7.8	0.91	0.78
CH2	153.5	135.0	17.2	8.2	0.93	0.69
CH3	156.7	136.9	18.4	7.6	0.94	0.73
CH4	123.5	107.1	15.1	6.9	0.95	0.83
CH5	125.3	107.6	16.3	6.6	0.92	0.86
CH6	125.5	107.6	16.6	6.4	0.88	0.78
CH7	136.4	119.2	16.0	7.5	0.88	0.76
CH8	141.7	123.0	17.3	7.1	0.95	0.75
CH9	116.7	99.4	15.9	6.0	0.94	0.90
CH10	135.8	117.2	17.1	6.7	0.95	0.85
CH11	129.7	109.6	18.5	5.9	0.95	0.85
CH12	95.9	78.0	16.2	6.7	0.55	1.00
CH14	131.6	111.7	18.4	6.6	0.93	0.79
CH15	113.8	97.2	15.3	7.2	0.84	0.84
CH16	154.5	136.7	16.6	9.4	0.97	0.67

CH17	135.6	118.8	15.6	8.1	0.96	0.70
CH18	143.7	127.6	15.0	8.8	0.98	0.67
CH19	151.6	135.9	14.7	10.2	0.94	0.58
CH20	137.8	124.3	12.6	11.3	0.89	0.56
CH21	147.8	133.4	13.5	11.2	0.95	0.59
Ganga river						
G1	117.4	105.3	11.2	9.4	0.93	0.65
G2	808.5	739.5	65.3	12.2	0.91	0.47
G3	156.0	139.9	15.1	9.3	0.95	0.58
G4	210.2	190.6	18.4	9.0	0.94	0.51
G5	156.7	142.4	13.2	12.4	0.83	0.71
G6	295.7	267.0	27.0	9.9	0.96	0.49
G7	236.5	214.8	20.3	11.5	0.96	0.54
Granites						
GR98-1	280.2	253.4	26.2	9.7	0.94	0.23
GR98-2	185.9	176.6	8.5	34.0	0.96	0.46
GR99-1	153.8	146.6	6.5	39.5	0.98	0.53
GR99-2	147.5	139.2	7.6	31.4	0.90	0.47

The Chambal sediments have Eu/Eu\* ratios between 0.56 and 1.0, some of the sediment sample values are similar to that of Deccan Trap basalts (0.96). In the Chambal sediments, a significant Eu enrichment with respect to PAAS is observed. Feldspars are essential constituents of most igneous rocks. The feldspars and their secondary products derived from Deccan Trap basalts, which are enriched in Eu, might be the cause of the changes in Eu anomaly values.

Assuming the Eu anomaly values are specific to the tributaries, one can calculate the contribution of bed sediments by knowing the Eu anomaly values of the main river before and after the confluence of a tributary. The fraction of sediments coming from the tributary, f, is calculated as:

$$fx + (1 - f)y = z \text{ and } f = (z - y)/(x - y)$$
 ....6.8

where x, y and z are the Eu anomaly values of the sediment samples from the tributary, and of the main stream before and after the mixing. In the case of the Purola river joining the main Yamuna river, the fraction of sediments coming from the tributary to the main stream is  $\sim$ 10%. On the other hand, Godu Gad mixing with the Tons river, the

calculated fraction of the sediments from the tributary to the Tons river is  $\sim$ 67% (Chapter 5, Fig. 5.9).

	(La/Yb) <sub>CN</sub>	(La/Sm) <sub>CN</sub>	(Gd/Yb) <sub>CN</sub>	Eu/Eu*	Ce/Ce*
Yamuna main stream	n (n=10)				
Min.	8.6	3.5	1.1	0.49	0.91
Max.	11.8	4.0	1.6	0.61	0.97
Average	9.5	3.7	1.4	0.54	0.95
Yamuna tributaries (	n=13)				
Min.	5.7	3.3	0.7	0.37	0.88
Max.	13.7	4.2	1.7	0.73	1.03
Average	8.7	3.7	1.3	0.56	0.96
Chambal river (n=20)					
Min.	5.9	2.3	1.1	0.56	0.55
Max.	11.3	3.6	1.7	1.	0.98
Average	7.8	2.9	1.4	0.76	0.91
Ganga river* (n=7)					
Min.	9.0	3.4	1.2	0.47	0.83
Max.	12.4	4.4	1.6	0.71	0.96
Average	10.5	3.8	1.4	0.56	0.93
All bed sediments (n	=50)				
Min.	5.7	2.3	0.72	0.37	0.55
Max.	13.7	4.4	1.7	1.00	1.03
Average	8.8	3.4	1.4	0.63	0.93
Granites (n=4)					
Min.	9.7	3.9	1.3	0.23	0.90
Max.	39.5	4.3	3.7	0.53	0.98
Average	28.7	4.2	2.9	0.42	0.95
Leucogranite <sup>#</sup>	5.7	2.3	-	0.61	0.98
Deccan Basalt @	5.2	2.0	2.2	0.96	0.99
(Toranmal section)					
PAAS	9.2	4.3	1.3	0.65	0.98

Table 6.16. Range and mean concentrations of chondrite normalized ratios and Eu and Ce anomalies of the sediments from the Yamuna and the Chambal river catchments.

\* Sampled during March 1982 and November 1983 (Sarin et al., 1992).

<sup>#</sup> Average values of leucogranites from HHC series (Ayres and Harris, 1997).

<sup>@</sup> Typical Deccan Basalt flow value (Mahoney et al., 2000).



Fig. 6.21. Distribution of chondrite normalized Ce and Eu anomalies in bed sediments of the Yamuna and the Chambal rivers. In the Chambal river, one sample (CH-12) has a low Ce/Ce\* value of 0.55 which is not included in the plot.



Fig. 6.22. PAAS normalized REE composition of (a) the Decan basalts (Sen Gupta and Deshmukh, 1996) and (b) bed sediments of the Chambal river and tributaries.



Fig. 6.23. PAAS normalized REE composition of (a) granite samples and average leucogranites from the Yamuna river (b) bed sediments from the Yamuna river. REE data for leucogranites are from Ayres and Harris, 1997.



Fig. 6.24. PAAS normalized REE composition of the bed sediments from the Yamuna tributaries.



Fig. 6.25. PAAS normalized REE composition of the bed sediments from the Ganga river and its tributaries .

The PAAS normalized REE patterns in upstream and downstream locations of the Yamuna and the Chambal rivers are shown in Fig. 6.26. It is evident that the LREE are enriched with respect to the HREE in the downstream samples:  $[La/Lu]_{20}$  /  $[La/Lu]_{33}$  = 1.26, the numbers 20 and 33 denote samples from the upstream (RS98-20) and downstream (RS98-33) of the Yamuna river, respectively. Since all the samples except one is from the tributaries of the Chambal river, one of its tributary, Kali Sindh is considered. In the Kali Sindh, a tributary of the Chambal river, the LREE are depleted with respect to the HREE along downstream:  $[La/Lu]_5$  /  $[La/Lu]_{17}$  = 0.8, the numbers 5 and 17 denote samples from the upstream (CH-5) and downstream (CH-17) of the Kali Sindh respectively. Sedimentary transport may also result in changing REE patterns due to heavy mineral (notably zircon and monazite) fractionation (McLennan, 1989).



Fig. 6.26. Distribution of PAAS normalized REE patterns in the upstream and downstream samples from the Yamuna river and the Kali Sindh, a tributary of the Chambal river. (a) HREE are enriched relative to LREE in the downstream bed sediments of the Yamuna river,  $(La/Lu)_{upstream}/(La/Lu)_{downstream} = 1.3$ . (b) In case of the Kali Sindh, HREE are depleted in the downstream sediments,  $(La/Lu)_{upstream}/(La/Lu)_{downstream} = 0.8$ .



Fig. 6.27. Scatter plots of Ce vs Fe and Ce vs Mn for the bed sediments of the Chambal, the Yamuna and the Ganga rivers.



Fig. 6.28. The variation in (a)  $\Sigma REE vs. AI_2O_3$  (wt. %) (b)  $\Sigma REE vs. P_2O_5$  (wt. %) (c) La (ppm) vs.  $AI_2O_3$  (wt. %) (d) Yb (ppm) vs.  $AI_2O_3$  (wt. %) (e)  $(La/Yb)_{CN} vs. CaO$  (Wt. %) and (f)  $(La/Yb)_{CN} vs. AI_2O_3$  (wt. %). The Yamuna and the Ganga samples show the highest degree of LREE enrichment. No trends are obvious except that on average, the Chambal samples contain less La than Yamuna samples.



*Fig. 6.29. Plot of La against P in bed sediment samples from the Chambal and the Yamuna rivers.* 

Bulk chemical analysis of the bed sediment samples of the Yamuna and the Ganga bed sediments indicate that La (La being used as a proxy for total REE) is showing an increasing trend with aluminosilicate content (as represented by  $Al_2O_3$ ). This can be attributed to the association of REE with siliciclastic component (Fig. 6.28). There is, however, a spread of La for a given  $Al_2O_3$  indicating the presence of other heavy minerals or adsorbed component. On the contrary, those of the Chambal river do not show a linearly increasing trend. The data show that REE in the Chambal river sediments are not solely residing in the clay mineral fractions. The REE fractionation associated with each of these rivers may be recognized from the (La/Lu)<sub>CN</sub> and (La/Yb)<sub>CN</sub> ratios for the varying La concentrations in different samples. The ratios are reasonably constant which is similar to the observations made by Elderfield et al. (1990) for other major river basins of the world. Fig. 6.29 illustrates the variation of La

with P in the sediments. Generally La shows an increasing trend with P in the Yamuna sediments whereas in the Chambal river no such trend is discernible.



Fig. 6.30. The variation of Eu against Sm of the bed sediments of the Chambal and the Yamuna river samples.

The Eu/Sm ratio varied from 0.06 to 0.28 with a mean of 0.17 in the bed sediments (Fig. 6.30). Egashira (1997) reported that the plot of Ce/Eu against Eu/Sm is useful to group sediments according to their sources. As shown in Fig. 6.31, these ratios are plotted on a log-log plot. For Chambal river sediments, Ce/Eu ranged between 16.4 and 68.5 and Eu/Sm from 0.16 to 0.28. The corresponding values for the Yamuna river sediments are 53.3 -119.8 and 0.10 - 0.20 respectively. Thus the Chambal and the Yamuna sediments by and large fall on different regions of the plot due to the difference in their lithologies.



Fig. 6.31. Plot of Ce/Eu against Eu/Sm of the bed sediments from the Yamuna and the Chambal rivers. They fall in different groups with the same slope.

#### 6.3.3 Enrichment factor for trace and rare earth elements

Trace and rare earth element composition of the bed sediments in the Yamuna and the Chambal rivers and their several tributaries is plotted in Fig. 6.32 after normalizing to upper continental crust (UCC) values (Taylor and McLennan, 1985). Such a representation has previously been used for the Congo basin by Dupre et al. (1996) and for the Amazon basin by Gaillardet et al. (1997). The UCC-normalized elemental plot exhibits ample variability in the Yamuna sediments. The primary constituents of the crystallines in the Yamuna catchment are



Fig. 6.32. UCC-normalized multi-elemental diagrams of the Yamuna and the Chambal river sediment samples (filled circles). Also shown are the UCC-normalized granite and basalt values (open circles) for comparison.

granites and gneisses whereas the sedimentary units are composed of carbonates, shales, slates and quartzites (Valdiya, 1998). Fe, Mg and to some extent Ti are basically unaffected and have concentrations similar to the UCC and those that are less fractionated during weathering and transport (e.g., the REE). In the Chambal river, the pattern of bed sediments are similar to that of Deccan Trap basalts.

Surface adsorption of trace elements in aqueous solution by colloidal hydroxides is a well-known phenomenon and is suggested to be an important process affecting the transport of trace elements in natural water systems. Processes that include weathering and adsorption-desorption generally control the distribution of elements in suspended matter and sediments along the course of a river (Forstner and Wittmann, 1986). It is shown by Andersson et al. (1998) that enrichment of trace elements like uranium in non-detrital phases of sediments is mostly linked to enrichments in Fe oxyhydroxides and/or in organic matter, since adsorption is likely to occur mainly on these phases. The organic carbon content for the Chambal bed sediments is low with a mean of 0.78% and ranges between 0.03% and 1.8% (Table 6.12). Concentrations of trace elements such as Cu, Ni, Co and Cr were high in the Chambal river sediments compared to the Ganga sediments as the Chambal river receives sediments from Bundelkhand gneiss and Deccan basalts that are enriched in these elements (Mahoney, 1988).

In order to estimate the contribution of elements to sediments from other than natural sources, enrichment factors (EF) with respect to the composition of PAAS (Taylor and McLennan, 1985) are calculated.

$$EF = (X/AI)_{sample}/(X/AI)_{PAAS} \qquad \dots [6.9]$$

where  $(X/AI)_{sample}$  denotes the measured element/aluminum ratio of the sample and  $(X/AI)_{PAAS}$  denotes the corresponding element/aluminum ratio in PAAS. Distribution of EF for the measured elements is shown in Fig. 6.33. A value of EF  $\leq$ 2 can be considered to be of natural origin and a value of >2 is suggestive of anthropogenic sources (Grousset et al., 1995). In both the Yamuna and Chambal river sediment

samples, all heavy metals have EF  $\leq$  2 suggesting that they are mainly of natural origin. K remained moderately depleted in the Chambal river samples probably due to the relatively low K-rich igneous rocks in the Deccan Traps.



Fig. 6.33. The variations of the enrichment factor of the different elements in the Chambal and the Yamuna bed sediments with respect to PAAS are shown box plot representing statistical values. The boundary of the box closest to zero indicates the 25<sup>th</sup> percentile, a line within the box marks the median and the boundary of the farthest from zero indicates the 75<sup>th</sup> percentile. Whiskers above and below the box indicate the 90<sup>th</sup> and 10<sup>th</sup> percentiles. PAAS data from Taylor and McLennan, 1985.

The proportion of enrichment of REE of the bed sediments remained similar with increasing atomic number. HREE are more soluble and more strongly complexed than middle or light REE and that the LREE are more strongly absorbed on most subtracts (Byrne and Kim, 1990). Another factor that might explain the LREE enriched pattern, which was also pointed out by Goldstein and Jacobsen (1988) is mechanical sorting of the stream water suspended material. The HREE are concentrated in many heavy minerals, e.g., zircon and garnet. Since these minerals are preferentially transported along the streambed they may not have been sampled.

### 6.4 Conclusions

Based on a synoptic study of the streams within the Chambal river, TDS values ranged from 132 to 509 mg L<sup>-1</sup>. Total dissolved cation charge ( $TZ^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$ ) and anion charge ( $TZ^- = CI^- + NO_3^- + HCO_3^- + 2SO_4^{2-}$ ) in the Chambal waters varied from 2416 to 7656 µEq and 2166 to 7062 µEq respectively. Among cations, Na is by far the most abundant (molar) and constitutes 35 - 54% of total cations. The order of cation abundance in these stream waters is Na > Ca > Mg > K.

Among the anions, the abundance order is  $HCO_3 > CI > SO_4 > NO_3$  both in the headwater and in the downstream samples, with  $HCO_3$  constituting 60-90% of the total anions. The range of (Ca+Mg)/HCO<sub>3</sub> equivalent ratio between 0.85 and 1.2, a relatively high contribution of (Ca+Mg) to the total cations (TZ<sup>+</sup>) and high (Ca+Mg)/(Na\*+K) ratio indicate that weathering of Deccan Trap basalts and Vindhyan carbonates could be the source of the major ions to these waters. In addition, alkaline/saline soils present in the catchment contribute major ions to the Chambal river. The dissolved Si concentration in the streams ranges from 157 to 607  $\mu$ M. Conventional approaches to derive silicate weathering rates could not be employed, as Na, Ca and Mg have multiple sources. Hence silicate weathering is calculated based on Si abundances in the Chambal river. The SWR and CWR of Chambal basin is 7.9 x 10<sup>3</sup> kg km<sup>-2</sup> y<sup>-1</sup> and 22.6 x 10<sup>3</sup> kg km<sup>-2</sup> y<sup>-1</sup>.

Yamuna river waters have variable dissolved REE contents ( $87 < \Sigma REE < 1374$  ng L<sup>-1</sup>, Mean = 289 ng L<sup>-1</sup>) and displays negative Eu anomaly (0.49 < Eu/Eu\* < 0.73, Mean = 0.63). In case of Ce, most of the samples do not show discernable anomalies. However, in a few of them, there is a negative anomaly. These samples are from the Yamuna (RW99-13, RW99-17, RW99-51 and RW99-54) and Aglar (RW99-52) rivers. One sample collected from the Yamuna river at Rampur Mandi (RW99-58) shows the positive Ce anomaly value of 1.16 and the spring sample from Shahashradhara. (RW99-60) has the lowest value of 0.25. A comparison of PAAS normalized REE patterns of river water and bed sediments suggests that dissolved composition of REE is strongly fractionated and is enriched in MREE (Nd-Gd) with respect to sediments, presumably due to preferential dissolution of phosphate minerals (apatite) during weathering processes while the PAAS normalized REE pattern of sediments is nearly flat.

Bed sediments of the Chambal river are characterized by  $\Sigma REE$  concentrations in the range of 96 to 157 µg g<sup>-1</sup> (mean = 134 µg g<sup>-1</sup>). Ratios of LREE/HREE in the Chambal sediments vary from 4.8 to 9.9 (geometric mean=7.3). These sediments are having PAAS normalized REE patterns similar to Deccan Trap basalts due to the weathering of these rocks in their catchment. Also these sediments show slight LREE enrichment with respect to the Deccan Trap basalts. This is seen in the Kali Sindh, a tributary of the Chambal river, where (La/Lu)<sub>upstream</sub>/(La/Lu)<sub>downstream</sub> = 0.8. There is Eu enrichment with respect to Deccan Trap basalts. Feldspars are essential constituents of most igneous rocks. This Eu enrichment in the Chambal bed sediments is due to increase of feldspars and their secondary products in the sediments, which are enriched in Eu.

The Yamuna bed sediments are characterized by  $\Sigma REE$  concentrations in the range of 78 to 291 µg g<sup>-1</sup> (mean = 165 µg g<sup>-1</sup>). LHREE/HREE ratios are between 7.2 and 11.8 (geometric mean=9.0). The Yamuna sediments are having PAAS normalized REE patterns similar to sedimentary rocks (meta-sediments and leucogranites of the HHC series). There is HREE enrichment with respect to granites at Hanuman Chatti at

the Yamuna catchment. HREE are enriched relative to LREE in the Yamuna sediments downstream, (La/Lu)<sub>upstream</sub>/(La/Lu)<sub>downstream</sub> = 1.3.

Major fraction of the sediments to the Bay of Bengal is from the Ganga-Brahmaputra river system. From the study of Nd, Sr and O isotopic signatures of the ODP Leg 116 core from the Bengal Fan, Galy et al. (1996) and France-Lanord and Derry (1997) had shown that the source for ~80% of the detritus material since 20 Myr ago were from the meta-sedimentary rocks of the High Himalayan Crystalline (HHC) sequence; clastic and carbonate sediments of the Lesser Himalaya (LH) and Tythian Himalaya are the other important sources of sediment to the Bengal Fan during this period. From the PAAS normalized REE patterns and (La/Yb)<sub>CN</sub> ratios of the Yamuna sediments, it can be inferred that the Yamuna mainstream sediments are derived mostly from meta-sediments and leucogranites of the HHC series compared to the granites at Hanuman Chatti. More studies on Sr and Nd isotopic signatures on these samples are required to substantiate the above findings.

In order to estimate the contribution of elements to sediments from other than natural sources, enrichment factors (EF) with respect to the composition of PAAS are calculated. In both the Yamuna and Chambal river sediment samples, all heavy metals have  $EF \leq 2$  suggesting that they are mainly of natural origin. K remained moderately depleted in the Chambal river samples probably due to the relatively low K-rich igneous rocks in the Deccan Traps. The proportion of enrichment of REE of the bed sediments remained similar with increasing atomic number.

Chemical weathering reactions on the continents leads to extensive fractionation between the dissolved REE composition of river waters and that of river sediments and continental rocks. Solution and surface chemistry play a major role in establishing the REE composition of freshwater. Such detailed study on the distribution of REE in rivers helps to elucidate the pattern of their supply to the oceans via rivers.

Sample Code	River	Location	La	Се	Nd	Sm	Eu	Gd	Dy	Но	Er	Yb	Lu
Yamuna Riv	ver & Tribut	aries											
RW98-20	Yamuna	Downstream of Paligad bridge	30.8	62.6	25.2	5.0	0.72	3.6	3.4	0.73	2.1	1.8	0.26
RW98-25	"	Barkot	31.2	62.0	23.9	5.3	0.79	3.9	3.9	0.81	2.3	2.3	0.28
RW98-22	"	Upstream of Naugaon	29.5	57.7	23.8	5.2	0.85	3.6	3.9	0.90	2.5	2.2	0.34
RW98-14	"	Downstream of Barni Gad's confluence	30.8	57.9	21.9	5.2	0.73	3.8	3.7	0.81	2.2	2.2	0.28
RW98-12	"	Downstream of Nainbaug	37.7	75.6	27.7	6.3	0.88	4.4	4.5	0.93	2.8	2.7	0.37
RW98-9	33	Downstream of Aglar's confluence	38.6	78.1	30.2	6.6	0.89	4.7	5.0	1.1	3.1	2.9	0.42
RW98-6	"	Upstream of Ton's confluence	32.7	62.3	25.2	5.3	0.85	4.2	4.2	0.89	2.3	2.3	0.32
RW98-1	"	Rampur Mandi, Paonta Sahib	43.7	86.6	32.9	6.9	0.94	4.6	5.2	1.2	3.5	3.5	0.53
RW98-4	33	Downstream of Bata's confluence	35.8	73.3	30.0	6.5	1.0	4.6	4.7	0.99	2.9	2.7	0.38
RW98-33	"	Yamunanagar, Saharanpur	32.0	63.2	27.3	5.2	0.87	3.6	4.0	0.81	2.2	2.2	0.34
RW98-18	Didar Gad	Hanuman Chatti – Barkot Road	59.3	125	52.9	11.1	1.3	7.7	8.1	1.7	4.8	3.7	0.54
RW98-19	Pali Gad	Pali Gad bridge	27.7	55.2	24.1	4.9	1.0	3.5	3.7	0.87	2.6	2.6	0.39
RW98-13	Barni Gad	Kuwa	31.3	64.5	25.4	6.0	1.2	4.9	4.6	0.95	2.8	2.8	0.38
RW98-21	Kamola	Between Naugaon and Pirola	28.9	57.1	22.4	4.6	0.60	3.0	2.8	0.60	1.6	1.4	0.23
RW98-26	Godu Gad	Purola – Mori Road	67.7	135	49.0	11.3	1.1	7.7	7.4	1.7	4.9	5.3	0.82
RW98-27	Tons	Mori	37.8	75.8	27.3	6.2	0.85	4.5	4.5	0.98	2.6	2.9	0.36
RW98-29	Tons	Tiuni	52.4	105	38.9	7.9	0.88	5.5	8.0	1.9	6.0	6.2	0.94

Appendix 6.1. Rare Earth Element (concentrations in µg g<sup>-1</sup>) data of bed sediments from the Yamuna and Chambal rivers and their tributaries.

RW98-31	Shej Khad	Minas	33.9	65.5	27.6	5.9	1.0	4.0	4.3	0.87	2.5	2.3	0.34
RW98-30	Tons	Minas	49.1	94.4	36.2	8.0	1.1	5.3	7.1	1.6	5.1	5.1	0.76
RW98-32	Tons	Kalsi, upstream of confluence	41.8	85.2	33.1	6.7	1.0	4.6	4.9	1.0	2.9	2.9	0.42
RW98-8	Aglar	Upstream of Yamuna bridge	17.8	33.0	14.8	3.3	0.58	2.1	2.6	0.51	1.6	1.5	0.20
RW98-2	Giri	Rampur Mandi	33.1	66.6	27.5	6.0	1.1	4.6	4.8	1.0	3.1	2.8	0.41
RW98-11	Asan	Simla Road bridge	34.0	72.9	26.7	6.2	1.1	4.6	4.4	0.96	2.7	2.6	0.39
Chambal Ri	ver & Tribut	aries											
CH-1	Chamla	Burnagar	27.0	52.9	24.8	5.9	1.2	3.6	4.4	0.91	2.6	2.3	0.41
CH-2	Chambal	Between Burnagar and Ujjain	32.9	65.8	29.5	6.8	1.3	4.9	5.1	1.1	3.1	2.7	0.43
CH-3	Gambir	ű	32.7	66.4	30.5	7.2	1.4	4.9	5.6	1.2	3.3	2.9	0.46
CH-4	Shibra	Ujjain-Agar Road	25.8	52.4	23.1	5.8	1.3	3.8	4.7	0.95	2.7	2.5	0.37
CH-5	Kalisindh	Upstream of barrage on Indore- Guna Road	26.0	51.7	23.7	6.1	1.4	4.1	5.1	1.0	3.0	2.7	0.40
CH-6	Lakunda	Near Chomachoma village	26.5	50.5	24.4	6.2	1.3	4.2	5.1	1.0	3.1	2.8	0.42
CH-7	Chota Kalisindh	Bat village	30.6	56.9	25.2	6.5	1.2	3.9	5.0	1.0	3.0	2.8	0.40
CH-8	Newaj	Pachor village	29.5	60.0	26.7	6.8	1.4	4.4	5.3	1.1	3.3	2.8	0.44
CH-9	Dhudhi	Dhudhi village Tributary of Newaj	23.4	47.8	22.2	6.0	1.4	3.8	5.0	1.1	3.0	2.7	0.38
CH-10	Newaj	Kisanghat village 5 km before Rajghar	27.7	57.0	26.0	6.5	1.5	4.4	5.3	1.1	3.1	2.8	0.42
CH-11	Charganga	~15 km before Aklera Tributary of Newaj	25.0	52.0	25.9	6.8	1.6	4.9	5.9	1.1	3.3	2.9	0.42
CH-12	Chhapi	Arnia village Tributary of Kalisindh	22.2	27.0	22.9	6.0	1.7	4.2	5.4	1.1	2.9	2.3	0.32
CH-14	Kalisindh	~20 km to Jhalewar	26.4	53.4	25.7	6.3	1.5	5.5	5.4	1.2	3.3	2.7	0.43
CH-15	Aav	Suket village Tributary of Kalisindh	25.1	44.9	21.5	5.7	1.3	4.1	4.8	0.95	2.7	2.4	0.36

CH-16	Aamjar	~50 km from Kota Tributary of Kalisindh	34.4	69.5	26.7	6.2	1.2	5.0	4.8	1.1	2.9	2.5	0.40
CH-17	Kalisindh	Kota-Kisanganj Road	28.0	58.1	26.7	6.0	1.2	4.8	4.6	0.92	2.5	2.4	0.34
CH-18	Parbati	~1 km before Kisankanj	30.5	63.9	27.2	6.0	1.2	4.6	4.4	0.93	2.4	2.3	0.31
CH-19	Tabra	Upstream of bridge on Kota- Bundi Road	33.6	67.1	29.2	6.0	0.98	4.5	4.4	0.89	2.4	2.2	0.31
CH-20	Guda- pachad	Bridge on the Kota-Bundi Road	32.0	60.2	26.6	5.6	0.88	4.1	3.6	0.77	2.0	1.9	0.26
CH-21	Mangli	Bridge on the Kota-Bundi Road	32.7	66.3	28.2	6.1	0.98	4.3	3.9	0.83	2.2	2.0	0.29
<u>Ganga Rive</u>	r & Tributari	es*											
G-1	Yamuna	Saharanpur	27.2	52.6	21.0	4.5	0.81	3.3	3.1	0.76	1.9	2.0	0.24
G-2	Ganga	Rishikesh	203	375	132.3	29.2	3.7	20	18.1	3.9	10.6	11.2	1.6
G-3	"	Gurmuktesh-war	36.4	71.3	26.2	6.0	0.99	4.6	4.2	0.98	2.3	2.7	0.33
G-4	Ghaghara	Ayodhya	49.2	96.3	36.7	8.4	1.2	5.6	5.4	1.2	3.1	3.7	0.42
G-5	Yamuna	Allahabad	40.7	68.3	26.5	6.8	1.2	3.8	4.1	0.77	2.0	2.2	0.30
G-6	Ganga	Varanasi	67.3	135	52.0	12.4	1.6	8.2	7.8	1.5	4.3	4.6	0.61
G-7	Gomti	Dobni	55.3	109	41.1	9.0	1.3	6.4	5.7	1.2	3.3	3.2	0.49
<u>Granites</u>													
GR98-1	Yamuna Bank	K Hanuman Chatti	65.0	128	50.1	10.5	0.66	7.1	7.5	1.6	5.0	4.5	0.58
GR98-2	Yamuna Bank	Sharjhar Ghad	46.8	91.7	31.3	6.8	0.76	3.8	2.3	0.48	0.95	0.93	0.11
GR99-1	5 km downstre	eam of Hanuman Chatti	38.0	76.5	26.6	5.6	0.70	3.0	1.7	0.42	0.72	0.65	0.08
GR99-2	5 km downstre	eam of Hanuman Chatti	37.7	69.3	26.3	5.9	0.68	3.4	2.2	0.42	0.78	0.81	0.09

\* Sampled during March 1982 and November 1983 (Sarin et al., 1992)

# **Chapter 7**

# U isotopes in the Chambal and the Yamuna rivers

#### 7.1 Introduction

Studies on uranium in river waters are motivated by several considerations such as determination of its flux from continents, its mass balance in the oceans and its hydrological applications (Sarin et al., 1990; Osmond and Ivanovich, 1992; Palmer and Edmond, 1993; Snow and Spalding, 1994; Vigier et al., 2001). Attempts have also been made to understand the source(s) of uranium to rivers and the weathering processes controlling its distribution (Bhat and Krishnaswami, 1969; Ku et al., 1977; Borole et al., 1982; Sarin et al., 1990 and 1992b; Palmer and Edmond, 1993; Pande et al., 1994; Windom et al., 2000; Chabaux et al., 2001; Singh et al., 2003). Reliable estimation of world average uranium riverine input to the oceans is complicated by the wide variability in its concentration in individual rivers; however, based on its measurement in a very large number of rivers draining through different lithological and climatological regions, a global average value of  $0.25 - 0.30 \ \mu g \ L^{-1}$  has been derived (Scott, 1982; Sarin et al., 1990; Klinkhammer and Palmer, 1991; Palmer and Edmond, 1993).

Several studies have been made on uranium isotopes in dissolved phase and suspended particles in rivers flowing through India: the Himalayan rivers – the Ganga-Brahmaputra-Indus (Bhat and Krishnaswami, 1969; Sarin et al., 1990 and 1992b; Pande et al., 1994) and the peninsular rivers – the Narmada, the Tapti (Borole et al., 1982), the Godavari, the Krishna and the Mahanadi (Bhat and Krishnaswami, 1969; Somayajulu et al., 1993). These investigations have brought out the interrelation between uranium and major ions in rivers, their mode of transport and their behaviour in the estuarine environment. These studies also have shown that a number of highland rivers (Bhagirathi, Gontak, Ghaghra and the upper reaches of Ganga) of the Himalaya have higher uranium concentrations and U/(major ion) ratios than lowland rivers (Chambal, Betwa, Ken and Son). The high U/(major ion) ratios are not compatible with the major lithology of their drainage basins and suggest a need for an additional source of uranium (Palmer and Edmond, 1993; Pande et al., 1994; Chabaux et al., 2001; Singh et al., 2003). The suggested sources include uranium-mineralized zones, black shales and other organic rich sediments. Dalai et al. (2002a) and Singh et al. (2003) suggested based on U and Re measurements in organic rich sediments that dissolved Re (and U) in the Yamuna river can be derived from weathering of these sediments.

In natural systems, <sup>234</sup>U and <sup>238</sup>U would be in radioactive equilibrium, i.e., activity ratio of <sup>234</sup>U/<sup>238</sup>U would be 1.0, if uranium is in a closed system such that its isotopic composition is altered only by radioactive decay. This, however, is hardly the case in aqueous systems. <sup>234</sup>U/<sup>238</sup>U activity ratios have been found to vary considerably in waters (Bhat and Krishnaswami, 1969; Sarin et al., 1990 and 1992b; Pande et al., 1994; Riotte and Chabaux, 1999), soils (Lowson et al., 1986), sediments (Plater et al., 1992) and uranium ores (Richter et al., 1999). The causes for such variation is preferential leaching of <sup>234</sup>U compared with <sup>238</sup>U from solid phase, caused by radiation damage of crystal lattice upon alpha decay of <sup>238</sup>U, oxidation of less soluble tetravalent <sup>234</sup>U to more soluble hexavalent <sup>234</sup>U, and alpha recoil of <sup>234</sup>Th (and its daughter <sup>234</sup>U) into solution phase (Cherdyntsev, 1971; Kigoshi, 1971; Hussain and Lal, 1986). <sup>234</sup>U/<sup>238</sup>U activity ratios in waters reportedly vary from 0.5 to 40 (Osmond and Ivanovich, 1992; Bourdon et al., 2003), while that in soil the typical range is from 0.5 to 1.2 (Goldstein et al., 1997). The <sup>234</sup>U/<sup>238</sup>U activity ratios of the Himalayan and peninsular rivers also show distinct differences, the Himalayan rivers generally have <sup>234</sup>U/<sup>238</sup>U activity ratio close to equilibrium value whereas the peninsular rivers have values in the range of 1.1 - 1.8 (Bhat and Krishnaswami, 1969; Sarin et al., 1990 and 1992b; Pande et al., 1994).

In this work, concentration of dissolved uranium and <sup>234</sup>U/<sup>238</sup>U activity ratios have been measured in the Yamuna and the Chambal rivers to study weathering and mobility of uranium in these watersheds. These two rivers have, as discussed in Chapter 4, distinctly different drainage lithologies and climate,

which provide a means of understanding their influence on the uranium geochemistry of rivers.

## 7.2 Dissolved U in the Chambal and the Yamuna river systems

The results on uranium concentration and <sup>234</sup>U/<sup>238</sup>U activity ratio in the water samples are summarized in Table 7.1. The errors are  $\pm 1\sigma$  standard deviation derived from counting statistics and uncertainties in <sup>232</sup>U spike calibration. Typical  $\pm 1\sigma$  uncertainty in the concentration measurements is  $\pm 3$  %. The range and mean concentrations of uranium and <sup>234</sup>U/<sup>238</sup>U activity ratios of the samples are given in Table 7.2. The river water uranium content in the Chambal watershed ranges from 0.2 to 1.74  $\mu$ g L<sup>-1</sup>, whereas that of the Yamuna watershed the range is from 0.13 to 3.18  $\mu$ g L<sup>-1</sup> in post-monsoon period and 0.09 to 3.61  $\mu$ g L<sup>-1</sup> in summer (Table 7.2, Fig. 7.1). These concentrations bracket the average values of 1.72 and 1.81  $\mu$ g L<sup>-1</sup> reported for the Yamuna and the Ganga river systems by Sarin et al. (1990). In general, uranium in the Yamuna and the Chambal are much higher than the global average uranium concentration, 0.3 µg L<sup>-1</sup> in river waters (Sarin et al., 1990; Palmer and Edmond, 1993). In the Yamuna main stream, uranium is highest at its source and decreases steadily along its course, from 3.18  $\mu$ g L<sup>-1</sup> at Hanuman Chatti to 0.67  $\mu$ g L<sup>-1</sup> at Batamandi, in the base of the Himalaya. The decrease results mainly from mixing of the mainstream with its tributaries, which are lower in uranium. In the Chambal river system only one sample from the main stream was analyzed. Remaining 15 samples were collected from its various tributaries and hence the impact of mixing in its distribution along the course of the main channel could not be assessed.

The variation in uranium content of the Yamuna river during the two seasons sampled is <30% (Table 7.1). This is much less than the 2 or 3 fold differences reported for some of the rivers from India, such as the Ganga, the Sabarmati and the Cauveri by Bhat and Krishnaswami (1969) and Sarin et al. (1990). The much lower temporal variability observed in this study is because

sampling has not been carried out during monsoon, when the water discharge is at its peak and elemental abundances are at their lowest. Intra-annual variations in water discharge exert direct control on the abundance of dissolved constituents.

Sample	Type <sup>\$</sup>	<sup>238</sup> U	<sup>234</sup> U	<sup>234</sup> U/ <sup>238</sup> U	U	Σcat* <sup>†</sup>
Code <sup>@</sup>		dpm	ו L <sup>-1</sup>	A.R.	µg L⁻¹	(mg L <sup>-1</sup> )
Yamuna ri	ver and	tributaries (O	ctober 1998)			
RW98-1	М	0.49±0.01	0.51±0.01	1.05±0.02	0.65	26.8
RW98-2	Т	0.62±0.03	0.78±0.03	1.25±0.05	0.83	98.6
RW98-3	Т	0.23±0.01	0.33±0.01	1.43±0.06	0.31	54.7
RW98-4	М	$0.50 \pm 0.02$	0.58±0.02	1.16±0.04	0.67	58.7
RW98-5	Т	0.09±0.01	0.15±0.01	1.56±0.07	0.13	39.4
RW98-6	М	$0.74{\pm}0.02$	0.81±0.03	1.09±0.03	1.00	37.1
RW98-8	Т	$0.56 \pm 0.02$	0.65±0.02	1.17±0.03	0.75	70.6
RW98-9	М	$0.80 \pm 0.02$	0.87±0.03	1.09±0.03	1.07	34.9
RW98-12	М	0.62±0.02	0.66±0.02	1.05±0.02	0.84	27.1
RW98-16	М	2.37±0.06	2.46±0.07	1.04±0.02	3.18	20.7
RW98-18	Т	0.33±0.01	0.31±0.01	0.95±0.03	0.44	6.10
RW98-19	Т	0.30±0.01	0.33±0.01	1.11±0.03	0.40	21.6
RW98-20	М	2.21±0.06	2.30±0.06	1.04±0.02	2.97	21.2
RW98-21	Т	0.19±0.01	0.23±0.01	1.22±0.05	0.25	30.9
RW98-22	М	1.25±0.04	1.31±0.04	1.05±0.03	1.05	23.0
RW98-25	М	1.39±0.04	1.47±0.04	1.06±0.02	1.86	22.2
RW98-28	Т	0.34±0.01	0.34±0.01	1.01±0.03	0.46	11.1
RW98-29	Т	0.52±0.02	0.54±0.02	1.03±0.03	0.70	12.8
RW98-30	Т	0.54±0.01	0.56±0.01	1.05±0.02	0.72	24.0
RW98-32	Т	0.59±0.02	0.63±0.02	1.06±0.02	0.80	46.9
RW98-33	М	0.97±0.03	1.04±0.03	1.08±0.02	1.30	53.4
RW98-34	G	1.37±0.04	1.39±0.04	1.01±0.02	1.83	26.0
Yamuna ri	ver and	tributaries (J	une 1999)			
RW99-2	М	0.45±0.01	0.46±0.02	1.02±0.03	0.60	39.8
RW99-3	Т	0.76±0.02	0.96±0.03	1.26±0.03	1.02	119
RW99-4	Т	0.46±0.01	0.60±0.02	1.30±0.03	0.62	70.1
RW99-5	М	0.60±0.02	0.73±0.03	1.22±0.04	0.80	61.2
RW99-6	G	1.98±0.05	1.94±0.05	0.98±0.01	2.65	25.5
RW99-7	М	1.24±0.04	1.31±0.04	1.06±0.02	1.66	55.8
RW99-10	Т	1.00±0.04	1.07±0.04	1.07±0.03	1.34	150

Table 7.1. Concentrations of uranium isotopes and  $^{234}U/^{238}U$  activity ratios (A.R.) of the Yamuna and Chambal river water samples.

RW99-11	Μ	1.51±0.04	1.58±0.05	1.05±0.02	2.02	30.6
RW99-13	Μ	2.27±0.06	2.33±0.06	1.03±0.02	3.05	20.2
RW99-17	Μ	2.69±0.07	2.76±0.07	1.03±0.01	3.61	22.9
RW99-18	Μ	1.89±0.06	2.00±0.06	1.05±0.02	2.54	26.6
RW99-19	Μ	1.98±0.06	1.94±0.06	0.98±0.02	2.65	23.3
RW99-22	Т	0.36±0.01	0.36±0.01	1.00±0.03	0.49	9.62
RW99-24	Т	0.41±0.01	0.45±0.01	1.11±0.03	0.55	45.5
RW99-26	Т	0.15±0.01	0.16±0.01	1.05±0.03	0.20	8.33
RW99-27	Т	0.07±0.002	0.07±0.003	1.0±0.05	0.088	14.0
RW99-29	Т	0.57±0.02	0.60±0.02	1.06±0.03	0.76	46.9
RW99-30	Μ	1.24±0.04	1.27±0.04	1.02±0.02	1.67	45.3
RW99-31	Μ	1.06±0.03	1.08±0.03	1.02±0.02	1.42	39.5
Chambal riv	ver an	d tributaries (S	September 19	98)		
CH-2	Т	0.57±0.02	0.77±0.02	1.35±0.03	0.77	56.3
CH-3	Т	0.46±0.01	0.59±0.02	1.30±0.03	0.61	57.1
CH-4	Т	0.69±0.02	0.87±0.03	1.26±0.03	0.92	105
CH-5	Т	0.38±0.02	0.46±0.02	1.23±0.05	0.50	81.3
CH-6	Т	0.48±0.02	0.58±0.02	1.20±0.03	0.65	88.2
CH-7	Т	0.35±0.01	0.44±0.01	1.24±0.03	0.47	41.3
CH-8	Т	0.74±0.02	0.88±0.03	1.19±0.02	0.99	76.3
CH-10	Т	0.65±0.02	0.98±0.03	1.51±0.04	0.87	68.8
CH-11	Т	0.15±0.01	0.18±0.01	1.15±0.05	0.20	67.4
CH-12	Т	0.23±0.01	0.27±0.01	1.21±0.05	0.30	68.7
CH-14	Т	0.37±0.01	0.43±0.02	1.17±0.04	0.50	71.0
CH-15	Т	0.45±0.01	0.56±0.02	1.23±0.03	0.61	68.6
CH-17	Т	0.42±0.02	0.58±0.02	1.39±0.04	0.56	64.3
CH-18	Т	0.47±0.02	0.79±0.02	1.67±0.04	0.63	60.6
CH-21	Т	1.30±0.04	1.82±0.05	1.40±0.02	1.74	72.4
CH-22	Μ	0.31±0.01	0.39±0.01	1.27±0.03	0.41	46.4

\* Yamuna river data from Dalai (2001).
\* M – Yamuna mainstream; T – Yamuna tributary; G – Ganga river at Rishikesh.

<sup>@</sup> Location details for the samples are given in Appendixes 5.1 and 5.2 (Chapter 5).

Uranium concentrations and <sup>234</sup>U/<sup>238</sup>U activity ratios in the Chambal, the Yamuna and the Ganga measured in this study are compared with those reported by Bhat and Krishnaswami (1969) and Sarin et al. (1990) for these rivers at the same locations (Table 7.3). The corresponding  $\Sigma$ cat\* values (mg L<sup>-1</sup>) are also listed for comparison. These data show measurable variations over decadal timescales in both uranium concentrations and <sup>234</sup>U/<sup>238</sup>U activity ratios in the Chambal river. Factors contributing to this variability could be differences in

monsoon intensity and seasonal changes. The sample in this study was collected during monsoon whereas one of that of Sarin et al. (1990) was collected during post-monsoon (November). As a result, the uranium and  $\Sigma$ cat\* is lower in the present sample. The variation in <sup>234</sup>U/<sup>238</sup>U activity ratio is also quite significant between these two samples. A likely explanation for this is the variation in relative proportions of major lithologies being weathered during different time periods.

	U	<sup>234</sup> U/ <sup>238</sup> U							
	(µg L⁻¹)	(A.R.)							
Yamuna River System (October 1998), n=22									
Mean	1.01±0.80								
Minimum	0.13	0.95							
Maximum	3.18	1.56							
Yamuna River System (June 1999), n=19									
Mean	1.46±1.04								
Minimum	0.09	0.98							
Maximum	3.61	1.30							
<b>Chambal River System</b>	(September 1998), n=16								
Mean	0.67±0.36								
Minimum	0.2	1.15							
Maximum	1.74	1.67							

Table 7.2. Range and mean values for dissolved uranium concentration and <sup>234</sup>U/<sup>238</sup>U (A.R.) in the Yamuna and Chambal river systems.

In contrast, in the Yamuna and the Ganga, the <sup>234</sup>U/<sup>238</sup>U activity ratios have remained nearly the same within errors of measurement over the past few decades, whereas uranium concentration shows measurable changes. These variations can result from changes in water discharge and ground water input. For example, in the Ganga sample from Rishikesh, the uranium concentration in June 1998 collection, when the water discharge is low, is higher than those measured in samples of October-November (post-monsoon) collection. More importantly, this comparison indicates that uranium concentration in the Yamuna and the Ganga rivers is not affected in a major way by changes in land use and anthropogenic (fertilizer) inputs over the past few decades.



Fig. 7.1 Distribution of dissolved uranium concentration in the Yamuna and the Chambal rivers. (a) and (b) The Yamuna river during Oct 1998 and Jun 1999 respectively, (c) the Chambal river and (d) all the samples.

Scatter plot of dissolved uranium vs.  $\Sigma$ cat\* [the sum of Na\* (Na\*=Na-Cl, Na corrected for cyclic salts), K, Mg and Ca concentrations measured in these waters] is given in Fig. 7.2. Borole et al. (1982) and Sarin et al. (1990) observed an overall linear trend between uranium concentration and  $\Sigma$ cat\* for the samples from the Ganga-Brahmaputra rivers, Narmada and Tapti basins. Such a linear trend would result if uranium and  $\Sigma$ cat\* are released to rivers from their drainage basins in a roughly constant ratio. There is a suggestion of a positive trend for the Chambal water data. For the Yamuna river, the results fall into two groups (Fig. 7.2b): (i) the tributary samples which show an overall positive trend with  $\Sigma$ cat\* and (ii) Yamuna mainstream samples (<sup>238</sup>U concentration  $\geq$ 0.6 µg L<sup>-1</sup>) which show decrease in <sup>238</sup>U with  $\Sigma$ cat\*. This mainstream data, as mentioned

earlier, can be understood in terms of mixing of uranium rich source water from the Hanuman Chatti with uranium poor, cation rich tributaries. The scatter in the U -  $\Sigma$ cat\* plots (Fig. 7.2a and c) can be influenced by several factors, such as (1) lithology of the basin. The river basins are multi-lithological and hence the U/Σcat\* ratios released to water from rocks/soil could have significant variability (2) non-conservative behaviour of Ca resulting from CaCO<sub>3</sub> precipitation. This will have impact on Ca concentration and  $\Sigma cat^*$  and to some degree on uranium. In effect, this could affect the  $U/\Sigma cat^*$  ratio. This could be important for Chambal and the Yamuna tributaries in lower reaches, which show calcite supersaturation. (3) the supply of recycled salts from alkaline/saline soils, especially in the Chambal river system. The impact of this on U- $\Sigma$ cat\* plot needs further study, however, the strong correlation between U-Cl and U-SO<sub>4</sub> in these rivers (see discussion below) is an indication that these salts could be influencing the uranium abundance of the rivers. (4) groundwater/anthropogenic inputs. Groundwater input could be seasonal. The role of anthropogenic input to uranium is difficult to assess, however, between the two basins, the Yamuna should be relatively free of this, as it is more pristine watershed, particularly its upper reaches. The Chambal on the other hand, has part of its drainage through agricultural land and urbanized regions. However, the observation that samples collected about 2 decades apart have similar uranium is an indication that anthropogenic input may not be a major source for uranium even for these waters. The role of uranium-rich minerals in its supply is another variable, the impact of which needs to be assessed.

Plots of uranium concentration against  $HCO_3$  in the Yamuna and Chambal rivers (Fig. 7.3) also show similar trend as U -  $\Sigma$ cat\*. Similarity of the plots of U vs.  $\Sigma$ cat\* and U vs.  $HCO_3$  can be understood in terms of linear relationship existing between  $\Sigma$ cat\* and  $HCO_3$  in both the Chambal and Yamuna rivers (Fig. 7.4). Similar trends between U- $\Sigma$ cat\* and U- $HCO_3$  are also reported for the Narmada, Tapti rivers (Borole et al., 1982) and for the world rivers (Mangini et al., 1979). Significant positive correlation between U and CI is observed for both the

Yamuna and the Chambal rivers (Fig. 7.5). Samples deviating from the general trend are from Rishikesh (RW98-34, RW99-6), Hanuman Chatti (RW98-16, RW99-13), Pali gad (RW98-20) and Kuthanur (RW99-17), which have high uranium contents with low CI (open circles, Fig. 7.5). It is tempting to interpret this correlation in terms of supply of uranium and CI from same source such as halite weathering, evaporated rain and saline soils. This idea needs further check through studies of soil profile from the region and their water leaches. It is also possible that CI aids in solubilizing uranium from river basins. It is known that U(VI) forms complexes with CI and SO<sub>4</sub> in groundwater in oxidizing conditions and these species become more stable due to the higher ionic strength (Lemire, 1988). Alternately, salts leached from saline soils along the stream may contribute to this trend. Such saline soils are known to be dispersed along the drainage basin of the Chambal but not in the Yamuna-Ganga drainage area in the Himalaya. Further, such a hypothesis would also require these salts contribute to uranium in these rivers. More studies are needed to understand the linear trend between U and CI (Fig. 7.5) as well as U and SO<sub>4</sub>.

<b>River/location</b>	Sample date	Σcat* <sup>†</sup> mg L <sup>-1</sup>	U µg L <sup>-1</sup>	<sup>234</sup> U/ <sup>238</sup> U activity ratio	Ref.
Yamuna	11/1983	86.0	2.52	1.07±0.03	2
@Saharanpur	10/1998	53.4	1.30	1.08±0.03	3
Yamuna	11/1983	43.4	1.72	1.01±0.03	2
@Musoorie	10/1998	70.6	1.07	1.09±0.03	3
Ganga	1/1968 <sup>\$</sup>	-	1.92	1.03±0.03	1
@Rishikesh	11/1983	32.2	2.25	1.04±0.03	2
	10/1998	26.0	1.83	1.01±0.02	3
	6/1999	25.5	2.65	0.98±0.01	3
Chambal	9/1982	50.6	0.88	1.41±0.04	2
@Dholpur	11/1983	79.0	1.61	1.58±0.04	2
	9/1998	64.3	0.56	1.39±0.04	3

Table 7.3. Decadal variations of U concentrations and <sup>234</sup>U/<sup>238</sup>U activity ratios in the Ganga, Yamuna and Chambal rivers.

<sup>†</sup> Σcat<sup>\*</sup> = (Na<sup>\*</sup>+K+Ca+Mg), where Na<sup>\*</sup> is Na corrected for chloride. Data for Yamuna and Ganga samples are from Dalai (2001).

1. Bhat and Krishnaswami, 1969.2. Sarin et al., 1990.3. This study.

<sup>&</sup>lt;sup>\$</sup> Sample is collected at Haridwar, close to Rishikesh.



Fig. 7.2. Plot of dissolved uranium concentration ( $\mu$ g L<sup>-1</sup>) vs.  $\Sigma$ cat\* (mg L<sup>-1</sup>) in (a) the Chambal and (b) the Yamuna mainstream and (c) Yamuna tributaries. In Figs. b and c, filled and open circles are samples collected during October 1998 and June 1999 respectively.  $\Sigma$ cat\* data for the Yamuna river are from Dalai et al., 2002.



Fig. 7. 3. Variations of uranium concentration ( $\mu$ g L<sup>-1</sup>) against HCO<sub>3</sub> ( $\mu$ M) in river water samples of (a) the Yamuna mainstream (b) the Yamuna tributaries and (c) the Chambal rivers and tributaries. In Fig. a and b, filled and open circles are samples during October 1998 and June 1999 respectively. There is an overall positive trend in the Chambal river samples. HCO<sub>3</sub> data for the Yamuna river are from Dalai et al., 2002.


Fig. 7. 4. Variation of  $\sum cat^*$  and HCO<sub>3</sub> (both in  $\mu Eqs.$ ) in (a) the Yamuna and (b) the Chambal rivers. There is a linear trend in both the Yamuna and Chambal rivers.  $\Sigma cat^*$  and HCO<sub>3</sub> data for the Yamuna river are from Dalai et al., 2002.



Fig. 7.5. Dissolved uranium ( $\mu$ g L<sup>-1</sup>) versus CI ( $\mu$ M) in (a) the Yamuna and (b) the Chambal rivers and their tributaries. In samples (open circles) from Rishikesh (RW98-34, RW99-6), Hanuman Chatti (RW98-16, RW99-13), Pali gad (RW98-20) and Kuthanur (RW99-17), the high uranium concentrations with corresponding low CI are due to mobilization of uranium from draining exposed black shales which have high uranium content. CI data for the Yamuna river are from Dalai et al., 2002.

#### 7.3 Sources of uranium to the Yamuna and the Chambal rivers

Uranium occurs as a trace element in rocks and minerals. During chemical weathering of these rocks and minerals, it is expected that uranium is released to solution along with major ions. This is because uranium forms soluble complexes with a number of anions in oxic, natural environments. Thus if uranium is distributed uniformly in rocks and minerals and the cations and uranium are released to rivers in approximately constant ratio, one would expect to have an overall linear relation between uranium and total cations in the rivers. But this may not be the case in general, as uranium in rocks could be associated with accessory minerals that are resistant to chemical weathering and/or in organicrich sediments and uranium minerals of the drainage basin, which could be heterogeneously distributed. As seen earlier, in the Yamuna main stream, uranium is highest at its source and decreases steadily along its course, from 3.18  $\mu$ g L<sup>-1</sup> at Hanuman Chatti to 0.67  $\mu$ g L<sup>-1</sup> at Batamandi, in the base of the Himalaya. The high concentration of uranium in the Yamuna river and generally in the Ganga-Brahmaputra river system (Singh et al., 2003) is intriguing. In the following discussion an attempt is made to constrain its sources to the Chambal and the Yamuna rivers.

The highest uranium concentration in the Yamuna river is in the sample from the Hanuman Chatti (Table 7.1), which is closest to source region of the Yamuna river. The lithology of the basin upstream of Hanuman Chatti is predominantly HHC and hence the high concentration of uranium in the Hanuman Chatti water has to be derived from HHC. Potential sources of dissolved uranium in the Yamuna headwaters are:

(i) Granites and meta-sediments. Granites and gneisses have uranium content typically of ~3  $\mu$ g g<sup>-1</sup>. The U/Na weight ratio in granites are ~0.3  $\mu$ g mg<sup>-1</sup> (Singh et al., 2003). Distribution of U/Na\* weight ratios in the Yamuna and the Chambal river water samples are shown in Fig. 7.6. Na\* is the Na concentration corrected for cyclic and halite contributions, i.e. Na\*=Na-Cl (Sarin et al., 1989).

The results show that in most samples U/Na<sup>\*</sup> weight ratios are < 0.5  $\mu$ g mg<sup>-1</sup>, similar to that in granites, though a significant number of samples from the Yamuna have higher U/Na<sup>\*</sup> weight ratios (upto 3.7  $\mu$ g mg<sup>-1</sup>). One possible source for the high U/Na<sup>\*</sup> in the headwaters could be local granites. Sharma et al. (1983) reported high uranium content in granites of the Ladakh batholith (leucogranites, aplites and porphyritic granites). Uraninite is known to be present (Cuney et al., 1984) in major minerals of leucogranites (such as muscovite, biotite, tourmaline, K-feldspar, plagioclase) and in the shear planes. As discussed in the Chapter 6, dissolved REE in the Yamuna river samples have MREE enrichment and this is attributed to dissolution of apatite minerals present in the granites. Uranium concentration in apatite is generally high (upto 0.02%, Altschuler, 1980; Kanai and Sakamaki, 1994; Jeanjean et al., 1995) where uranium substitutes for Ca in the apatite structures. Apatites being an easily weatherable mineral, it can contribute to uranium.

(ii) Uranium mineralized zones in the source regions. Saraswat and Mahadevan (1989) and Pachauri (1992) had suggested that occurrence of uranium mineralization is widespread in plutonic rocks above Main Central Thrust (MCT) in the Himalaya such as granites from Badrinath, Gangotri and Yamunotri. This localized U-mineralization can be a potential source of dissolved uranium to specific streams.

(iii) Organic rich sediments/black shales, which are generally rich in uranium. Singh et al. (2003), based on average concentration of uranium in black shales (~37  $\mu$ g g<sup>-1</sup>), have shown that their weathering can contribute significantly to the dissolved uranium of the Ganga river water, if their abundances in the drainage basin are in the range of 1-2%.

With a view to assess the role of organic rich sediments in contributing to uranium in the Yamuna river, the relation between dissolved rhenium and uranium is studied. It is known that uranium and rhenium are incorporated in organic rich sediments during their formation (Colodner et al., 1993). As a result, the concentration of these elements in such sediments are higher than that in common rocks and their oxidative weathering releases these elements to aqueous phases. Colodner et al. (1993) measured rhenium in the Ganga and the Brahmaputra and proposed black shales as a possible source to these rivers. Dalai et al (2002a) suggested that bulk of the dissolved rhenium in the Yamuna river system is derived from weathering of black shale/carbonaceous sediments. If rhenium and uranium are released to rivers from black shales, an overall positive trend between these elements can be expected. Analyzing the available data, however, do not show any discernable relationship between uranium and rhenium (Dalai, 2001) in the Yamuna river system (Fig. 7.7a and b). The lack of correlation between dissolved rhenium and uranium in the Yamuna river samples can result if (i) black shale weathering is not a major source of dissolved uranium in the Yamuna river system and/or (ii) black shales have widely different U/Re ratios. The U/Re ratios in the black shales from the Lesser Himalaya have a wide range between 0.07 – 30  $\mu$ g ng<sup>-1</sup> (Singh et al., 1999; Singh et al., 2003). Thus, from the available data, it is difficult to conclude that the scatter in Fig. 7.7a and b is due to the lack of supply of uranium and rhenium from organic rich sediments or because of variations in U/Re ratios in them.

In the case of the Chambal river, most of the samples have uranium concentration in the range of  $0.2 - 1.0 \ \mu g \ L^{-1}$  except one sample (CH-21) from Banas, which is having uranium content of 1.74  $\mu g \ L^{-1}$ . Deccan Trap basalts have low uranium concentration. The high uranium concentration found in the Banas river sample (CH-21) could be due to the presence of gneiss and schist of the Pre Aravallis rocks in its catchment area.

#### 7.4 Variation in uranium isotope ratios

The sedimentary units in the Yamuna catchment are made of carbonates, shales, slates and quartzites whereas granites and gneisses are the primary constituents of the crystallines (Valdiya, 1998). In general, during weathering

process, <sup>234</sup>U from the rocks is expected to be released preferentially to solution leading to <sup>234</sup>U/<sup>238</sup>U activity ratio in excess of equilibrium value in rivers.



Fig. 7.6. U/Na\* weight ratios in the Chambal and the Yamuna rivers. Na\* data for the Yamuna river are from Dalai et al., 2002.

The <sup>234</sup>U/<sup>238</sup>U activity ratios of samples from the Chambal watershed are in the range of 1.15 to 1.67 while those of the Yamuna watershed are lower (range = 0.95 to 1.56, during post-monsoon and 0.98 to 1.30, during summer, Table 7.2, Fig. 7.8). In the Yamuna drainage basin, the <sup>234</sup>U/<sup>238</sup>U activity ratios in many rivers show only marginal excess of <sup>234</sup>U or radioactive equilibrium value. <sup>234</sup>U concentration in excess of the equilibrium value, <sup>234</sup>U<sub>xs</sub>, can be expressed as:

$$^{234}U_{xs} = (R - 1) \times U_{conc}$$
 ...[7.1]

For a given  ${}^{234}U_{xs}$  in the waters, the  ${}^{234}U/{}^{238}U$  activity ratio (R) could be less pronounced when they have high  ${}^{238}U$  concentration. This may be a contributing factor for the lower  ${}^{234}U/{}^{238}U$  activity ratios in the Yamuna river compared to the Chambal river system.

Chabaux et al. (2001) had shown that dissolved <sup>234</sup>U/<sup>238</sup>U activity ratio in the Himalayan rivers are significantly different in the various main structural units: slightly lower values from 1.0 (equilibrium value) in the TSS area, slightly higher than 1 in the LH and HHC regions and much higher in the Siwaliks area. In this study, all but one of the tributaries of the Yamuna river show  $^{234}U_{xs}$  with two of them, the Bata and the Amlawa (RW98-3, RW98-5), having quite high <sup>234</sup>U/<sup>238</sup>U activity ratio, 1.43  $\pm$  0.06 and 1.56  $\pm$  0.07 during the post-monsoon period. The source of <sup>234</sup>U<sub>xs</sub> in these rivers is intriguing. These two tributaries, flow predominantly through carbonates in the Lesser Himalaya/Siwaliks area and have the lowest uranium concentration among the samples measured. Considering that carbonates are easily weatherable, such high ratios are not expected in the rivers draining them. The U/Ca weight ratio in these rivers are 8.1 and 4.4 ng mg<sup>-1</sup>, which fall within the range of U/Ca weight ratio measured in Precambrian carbonates of the Himalaya (Singh et al., 2003). These authors also reported carbonates with  $^{234}$ U/ $^{238}$ U activity ratio of 1.19  $\pm$  0.03 from Gangolihat-Pithoragarh region. They hypothesized that the high <sup>234</sup>U/<sup>238</sup>U activity ratio in the carbonates may be due to incorporation of fluids containing <sup>234</sup>U excess (groundwater, surface water and metamorphic fluids) into the carbonates during metamorphism. The Song river, a tributary of the Ganga, flowing through Siwaliks has a high  $^{234}$ U/ $^{238}$ U activity ratio of 1.44 ± 0.04 (Sarin et al., 1992). Low  $^{234}$ U/ $^{238}$ U activity ratio in the rivers flowing in the HHC-LH area and high  $^{234}$ U/ $^{238}$ U activity ratio in the rivers flowing in Siwaliks are explained by Chabaux et al. (2001) in terms of differences in water-rock interactions in subsurface environments. The Higher Himalayan Crystalline series and Lesser Himalaya (HHC-LH) formations consist of shale and gneisses that have low water storage capabilities. In contrast, the Siwaliks region consists of interbedded argillaceous and sandy rocks, the latter serving as good aquifers. As a result, tributaries flowing through the Siwaliks are likely to have more pronounced <sup>234</sup>U/<sup>238</sup>U disequilibrium. Also the role of groundwater and Precambrian carbonates in contributing to high <sup>234</sup>U/<sup>238</sup>U activity ratios to these tributaries needs further study.

The plot of <sup>234</sup>U/<sup>238</sup>U activity ratio versus HCO<sub>3</sub> shows an increasing trend especially for the samples collected after the monsoon (October 1998). The HCO<sub>3</sub> content of Yamuna waters increases downstream and in its tributaries in the lower reaches, due to weathering of limestone and dolomites (Fig. 6.7d). This is also seen in the mixing plot of <sup>234</sup>U/<sup>238</sup>U activity ratio versus <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratio plot (Fig. 7.7c). The data show an inverse trend, samples with high <sup>87</sup>Sr/<sup>86</sup>Sr ratios have low <sup>234</sup>U/<sup>238</sup>U activity ratios and vice versa. The end members contributing to low <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratios can be Precambrian carbonates, evaporites and phosphates and the other end member, the silicates and calcsilicates of the HHC-LH which are having elevated <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratios (Bickle et al., 2001; Dalai, 2003). The samples with lower <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratios, characteristic of tributaries from lower reaches draining carbonates, have higher <sup>234</sup>U/<sup>238</sup>U activity ratio. Consequently, the trend in Fig. 7.7c requires that lithologies contributing to high <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio have to supply uranium to water with near equilibrium <sup>234</sup>U/<sup>238</sup>U activity ratio.

The observed <sup>234</sup>U/<sup>238</sup>U activity ratios in the Yamuna and the Chambal rivers bracket the range (0.95 – 1.67) for world rivers given by Scott (1982), as well as for the rivers Ganga and Indus (Sarin et al., 1990 and 1992; Pande et al., 1994). Sarin et al. (1990) reported for the Ganga river system a distinct difference in <sup>234</sup>U/<sup>238</sup>U activity ratio between the lowland (Chambal, Betwa, Ken and Son) and highland waters (Gontak, Ghaghra and the upper reaches of Ganga) and attributed the difference to the variation in the geology of their drainage basins and the type of weathering processes. The near equilibrium value of <sup>234</sup>U/<sup>238</sup>U activity ratio in the highland rivers is similar to that observed in many rivers of the Yamuna river system in this study.

Plots of <sup>234</sup>U/<sup>238</sup>U activity ratio versus 1/U of the Yamuna and the Chambal rivers are shown to assess mixing relationship between various end members (Fig. 7.9). The data from samples of the Yamuna mainstream and tributaries (collected during October 1998) and the Chambal river system (September 1998)

seem to fall on an overall mixing trend, with significant scatter. The scatter may be due to multiple end members, with their own characteristic <sup>234</sup>U/<sup>238</sup>U activity ratio and uranium concentration. The mixing trend of the Yamuna shows that its low concentration end member has high <sup>234</sup>U/<sup>238</sup>U activity ratio contrary to that in the Chambal river.



Fig. 7.7. Plot showing (a) and (b) Re versus U in the Yamuna maistream and tributaries, (c)  $^{234}U/^{238}U$  activity ratio versus  $^{87}Sr/^{86}Sr$  isotopic ratio and (d)  $^{234}U/^{238}U$  activity ratio versus HCO<sub>3</sub> of the Yamuna river water samples. Filled and open circles denote samples collected during October 1998 and June 1999 respectively. There is no discernable relation between rhenium and uranium. Re, Sr and  $^{87}Sr/^{86}Sr$  isotopic ratio data are from Dalai (2001).

Concentrations of dissolved uranium (in  $\mu g L^{-1}$ ) as well as  $^{234}U/^{238}U$  activity ratios are plotted as river flow diagram showing uranium variation downstream of the Chambal and the Yamuna rivers (Fig. 7.10 and 7.11). Sample from Hanuman Chatti (RW98-16) has U concentration of 3.18 µg L<sup>-1</sup> with <sup>234</sup>U/<sup>238</sup>U activity ratio of 1.04  $\pm$ 0.02. The uranium concentration in the water samples of the Yamuna river steadily decreases from this value to 0.67  $\mu$ g L<sup>-1</sup> (RW98-4) along downstream. Except Didar Gad and Tons, all the other tributaries are bringing waters with  $^{234}$ U/ $^{238}$ U activity ratio >1.1 to the Yamuna river.

Table 7.4. Dissolved uranium concentrations and uranium weathering rates in the Yamuna and the Chambal rivers compared with the major Indian rivers.

River	Area 10 <sup>6</sup>	Water flow	Uranium Conc.	Uranium weathering rate		Ref.
	km <sup>2</sup>	km³ y⁻¹	µg L⁻¹	10 <sup>6</sup> g y⁻¹	kg km <sup>-2</sup> y <sup>-1</sup>	
Indian rivers						
Yamuna	0.0096	10.8	1.46	16	1.67	1
@Batamandi						
Yamuna	0.140	93	1.72	160	1.14	3
@Allahabad						
Chambal @Udi	0.139	30	0.67	20	0.14	1
Chambal @Udi	0.139	30	1.04	31	0.22	3
Gomti	0.030	8	8.06	61	2.0	3
Betwa	0.046	10	2.88	29	0.63	3
Ken	0.028	11	1.80	20	0.70	3
Son	0.071	32	0.49	16	0.22	3
Gandak	0.045	52	2.33	121	2.62	3
Ghaghara	0.128	94	1.71	161	1.26	3
Ganga	0.975	393	3.97	1789	1.83	3
Brahmaputra	0.58	609	1.69	1019	1.76	3
Godavari	0.303	84	0.77	65	0.21	2
Krishna	0.260	67	1.16	78	0.30	2
Narmada	0.090	41	0.50	20	0.22	2
Tapti	0.062	18	0.22	4	0.06	2
Mahanadi	0.142	67	0.25	65	0.46	2
Indus	0.97	238	2.21	526	0.54	4
1. This work	is work 3. Sarin et al., 1990					

2. Borole et al., 1982

3. Sarin et al., 1990

4. Pande et al., 1994



Fig. 7.8. Histograms showing dissolved <sup>234</sup>U/<sup>238</sup>U (A.R.) in the Yamuna river during October 1998, June 1999 and the Chambal river during September 1998.



Fig. 7.9. Plot of  ${}^{234}U/{}^{238}U$  activity ratio versus reciprocal uranium concentration in (µg  $L^{-1})^{-1}$ , for river water samples from the Yamuna and the Chambal watersheds. The samples were collected during (a) October 1998 and (b) June 1999 and (c) September 1998. In the mixing diagram (a), a trend of mixing of water with more dilute runoff waters with higher  ${}^{234}U/{}^{238}U$  activity ratio contrary to that in the Chambal river system (c) is seen.



Fig. 7.10. River flow diagram showing uranium variation downstream of the Chambal river. Concentration of dissolved uranium ( $\mu$ g L<sup>-1</sup>) is shown in black and <sup>234</sup>U/<sup>238</sup>U activity ratio in red. Only tributaries that are sampled for uranium isotopes are shown.



Fig. 7.11. River flow diagram showing uranium variation downstream of the Yamuna river. Concentration of dissolved uranium ( $\mu$ g L<sup>-1</sup>) is shown in black and <sup>234</sup>U/<sup>238</sup>U activity ratio in red. Only tributaries that are sampled for uranium isotopes are shown.

#### 7.5 Uranium weathering rates from the Yamuna and the Chambal rivers

Using the average uranium concentration (Yamuna: 1.46  $\mu$ g L<sup>-1</sup>; Chambal: 0.67  $\mu$ g L<sup>-1</sup>) and water discharge data (Table 7.4), it can be estimated that ~16 and ~20 tons of uranium are transported annually in the dissolved form from the Yamuna river at Batamandi (the foothills of the Himalaya) and the Chambal river at Udi respectively. Uranium weathering rates to the Bay of Bengal through the major Indian rivers are dominated by the Ganga-Brahmaputra rivers. In this study, the weathering rate of uranium in the Yamuna river is 1.67 kg km<sup>-2</sup> y<sup>-1</sup> at Batamandi in the foothills of the Himalaya. The Himalayan rivers (Ganga, Brahmaputra, Yamuna, Gomti, Gandak and Ghaghara) have uranium weathering rate of 1 – 2 kg km<sup>-2</sup> y<sup>-1</sup> (Sarin et al., 1990), much higher than that of the Peninsular rivers (Chambal, Betwa, Ken, Son, Narmada, Tapti, Mahanadi, Godavari and Krishna, 0.1 - 0.5 kg km<sup>-2</sup> y<sup>-1</sup>). In the Chambal river, the uranium weathering rate is 0.14 kg km<sup>-2</sup> y<sup>-1</sup>.

Uranium weathering rate of the Chambal river (0.14 kg km<sup>-2</sup> y<sup>-1</sup>) is a factor of ~4 lower to that of the other lowland tributaries of the Yamuna, such as the Betwa and the Ken (0.63 and 0.70 kg km<sup>-2</sup> y<sup>-1</sup> respectively) most likely due to the low uranium concentration in the Deccan Trap basalts. The observed low uranium weathering rate of the lowland rivers (Chambal, Betwa, Ken, Son) compared to that of the highland rivers (Yamuna, Gomti, Gandak and Ghaghara) reinforces the earlier finding that the uranium fluxes to the Ganga-Brahmaputra originates mainly from weathering of the HHC along with associated minerals, uraninites/apatites in leucogranites and uranium mineralized zones (Sarin et al., 1990; Chabaux et al., 2001; Singh et al., 2003).

#### 7.6 Anthropogenic input of uranium

One of the issues pertaining to uranium distribution in rivers is its potential contribution from anthropogenic sources. Uranium is a trace constituent of many phosphate fertilizers (Guimond and Hardin, 1989). It is known that rivers draining highly fertilized regions can have high uranium (Snow and Spalding, 1994;

Zielinski et al., 1997 and 2000). Goldstein et al. (1997) found depleted  $^{234}$ U/ $^{238}$ U ratios in soil samples of elevated uranium concentrations and considered it to be a contribution from anthropogenic uranium. Average crustal abundance of uranium is ~1 µg g<sup>-1</sup> (Taylor and McLennan, 1985). Phosphatic fertilizers have uranium concentrations in the range of 20 to 200 µg g<sup>-1</sup>. In these fertilizers, the uranium content correlates positively with percentage of P<sub>2</sub>O<sub>5</sub> (Spalding and Sackett, 1972); these uranium concentrations are comparable to the range of uranium found in phosphate rock from major phosphate fertilizer producing areas of the world (Menzel, 1968). The considerable enrichment of uranium in fertilizers compared to soils suggests that fertilizers could contribute to dissolved uranium in rivers having their catchments in agricultural areas (Mangini et al., 1979).

The Chambal basin, particularly its lower reaches, have agricultural areas and hence anthropogenic supply of uranium from the use of phosphatic fertilizers is of concern. Attempts to assess this based on variation in uranium concentration under decadal timescales have not been fruitful. The value in 1998 is significantly lower than that in 1983, even in samples collected during the same month. Considering that the average concentration of uranium in Chambal river system is ~0.7  $\mu$ g L<sup>-1</sup> and has similar values over the past two decades, uranium content in the Chambal river is not significantly affected by anthropogenic phosphate fertilizer use.

#### 7.7 Conclusions

The river water uranium content of the Chambal watershed ranged from 0.2 to 1.74  $\mu$ g L<sup>-1</sup>, whereas that of the Yamuna watershed, it ranged from 0.13 to 3.18  $\mu$ g L<sup>-1</sup> in post-monsoon period and 0.09 to 3.61  $\mu$ g L<sup>-1</sup> in summer. These data overlaps with the value of ~1.81  $\mu$ g L<sup>-1</sup> reported for the Ganga river system. However, the global average uranium concentration in river waters is 0.3  $\mu$ g L<sup>-1</sup>, less by about an order of magnitude. About 16 and 20 tons of uranium are transported annually in the dissolved form from the Yamuna river at Batamandi in the foothills of the Himalaya and the Chambal river at Udi respectively.

In the Yamuna main stream, uranium is highest at its source and decreases steadily along its course, from  $3.18 \ \mu g \ L^{-1}$  at Hanuman Chatti and 0.67  $\ \mu g \ L^{-1}$  at Batamandi, in the base of the Himalaya. The decrease results mainly because of mixing of the mainstream with its tributaries, which are lower in uranium. The high concentration of uranium in the Hanuman Chatti water has derived from weathering of the HHC and associated accessory minerals and uranium mineralized zones.

The poor correlation between dissolved rhenium and uranium in the Yamuna river samples suggests that either black shale weathering is not a major source of dissolved uranium in the Yamuna river system or that the variability of Re/U ratio in the sediments is too high to discern their importance in supplying uranium to the Yamuna river system.

In the Yamuna drainage basin, the <sup>234</sup>U/<sup>238</sup>U activity ratios in many rivers show only marginal excess of <sup>234</sup>U or radioactive equilibrium value. However, two tributaries, the Bata and the Amlawa, flowing through Precambrian carbonates of Lesser Himalaya/Siwaliks, have low uranium with high <sup>234</sup>U/<sup>238</sup>U activity ratios. The cause for the excess <sup>234</sup>U from the equilibrium value is presently unclear but this suggests the need to study the importance of Precambrian carbonates in supplying uranium with high <sup>234</sup>U/<sup>238</sup>U activity ratio. The plot of <sup>234</sup>U/<sup>238</sup>U activity ratio versus HCO<sub>3</sub> shows an increasing trend. The samples with lower <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratios, characteristic of tributaries from lower reaches draining carbonates, have higher <sup>234</sup>U/<sup>238</sup>U activity ratio. There is an overall inverse trend between <sup>234</sup>U/<sup>238</sup>U activity ratio and <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio in the Yamuna river system.

The Chambal river and tributaries have low uranium and higher <sup>234</sup>U/<sup>238</sup>U activity ratios due to fresh rock surface exposures and weathering of Deccan Trap basalts where radiogenic <sup>234</sup>U is preferentially leached relative to <sup>238</sup>U.

## **Chapter 8**

# Synthesis and scope for future research

#### 8.1 Important results of this study

#### 8.1.1 Ra isotopes in the ocean

Radium isotopes have found extensive application in seawater circulation studies. <sup>228</sup>Ra and <sup>226</sup>Ra were measured in surface waters of the western Bay of Bengal and the Arabian Sea during ten cruises. The ranges and mean (in parenthesis) concentrations for <sup>228</sup>Ra and <sup>226</sup>Ra in the Bay of Bengal are 6.8-42.1 (17.8±7.9) dpm/100 kg and 6.0-16.7 (9.2±2.2) dpm/100 kg respectively. (<sup>228</sup>Ra/<sup>226</sup>Ra) activity ratio ranges from 0.8 to 3.4 with a mean of 1.9±0.5. Both <sup>228</sup>Ra and <sup>226</sup>Ra and <sup>226</sup>Ra show inverse correlation with salinity.

The Ra isotope data were used to determine lateral and vertical mixing in the Bay of Bengal and the Arabian Sea. The horizontal eddy diffusivities in the Bay of Bengal derived using a one-dimensional diffusion model to coast-to-openocean horizontal transects of <sup>228</sup>Ra range from 5.1 x 10<sup>6</sup> to 2.5 x 10<sup>7</sup> cm<sup>2</sup> s<sup>-1</sup>.

To improve the understanding of mixing processes in these waters, the Ra isotope data were also modelled using a surface 2-D diffusion-advection model. A bivariate function,

$$C_{(x,y)} = C_{\theta} e^{-Ax} \cdot e^{-By}$$

where C<sub>0</sub>, A and B are constants, is fitted to the <sup>228</sup>Ra and <sup>226</sup>Ra data C<sub>(x,y)</sub>. Substituting C<sub>(x,y)</sub> in the two dimensional steady-state diffusion equation of Ra, the estimated values of the constants A and B can be related to eddy diffusivities and advection velocities in the zonal (x) and meridional (y) directions. From this relationship, the horizontal eddy diffusivities in the zonal and meridional directions are inferred to be  $1.3 \times 10^7$  and  $2.1 \times 10^8$  cm<sup>2</sup> s<sup>-1</sup> respectively in the absence of advection terms. Similarly, neglecting the influence of diffusion, advection velocities, w<sub>x</sub> and w<sub>y</sub> in the zonal and meridional directions, are derived to be 0.2 and 1.1 cm s<sup>-1</sup> respectively. The model-fit values C<sub>(x,y)</sub> of <sup>228</sup>Ra

concentrations are in good agreement with the measured values except in regions showing exceptionally high and low concentrations. Incorporating both the advection and eddy diffusion terms into the equation, it is found that increase in advection velocities in the zonal and meridional directions can change the eddy diffusivities and that such changes are more effective in the meridional direction compared to zonal direction in the region of study.

The eddy diffusivities,  $K_x$  and  $K_y$  (without advection) derived for the Bay of Bengal are higher by about an order of magnitude than the values obtained for the Arabian Sea. This is not unexpected considering the large volume of freshwater inflow and the turbulent conditions prevailing in the Bay of Bengal for most of the year. The eddy diffusivities derived are the first sets of such measurements in the Bay of Bengal.

Vertical diffusivities from 0.011 to 10.3 cm<sup>2</sup> s<sup>-1</sup> are obtained from <sup>228</sup>Ra depth profiles of the Bay of Bengal and the Arabian Sea. Higher values of vertical eddy diffusivities are more common in the Arabian Sea and can be explained in terms of intense upwelling regions in the Arabian Sea. These vertical mixing parameters derived using Ra isotopes are from the first studies in these regions.

#### 8.1.2. U and REE in the Yamuna and Chambal rivers

A study of the major cations and anions in the upstream of Chambal river has been carried out to assess the weathering processes occurring mostly in the Deccan Trap basalts. Total dissolved solids (TDS) in the Chambal river range from 132 to 509 mg L<sup>-1</sup>. The order of cation abundance in these stream waters is Na  $\approx$  Ca > Mg > K. Among the anions, the abundance order is HCO<sub>3</sub> > Cl > SO<sub>4</sub> > NO<sub>3</sub> both in the headwater and in the downstream samples, with HCO<sub>3</sub> constituting 60-90% of the total anions. Conventional approaches in the Chambal catchment to derive silicate weathering rates could not be employed, as Na, Ca and Mg have multiple sources. Hence silicate weathering is calculated based on Si abundances in the Chambal river. The silicate and carbonate weathering rates (SWR and CWR) of Chambal basin is 7.9 x  $10^3$  kg km<sup>-2</sup> y<sup>-1</sup> and 22.6 x  $10^3$  kg km<sup>-2</sup> y<sup>-1</sup> respectively. The flux of CO<sub>2</sub> consumed during silicate weathering,  $\Phi$ CO<sub>2</sub>, is (1.7±1.3) x  $10^5$  moles km<sup>-2</sup> y<sup>-1</sup>.

Dissolved uranium in the Chambal river ranged from 0.2 to 1.74  $\mu$ g L<sup>-1</sup>, whereas that of the Yamuna river ranged from 0.13 to 3.18  $\mu$ g L<sup>-1</sup> in postmonsoon period and 0.09 to 3.61  $\mu$ g L<sup>-1</sup> in summer. About 16 and 20 tons of uranium are transported annually in the dissolved form from the Yamuna river at Batamandi in the foothills of the Himalaya and the Chambal river at Udi respectively.

In the Yamuna drainage basin, the <sup>234</sup>U/<sup>238</sup>U activity ratios in many rivers show only marginal excess of <sup>234</sup>U or radioactive equilibrium value. However, two tributaries, flowing through Precambrian carbonates, have low uranium with high <sup>234</sup>U/<sup>238</sup>U activity ratios. The Chambal river and tributaries have low uranium and higher <sup>234</sup>U/<sup>238</sup>U activity ratios due to the exposure of fresh rock surfaces and weathering of basalts where radiogenic <sup>234</sup>U is preferentially leached relative to <sup>238</sup>U.

Dissolved rare earth elements (REE) in the headwaters of the Yamuna river draining through the southern slopes of Himalaya were measured for the first time in this study. Yamuna river water samples have relatively high and variable dissolved REE contents ( $87 < \Sigma REE < 1374$  ng L<sup>-1</sup>) compared to world average (Martin and Meybeck, 1979) and display negative Eu anomaly (0.49 < Eu/Eu\* < 0.73). In case of Ce, most of the samples do not show measurable anomalies. The REE concentrations in these samples vary widely.

The shale normalized REE pattern shows a distinct MREE enrichment. Preferential weathering/dissolution of minor phases in the basin, such as phosphatic minerals (apatite) can result in extensive REE fractionation, leading to river waters with MREE enrichments.

Bed sediments in the Yamuna and the Chambal rivers are characterized by  $\Sigma$ REE concentrations in the range of 78 to 291 µg g<sup>-1</sup> and 96 to 157 µg g<sup>-1</sup> respectively. The most remarkable characteristics observed in the REEnormalized patterns of bed sediments is the strong HREE enrichment with respect to the granites at Hanuman Chatti in the Yamuna river catchment. In contrast, the samples of the Chambal river show significant LREE enrichment and Eu enrichment with respect to the Deccan basalts at its catchment. The feldspars derived from Deccan Trap basalts present in the bed sediments, which are rich in Eu, might be the cause of the Eu enrichment.

HREE are enriched relative to LREE in the downstream bed sediments of the Yamuna river,  $(La/Lu)_{upstream}/(La/Lu)_{downstream} = 1.3$ . In the Kali Sindh, a tributary of the Chambal river, HREE are depleted in the downstream sediments,  $(La/Lu)_{upstream}/(La/Lu)_{downstream} = 0.8$ . HREE are more soluble and more strongly complexed than LREE, LREE are strongly absorbed onto sediments and mechanical sorting of the stream water suspended material could lead to these differences in the Chambal and the Yamuna bed sediments.

In order to estimate the contribution of elements to sediments from other than natural sources, enrichment factors (EF) with respect to the composition of PAAS are calculated. In both the Yamuna and Chambal river sediment samples, all heavy metals have  $EF \le 2$  suggesting that they are mainly of natural origin. K remained moderately depleted in the Chambal river samples probably due to the relatively low K-rich igneous rocks in the Deccan Traps. The proportion of enrichment of REE of the bed sediments remained similar with increasing atomic number.

Chemical weathering reactions on the continents lead to extensive fractionation between the dissolved REE composition of river waters and that of river sediments and continental rocks. Solution and surface chemistry play a major role in establishing the REE composition of freshwater. Such detailed study on the distribution of REE in rivers helps to elucidate the pattern of their supply to the oceans via rivers.

#### 8.2 Scope of future research

#### Radium isotopes in the Bay of Bengal:

It is well recognized that the Bay of Bengal is a unique oceanographic basin dominated by freshwater inputs from six large rivers. It is thus important to understand the general surface circulation features, where surface currents change directions during the southwest and northeast monsoon periods. Further studies should aim for systematic and closer sampling (preferably 1° x 1° grid size) covering the two different seasons in conjunction with data from CTD profiles and current meter measurements. Such an approach would reduce the uncertainties in estimating eddy diffusivities especially in the zonal direction in the model calculations using Ra isotopes.

In addition, the future studies should take into consideration the role of submarine groundwater discharge (SGD) to the Bay of Bengal. Recent studies (Moore, 1996; Buddemier, 2000) have addressed these issues and have demonstrated that groundwater may account for a significant fraction (~10%) of the freshwater inflow to the coastal ocean. Also, it is an important pathway for nutrients, trace elements and inorganic carbonates into the coastal areas (Moore 1997; Basu et al., 2001).

Ra isotopes, as tracers, have higher concentrations in the groundwater relative to seawater and low reactivity in the coastal ocean. These tracers integrate the groundwater signal over a significantly large region. Under steadystate conditions, the rate at which Ra isotopes are lost by mixing offshore is equal to the rate at which it is being added to the coastal region. From the concentration of Ra isotopes in the groundwaters and the rate of mixing of coastal waters, groundwater flux to the coastal region can be estimated.

#### Rare earth elements in river basins:

One of the significant aspects emerging from the pattern of dissolved REEs of the present data set requires that rigorous study of both the dissolved and suspended matter REE composition be extended to major river basins of India characterized by diverse geologic and lithologic terrains. The seasonal data would help to elucidate mechanisms controlling mobility of REE through surface and sub-surface flows. To understand controls on dissolved REE concentrations in the river waters, speciation modeling is required which will provide the complexing species likely to dominate the solution chemistry of REE in these rivers.

Several studies of Nd and Sr isotopes in rivers have provided important information on weathering processes as well as crustal evolution and composition (Goldstein et al., 1984; Goldstein and Jacobsen, 1987a and 1987b; Allegre et al., 1996; Aubert et al., 2001; Singh et al., 2002). When coupled with the signature of lanthanide concentrations, the Nd isotopic composition of rocks and minerals is an excellent indicator of differentiation and chemical evolution of the earth and of the provenance of the detrital minerals in the oceans.

Clay mineralogical studies in the Ganga-Brahmaputra rivers and continental shelf of the Bay of Bengal (Sarin et al., 1989; Raman et al., 1995; Heroy et al., 2003) revealed that the Himalayan province is characterized by abundant illite followed by chlorite, and the Deccan Province by abundant smectite, from the Deccan basalts. Chlorite is absent in the Peninsular rivers. Studies on the sediment cores from the Bay of Bengal have shown variations in clay mineral abundances that can be related to their supply, which may vary depending on the Himalayan uplift and erosion as well as climate change. Comprehensive studies on REE composition in conjunction with Sr and Nd isotopic composition on bedrock, soil weathering profiles, stream water and bed sediments of the Himalayan and Peninsular rivers would help to quantify transport and place constraints on the sources of sediments to the Bay of Bengal and their dispersion from the continental source regions to deposition in the marine environment over time.

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