Aquatic Geochemistry (2006) 12:73–101
DOI 10.1007/s10498-005-1421-4

Dissolved Uranium and $^{234}U/^{238}U$ in the Yamuna and the Chambal rivers, India

R. RENGARAJAN★, M. M. SARIN and S. KRISHNASWAMI
Planetary & Geosciences Division, Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India

(Received 5 January 2005; accepted 27 July 2005)

Abstract. Dissolved uranium concentration and $^{234}U/^{238}U$ activity ratio have been measured in two distinctly different Indian drainage systems: the Yamuna headwaters in the Himalaya and the Chambal river system in the plains to study the weathering and mobility of uranium in these watersheds. The dissolved uranium in the Chambal river system ranges from 0.2 to 1.74 μg L^{-1} during September (tail end of monsoon), whereas in the Yamuna river system, its concentration varies from 0.1 to 3.18 μg L^{-1} during October (post-monsoon) and from 0.09 to 3.61 μg L^{-1} in June (summer). In the Yamuna main stream, uranium is highest at its source and decreases steadily along its course, from 3.18 μg L^{-1} at Hanuman Chatti to 0.67 μg L^{-1} at Batamandi, at the base of the Himalaya. This decrease results mainly from mixing of the Yamuna mainstream with its tributaries, which are lower in uranium. The high concentration of uranium at Hanuman Chatti is derived from weathering of the Higher Himalayan Crystalline series (HHC) and associated accessary minerals, which may include uranium-mineralised zones. The $^{234}U/^{238}U$ activity ratios in the samples from the Chambal watershed are in the range of 1.15 ± 0.05 to 1.67 ± 0.04; whereas in the Yamuna the ratios vary from 0.95 ± 0.03 to 1.56 ± 0.07, during post-monsoon and from 0.98 ± 0.01 to 1.30 ± 0.03, during summer. The relatively high $^{234}U/^{238}U$ activity ratios in the Yamuna system are in its tributaries from the lower reaches viz., the Amlawa, Aglar, Bata, Tons and the Giri. It is estimated that $\sim 9 \times 10^3$ and $\sim 12 \times 10^3$ kg of dissolved uranium are transported annually from the Yamuna at Batamandi and the Chambal at Udi, respectively. This corresponds to uranium weathering rates of 0.9 and 0.09 kg U km^{-2} y^{-1} in the basins of the Yamuna and the Chambal headwaters. This study confirms that uranium weathering rate in the Himalaya is far in excess (by about an order of magnitude) of the global average value of ~0.08 kg U km^{-2} y^{-1}.

Key words: Dissolved uranium, $^{234}U/^{238}U$ disequilibrium, Indian rivers, uranium, weathering

1. Introduction

Studies on uranium isotopes in dissolved and suspended phases in rivers draining the Himalaya; – the Ganga-Brahmaputra, Indus, Narayani and the Karnali (Bhat and Krishnaswami, 1969; Chabaux et al., 2001; Pande et al., 1994; Sarin et al., 1990, 1992a) show that many of them have dissolved

★Author for correspondence (e-mail: rajan@prl.ernet.in)

uranium concentration, of a few μg L^{-1}, several times higher than that in "average" global river water (Palmer and Edmond, 1993; Sarin et al., 1990). Such high dissolved uranium concentrations in rivers are difficult to account for by chemical weathering of major lithological units in these river basins, which mainly consist of carbonates, sedimentary silicates and crystallines (Singh et al., 2003). This has led to the suggestion that part of the dissolved uranium in these rivers could be derived from uranium rich organic sediments of the basin and from the minor phases (uranium-mineralized zones) dispersed in HHC. Dalai et al. (2002a) and Singh et al. (2003) suggested that weathering of black shales can be a potential source of dissolved uranium in the Ganga-Indus headwaters based on its abundance in black shales from the Himalaya and the similarity in the geochemical behaviour of U and Re in oxic surface waters. Chabaux et al. (2001) have also alluded to black shales as a possible source to account for high dissolved uranium in the Kali-Gandaki waters of the Narayani river basin in Nepal. The $^{234}U/^{238}U$ activity ratios of dissolved uranium in many of these rivers are close to equilibrium value, however, a few of them have distinct ^{234}U excess. Similar to the uncertainties in determining the source(s) of dissolved uranium to these waters, the process(es) contributing to the variability in $^{234}U/^{238}U$ activity ratio among them is also not well constrained, though lithology of the basin has been suggested as a factor (Bhat and Krishnaswami, 1969; Chabaux et al., 2001; Sarin et al., 1990, 1992a).

In this study, concentration of dissolved uranium and $^{234}U/^{238}U$ activity ratios have been measured in the Yamuna headwaters in the Himalaya and the Chambal headwaters in the plains to study weathering and mobility of uranium in these watersheds. This study forms a part of our ongoing investigations on the chemical and isotopic composition of rivers draining India. The Yamuna is a major river draining the Himalaya and the Chambal is one of its tributaries in the plains. These two rivers have distinctly different drainage lithologies and climate, which provide an opportunity to study the influence of environmental and geological factors on the uranium budget of rivers. Data for dissolved major ions and selected trace elements (Ba, Re, Sr and $^{87}Sr/^{86}Sr$) for these samples are available for suitable interpretation of the U data (Dalai et al., 2002, 2003; Rengarajan, 2004). Further, the study of the Yamuna headwaters in the Himalaya allows the comparison of its uranium abundance and isotope composition with those reported for the Ganga headwaters (Sarin et al., 1990, 1992a) flowing a few hundred kilometres east of the Yamuna.

2. Overview of the Yamuna and Chambal river basins

2.1. YAMUNA RIVER SYSTEM

The Yamuna originates from the Yamunotri Glacier at the base of the Bandapunch peak in the Higher Himalaya (Dalai et al., 2002; Negi, 1991)

and flows through the Himalaya and the alluvial plains before joining the Ganga at Allahabad. The prominent tributaries of the Yamuna in the Himalaya are the Tons, Giri, Aglar, Asan and the Bata (Figure 1). In the lower reaches, the Chambal, Sindh, Betwa, and the Ken are its major tributaries joining it in the plains from the right bank. The Yamuna receives waters from glacier/snow melt in the source region, from monsoon rains and from springs and several tributaries along its course. Near its source in the Higher Himalaya, the Yamuna drains mainly crystallines of the Ramgarh and Almora groups (Gansser, 1964; Valdiya, 1980). From the Higher Himalaya, the Yamuna flows in the southwest direction and enters the Lesser Himalaya, where it drains a variety of lithologies; including crystallines, carbonates and other sediments, mainly shales. Many of the major tributaries of the Yamuna (the Tons, Aglar, Giri, Bata and the Asan) have most of their drainage in the Lesser Himalaya (Figure 1). Southwest of Kalsi, the Yamuna flows through the Siwaliks comprising of channel and floodplain deposits. In the Lesser Himalaya, exposures of organic rich shales are reported in the catchments of the Yamuna and its tributaries, prominent among them being at Maldeota and Durmala, near Dehradun (Dalai et al., 2002; Valdiya, 1980). A significant part of the study area in the Yamuna drains through the Lesser Himalaya. The major lithologies of the Yamuna basin though are known, their aerial coverage are not well characterized. Dalai et al. (2002), based on major ion composition of rivers and invoking various assumptions, estimated that on average $\sim$20–25% of dissolved cations in the Yamuna rivers is of silicate origin, $\sim$50% is from carbonates and the balance from evaporites and atmospheric deposition. The contribution of these lithologies to the cation budget of individual rivers may, however, vary from the average cited above.

The drainage basins of the Yamuna and its tributaries experience tropical monsoon climate (Devi, 1992). The Yamuna river drains an area of about 9600 km^2 in the Himalaya with an annual water flow of 10.8×10^{12} L at Tajewala (Jha et al., 1988; Rao, 1975; Figure1). Most of the water discharge occurs during the southwest monsoon, late June to September. The water discharge during post-monsoon and summer are each $\sim$10% of the total discharge. The Yamuna's annual discharge at Allahabad, before confluence with the Ganga is 93×10^{12} L (Rao, 1975).

2.2. CHAMBAL RIVER SYSTEM

The Chambal is the principal tributary of the Yamuna in the plains. It rises near Mhow (Figure 2), at an elevation of 354 m, in the Vindhyan Range (Krishnan, 1982). The Banas, Kalisindh, Sipra, Newaj and the Parbati are its chief tributaries. The headwaters of the Chambal and many of its tributaries drain Deccan Trap tholeiitic basalt. Large inliers of sandstone, limestone and dolomite belonging to the Archaeans, Vindhyan and the Gondwana outcrop

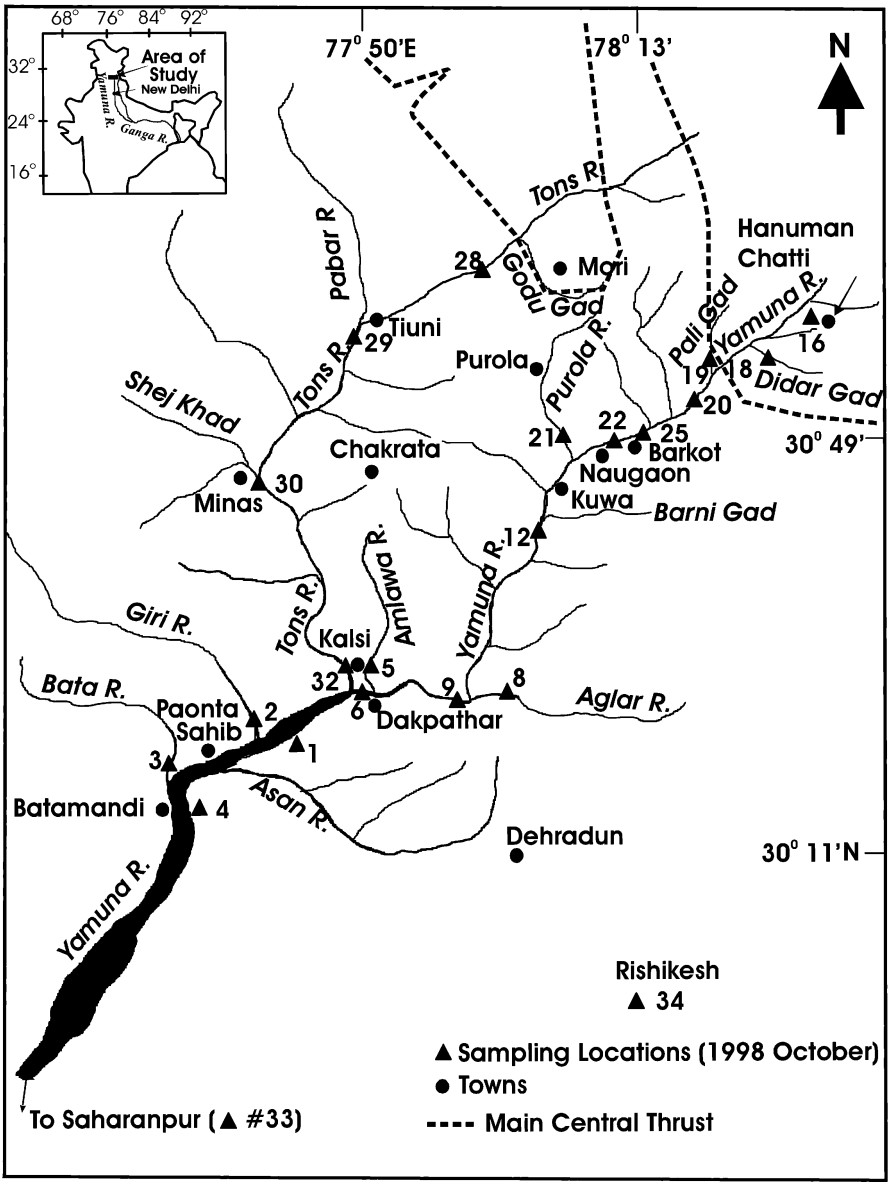

Figure 1. Sampling locations of the Yamuna river system. The location numbers given along the filled triangles are only for the October 1998 collection. Only those tributaries that are sampled for uranium are shown.

within the Deccan Trap basalts (Ghosh, 1976; Krishnan, 1982). At many locations, where the Traps are highly eroded, paleo-erosional planes between the Vindhyan and the Deccan lavas are exposed (Valdiya et al., 1982). The Chambal river has cut deep gorges through the plateau. Downstream of the

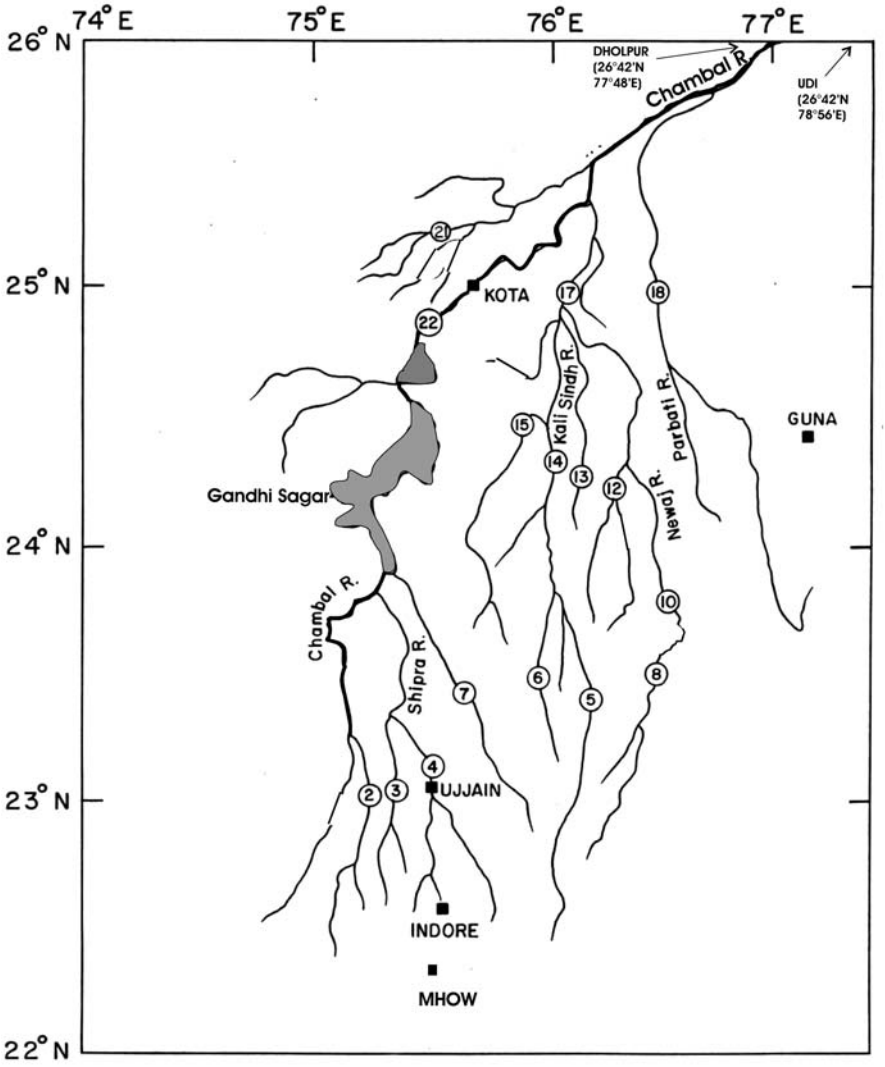

Figure 2. Sampling locations of the Chambal river basin. The location numbers are shown encircled. Only those tributaries that are sampled for uranium are shown. The samples were collected during September 1998 (tail end of monsoon season).

Gandhi Sagar Dam, the Chambal flows mainly through the Vindhyan system. The tributaries, the Kali Sindh, Newaj and the Parbati also drain the Vindhyan system and alluvial sediments prior to merging with the Chambal. The Banas (CH-21), a major tributary, originates in the Aravalli and Vindhyan systems and flows through them before merging with the Chambal. The alluvial plains, through which the Chambal traverses, contain alkaline and saline soils (Sarin et al., 1989). These soils are a source of salinity to the

Chambal and some of its tributaries. The Chambal catchment exhibits a wide range of land-use, with large areas of intensely farmed agricultural land, urbanized and industrial regions and open uplands (CBPCWP, 1982). Analogous to the Yamuna, the aerial coverage of various major and minor lithologies in the Chambal basin is also not well characterized. Attempts to determine the role of silicates and carbonates in contributing to the water chemistry have also met with only limited success, because of uncertainties associated with the use of common proxies (e.g. Na^+ for silicates, Rengarajan, 2004). In spite of this, constraints have been placed on the average contribution of silicates and carbonates to be ~22 and ~52%, respectively in the Chambal basin (Rengarajan, 2004).

The climate of the Chambal basin is warm and humid, with mean annual minimum and maximum temperatures of ~19 °C and ~32 °C, respectively. The average rainfall is ~100 cm in this region, of which nearly 90% is received during the SW monsoon, from late June to September. The Chambal river has a catchment area of $\sim 1.4\times10^5$ km^2 and mean annual runoff of 31.4×10^{12} L at Udi (CBPCWP, 1982; Rao, 1975).

3. Methodology

Chemical and isotopic studies of rivers draining the Himalaya and the Deccan Traps are an ongoing programme of our group. These investigations are being carried out to determine the sources of major and minor elements to these rivers, weathering rates of various lithologies and associated atmospheric CO_2 drawdown (Dalai et al., 2002; Krishnaswami et al., 1992; Krishnaswami et al., 1999; Pande et al., 1994; Rengarajan, 2004; Sarin et al., 1989, 1990, 1992a). In this study, dissolved uranium concentration and $^{234}U/^{238}U$ activity ratio have been measured to identify uranium sources and determine uranium-weathering rates. The Yamuna river and its tributaries were sampled (Figure 1) during October 1998 from 22 locations and June 1999 from 19 locations (Dalai et al., 2002). The headwaters of the Yamuna receive significant input from snowmelt during May and June. The Chambal and its tributaries were sampled during September 1998 from 16 headwater streams (Rengarajan, 2004; Figure 2) when the river stage is high.

For dissolved uranium and $^{234}U/^{238}U$ activity ratio measurements, ~10 L of water samples were collected from the mid-stream and filtered at site using 1 μM Gelman cartridge filters into clean polypropylene containers within a few hours of their collection. The filtered samples were acidified with conc. HNO_3 to pH of ~2. This was followed by the addition of ~100 mg of Fe carrier (as $FeCl_3$) and ^{232}U tracer (1 mL of 9.0 ± 0.16 dpm mL^{-1}). Subsequently, the samples were continuously stirred and purged with air to break the uranyl carbonate complex and establish tracer equilibrium with river water uranium. After 3–4 h, the pH of the sample was raised to ~8 by

adding concentrated NH_4OH and uranium was co-precipitated along with $Fe(OH)_3$. The $Fe(OH)_3$ precipitate containing uranium was filtered and uranium was separated from Fe^{3+} on an AG-1X8 anion exchange column (in 7.5 N HNO_3), purified and assayed by alpha spectrometry (Krishnaswami and Sarin, 1976; Sarin et al., 1992). The major ion composition of the Yamuna and the Chambal water samples are reported in Dalai et al. (2002) and Rengarajan (2004), respectively.

4. Results

The dissolved uranium concentration and $^{234}U/^{238}U$ activity ratio in the Yamuna and Chambal river systems are summarized in Table I. The errors given are $\pm 1\sigma$ standard deviation derived from counting statistics and uncertainties in ^{232}U spike calibration. Typical $\pm 1\sigma$ uncertainty in the concentration measurements is $\pm 3\%$. The precision of uranium concentration measurements based on repeat measurements of the water samples is $\pm 3\%$ (Rengarajan et al., 2003). The dissolved uranium in the Chambal system ranges from 0.2 to 1.74 μg L^{-1}, whereas in the Yamuna system, it varies from 0.13 to 3.18 μg L^{-1} in the post-monsoon samples and from 0.09 to 3.61 μg L^{-1} in summer (Figure 3). In general, uranium in the Yamuna and the Chambal are higher than the global average river water uranium concentration, 0.3 μg L^{-1} (Palmer and Edmond, 1993; Sarin et al., 1990). In the Yamuna main stream, uranium is highest at its source and decreases steadily along its course, from 3.18 μg L^{-1} at Hanuman Chatti to 0.67 μg L^{-1} at Batamandi, at the base of the Himalaya (Figure 4). The decrease results mainly from mixing of the Yamuna mainstream with its tributaries, which are lower in uranium (Table I). All but two samples of the tributaries have dissolved uranium ≤ 0.8 μg L^{-1}. Uranium abundance of the Yamuna mainstream during the two seasons sampled, summer and post-monsoon, with roughly similar but low water discharge is, on average, within $\pm 30\%$ of each other. This range is much less than the 2 to 3 fold intra-annual variability reported for the Ganga, Sabarmati and the Cauvery by Bhat and Krishnaswami (1969) and Sarin et al. (1990). The much lower temporal variability observed in this study is because sampling did not include the monsoon season, when the water discharge is at its maximum and elemental abundances are at their lowest.

In the Chambal system, two samples from the mainstream (CH-2 and CH-22) were analysed. The dissolved uranium concentration in the downstream sample collected after the Gandhi Sagar reservoir (CH-22, Figure 1b) is lower than that of the upstream sample by a factor of ~ 2. This can be attributed to mixing of the Chambal mainstream with its tributaries, which have lower uranium concentration and dilution along the mainstream and in the reservoir.

Table I. Dissolved uranium and $^{234}U/^{238}U$ activity ratios in the Yamuna and the Chambal rivers

Sample code	River	Location	Sampling season*	U ($\mu g\ L^{-1}$)	$^{234}U/^{238}U$ (Activity ratio)	ΣCat*[a] ($mg\ L^{-1}$)	Na*[a] ($mg\ L^{-1}$)
Yamuna mainstream							
RW98-16	Yamuna	Hanuman Chatti	PM	3.18 ± 0.08	1.04 ± 0.02	20.7	0.86
RW99-13	Yamuna	Hanuman Chatti	S	3.05 ± 0.08	1.03 ± 0.02	20.2	0.83
RW98-20	Yamuna	Downstream of Pali Gad Bridge	PM	2.97 ± 0.08	1.04 ± 0.02	21.2	1.23
RW98-25	Yamuna	Barkot	PM	1.86 ± 0.05	1.06 ± 0.02	22.2	1.34
RW99-19	Yamuna	Barkot	S	2.65 ± 0.08	0.98 ± 0.02	23.3	1.82
RW99-17	Yamuna	Kuthnaur village	S	3.61 ± 0.09	1.03 ± 0.01	22.9	1.82
RW98-22	Yamuna	Upstream of Naugaon	PM	1.05 ± 0.05	1.05 ± 0.03	23.0	1.48
RW99-18	Yamuna	Near Lakhmandal	S	2.54 ± 0.08	1.05 ± 0.02	26.6	1.71
RW99-11	Yamuna	Downstream of Barni Gad's confluence	S	2.02 ± 0.06	1.05 ± 0.02	30.6	1.93
RW98-12	Yamuna	Downstream of Nainbag	PM	0.84 ± 0.02	1.05 ± 0.02	27.1	2.07
RW98-9	Yamuna	Downstream of Aglar's confluence	PM	1.07 ± 0.03	1.09 ± 0.03	34.9	1.87
RW98-6	Yamuna	Upstream of Ton's confluence	PM	1.00 ± 0.03	1.09 ± 0.03	37.1	2.19
RW99-30	Yamuna	Upstream of Ton's confluence	S	1.67 ± 0.05	1.02 ± 0.02	45.3	2.54
RW99-31	Yamuna	Downstream of Ton's confluence	S	1.42 ± 0.04	1.02 ± 0.02	39.5	2.30
RW98-1	Yamuna	Rampur Mandi, Paonta Sahib	PM	0.65 ± 0.02	1.05 ± 0.02	26.8	1.90
RW99-2	Yamuna	Rampur Mandi	S	0.60 ± 0.02	1.02 ± 0.03	39.8	3.80
RW98-4	Yamuna	Downstream of Bata's confluence	PM	0.67 ± 0.02	1.16 ± 0.04	58.7	4.49
RW99-5	Yamuna	Downstream of Bata's confluence	S	0.80 ± 0.03	1.22 ± 0.04	61.2	5.35
RW98-33	Yamuna	Yamuna Nagar, Saharanpur	PM	1.30 ± 0.04	1.08 ± 0.02	53.4	3.56
RW99-7	Yamuna	Yamuna Nagar, Saharanpur	S	1.66 ± 0.05	1.06 ± 0.02	55.8	4.27
Yamuna tributaries							
RW98-18	Didar Gad	Hanuman Chatti-Barkot Road	PM	0.44 ± 0.01	0.95 ± 0.03	6.10	0.63
RW98-19	Pali Gad	Pali Gad Bridge	PM	0.40 ± 0.01	1.11 ± 0.03	21.6	0.71

RW98-21	Purola	Between Naugaon and Purola	PM	0.25 ± 0.01	1.22 ± 0.05	30.9	1.60
RW99-27	Pabar	Upstream of confluence with Tons	S	0.088 ± 0.003	1.00 ± 0.05	14.0	1.43
RW99-22	Tons	Mori	S	0.49 ± 0.01	1.00 ± 0.03	9.62	0.84
RW98-28	Tons	Downstream of Mori	PM	0.46 ± 0.01	1.01 ± 0.03	11.1	1.09
RW99-26	Tons	Before Pabar joins	S	0.20 ± 0.01	1.05 ± 0.03	8.33	0.79
RW98-29	Tons	Tiuni	PM	0.70 ± 0.02	1.03 ± 0.03	12.8	1.26
RW98-30	Tons	Minus, after confluence	PM	0.72 ± 0.02	1.05 ± 0.02	24.0	1.55
RW99-24	Tons	Minus, after confluence	S	0.55 ± 0.02	1.11 ± 0.03	45.5	2.22
RW98-5	Amlawa	Kalsi-Chakrata Road	PM	0.13 ± 0.01	1.56 ± 0.07	39.4	3.87
RW98-32	Tons	Kalsi, upstream of confluence	PM	0.80 ± 0.02	1.06 ± 0.02	46.9	2.83
RW99-29	Tons	Kalsi, upstream of confluence	S	0.76 ± 0.02	1.06 ± 0.03	46.9	2.86
RW98-8	Aglar	Upstream of Yamuna Bridge	PM	0.75 ± 0.02	1.17 ± 0.03	70.6	2.65
RW99-10	Aglar	Upstream of Yamuna Bridge	S	1.34 ± 0.05	1.07 ± 0.03	150	4.01
RW98-2	Giri	Rampur Mandi	PM	0.83 ± 0.03	1.25 ± 0.05	98.6	4.86
RW99-3	Giri	Rampur Mandi	S	1.02 ± 0.03	1.26 ± 0.03	119	5.69
RW98-3	Bata	Bata Mandi	PM	0.31 ± 0.01	1.43 ± 0.06	54.7	4.57
RW99-4	Bata	Bata Mandi	S	0.62 ± 0.02	1.30 ± 0.03	70.1	7.32
Ganga							
RW98-34	Ganga	Rishikesh	PM	1.83 ± 0.05	1.01 ± 0.02	26.0	1.74
RW99-6	Ganga	Rishikesh	S	2.65 ± 0.07	0.98 ± 0.01	25.5	1.88
Chambal river system							
CH-2	Chambal	Between Burnagar and Ujjain	LM	0.77 ± 0.02	1.35 ± 0.03	56.3	14.9
CH-3	Ghambir	Between Burnagar and Ujjain	LM	0.61 ± 0.02	1.30 ± 0.03	57.1	14.0
CH-4	Shipra	Between Ujjain and Agar	LM	0.92 ± 0.03	1.26 ± 0.03	105	11.2
CH-5	Kalisindh	Sarangpur	LM	0.50 ± 0.02	1.23 ± 0.05	81.3	10.5
CH-6	Lakimdar	Choma village	LM	0.65 ± 0.02	1.20 ± 0.03	88.2	16.5
CH-7	Chota Kalisindh	Bat village	LM	0.47 ± 0.01	1.24 ± 0.03	41.3	7.25

Table I. Continued

Sample code	River	Location	Sampling season*	U (μg L^{-1})	$^{234}U/^{238}U$ (Activity ratio)	ΣCat*[a] (mg L^{-1})	Na*[a] (mg L^{-1})
CH-8	Newaj	Pachor village	LM	0.99 ± 0.03	1.19 ± 0.02	76.3	12.4
CH-10	Newaj	Kisangarh	LM	0.87 ± 0.03	1.51 ± 0.04	68.8	11.9
CH-11	Gherganga	Aklera	LM	0.20 ± 0.01	1.15 ± 0.05	67.4	7.27
CH-12	Chappi	Before confluence of Newaj	LM	0.30 ± 0.01	1.21 ± 0.05	68.7	8.83
CH-14	Kalisindh	Jalawar	LM	0.50 ± 0.02	1.17 ± 0.04	71.0	10.5
CH-15	Aav	Suket village	LM	0.61 ± 0.02	1.23 ± 0.03	68.6	14.8
CH-17	Kalisindh	Kota-Kisankanj Rd.	LM	0.56 ± 0.02	1.39 ± 0.04	64.3	9.73
CH-18	Parbati	Kisanganj	LM	0.63 ± 0.02	1.67 ± 0.04	60.6	10.6
CH-21	Mangli	Overbridge on Kota – Buti highway	LM	1.74 ± 0.05	1.40 ± 0.02	72.4	21.8
CH-22	Chambal	Upstream of Jawahar Sagar Dam	LM	0.41 ± 0.01	1.27 ± 0.03	46.4	9.36

[a]The Yamuna river data from Dalai et al. (2002) and the Chambal river data from Rengarajan (2004).
*PM: Post-monsoon; S: Summer; LM: Late monsoon.

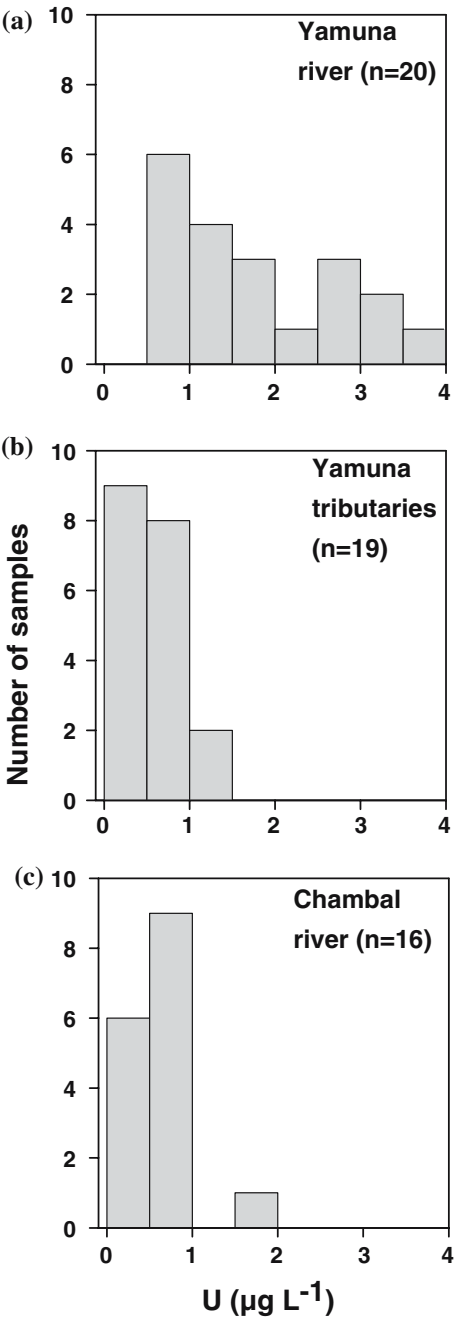

Figure 3. Frequency distribution of dissolved uranium concentration in (a) the Yamuna river, (b) its tributaries and (c) the Chambal river system.

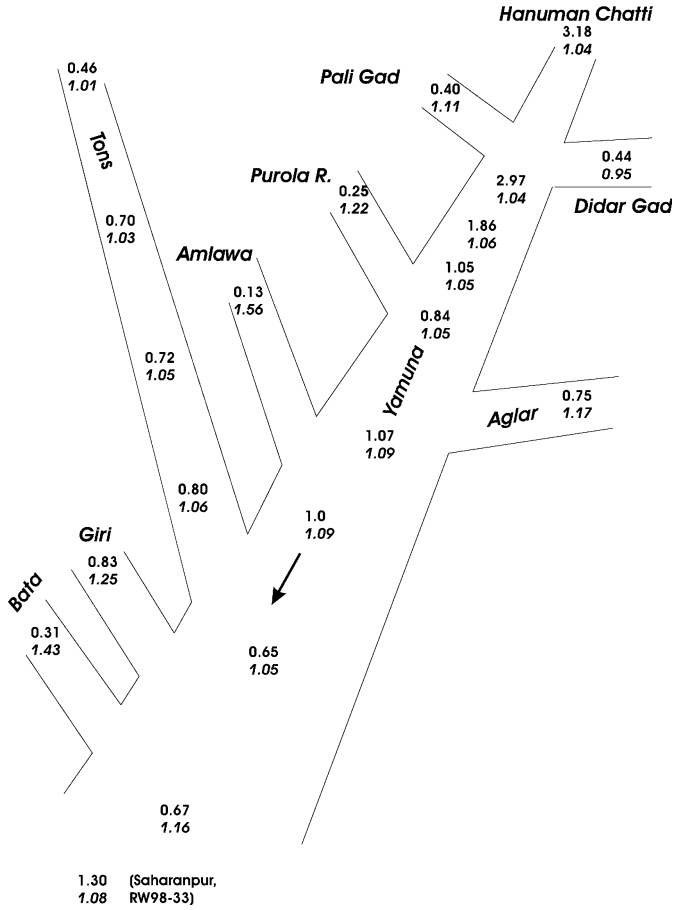

Figure 4. River flow diagram showing uranium and $^{234}U/^{238}U$ activity ratio along the Yamuna river in samples collected during October 1998. Concentration of dissolved uranium ($\mu g\ L^{-1}$) is shown in bold and $^{234}U/^{238}U$ activity ratio in italics.

5. Discussion

5.1. URANIUM AND MAJOR IONS

During chemical weathering of rocks and minerals, uranium is released to solution in the form of soluble complexes with a number of anions in oxic, natural environments. An overall positive correlation between dissolved uranium and dissolved cations is expected in rivers if during chemical weathering of rocks and minerals, cations and uranium are released to them in approximately constant ratio. Borole et al. (1982) and Sarin et al. (1990) have reported such a trend between uranium and ΣCat* for samples from the Narmada and Tapti basins and from the Ganga-Brahmaputra rivers (ΣCat*

is the sum of Na*, K, Mg and Ca concentrations in mg L^{-1} in these waters, where $Na^* = Na_{total} - Na$ from NaCl). Scatter plots of dissolved uranium vs. ΣCat* for samples analysed in this study are given in Figure 5. For the Yamuna system, the results fall into two groups: (i) the mainstream samples (all of which have ^{238}U concentration ≥ 0.6 μg L^{-1}, Table I) which show decrease in ^{238}U with ΣCat* (Figure 5a) and (ii) the tributary samples which show an overall positive trend with ΣCat* (Figure 5b). The 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 tributary waters. This trend is a reflection of changes in the U/ΣCat ratios in the drainage basin along the course of the Yamuna. In the Lesser Himalaya, where the Yamuna merges with many of its tributaries, the Tons, Aglar, Bata, Giri and the Asan (Figures 1 and 4), the drainage basin has relatively more areal coverage of carbonates, which are easily weatherable, but generally have lower uranium than silicates (granites/gneisses). The Precambrian carbonates, which are abundant in the Lesser Himalaya (Valdiya, 1980), have average uranium of ~0.71 μg g^{-1} (Singh et al., 2003), significantly lower than that in typical granites, ~3 μg g^{-1}. In contrast to the Yamuna mainstream, the dissolved uranium in the Bhagirathi, the Ganga source waters in the Himalaya, is nearly uniform, 2.5 ± 0.5 μg L^{-1} along its course (Sarin et al., 1992a). In the case of the Chambal, there is a suggestion of an overall positive trend between uranium and ΣCat* (Figure 5c) though the data show significant scatter.

The U-ΣCat* plots of both the Yamuna mainstream (Figure 5a) and the Bhagirathi system (Sarin et al., 1992a) show significant scatter. This can result from several factors, such as (1) diverse lithology of the basin. These river basins are multi-lithological and hence the U/ΣCat* ratios released to water from the bedrocks/soil could have significant variability. Further, uranium in the basin rocks/sediments can be associated with minerals that are variably resistant to chemical weathering. (2) non-conservative behaviour of Ca and Mg resulting from carbonate precipitation. This can impact on U/ΣCat* by altering both ΣCat* and dissolved uranium abundances. The extent of uranium removal, however, is expected to be low as its partition coefficient is generally $\ll 1$ (Meece and Benninger, 1993). $CaCO_3$ precipitation could be important for the Chambal and the Yamuna tributaries in the lower reaches, which show calcite supersaturation (Dalai et al., 2002; Rengarajan, 2004). (3) supply of recycled salts from alkaline/saline soils, especially in the Chambal river system. These can impact on the uranium and/or ΣCat* budgets. (4) groundwater/anthropogenic inputs. The headwaters of the Yamuna and the Ganga should be less influenced by anthropogenic input of uranium, as they are relatively pristine watersheds. In the Yamuna river system, however, some of its tributaries in the lower reaches (e.g. the Asan) have high nitrate concentration (Dalai et al., 2002), which raises concern about potential

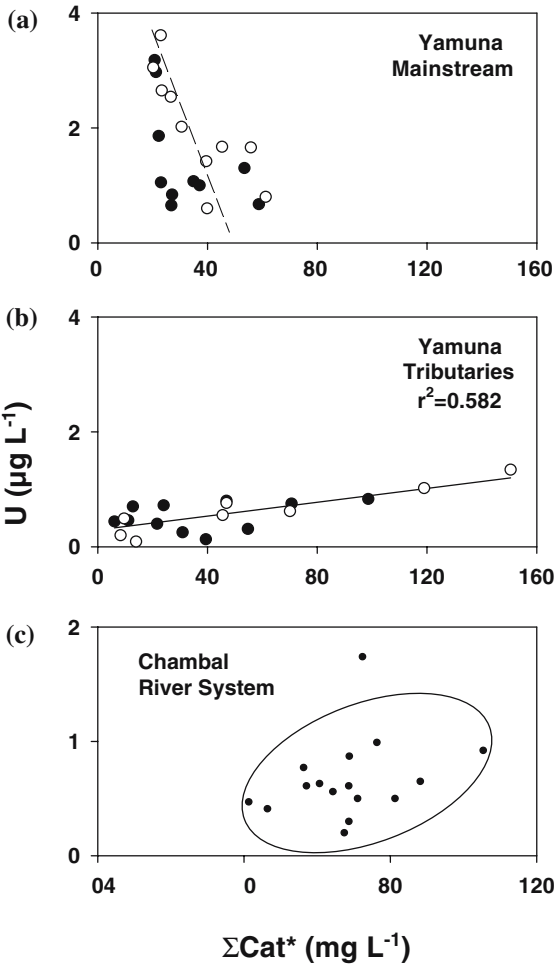

Figure 5. Plot of dissolved uranium concentration (µg L^{-1}) vs. ΣCat* (mg L^{-1}) in (a) the Yamuna mainstream, (b) the Yamuna tributaries and (c) the Chambal river system. In Figure a and b, filled and open circles are samples collected during October 1998 and June 1999, respectively. In Figure c, the encircled Chambal river system data shows an increasing trend. ΣCat* data for the Yamuna and the Chambal rivers (Table I) are from Dalai et al. (2002) and Rengarajan (2004).

anthropogenic contribution. Similarly, the Chambal has part of its drainage through agricultural land and urbanized regions. This coupled with the presence of high nitrate in some of the Chambal system rivers points to the influence anthropogenic inputs may have in its water chemistry.

In Table II, uranium concentrations and $^{234}U/^{238}U$ activity ratios in the Chambal, Yamuna and the Ganga obtained in this study are compared with those reported by Sarin et al. (1990) for these rivers at the same locations and sampled roughly during the same period nearly two decades ago. The table

also lists the corresponding ΣCat* values. These data show measurable variations over decadal timescales in uranium concentration in these rivers, with samples collected in 1998 having less uranium than those sampled in 1982–1983 (Table II). These comparisons, however, are inadequate to infer the importance and presence of any trends due to anthropogenic activities and/or natural causes in modifying uranium in these rivers. The $^{234}U/^{238}U$ activity ratios in these rivers have remained nearly the same, within errors of measurement, over the past two decades.

Similar to the U-ΣCat* trend, dissolved uranium also exhibits positive correlation with a few other dissolved constituents that are largely conserved in solution. These include U-HCO_3^- (Figure 6) and U–Cl. Similar trends between U-HCO_3^- are also reported for the Narmada, Tapti rivers (Borole et al., 1982) and for the world rivers (Mangini et al., 1979). HCO_3^- concentration in rivers is an index of chemical weathering of the basin. The correlation between uranium and HCO_3^- therefore relates the release of uranium and major cations during chemical weathering. Further, formation of uranyl carbonate complexes in oxic environments also contributes to this correlation. In both the Yamuna and the Chambal rivers, in addition to HCO_3^-, uranium also correlates with Cl^-. This correlation is difficult to interpret in terms of association of uranium and Cl^- as uranium is not incorporated in halites (Yadav, 1995) and because $UO_2(CO_3)_2$ complex is more significant in natural waters (Herczeg et al., 1988; Langmuir, 1978) than its chloro complex. This correlation therefore has to be explained in terms of overall chemical erosion of the basins in which dissolution of chloride and carbonic acid mediated weathering are related. Indeed, Cl^- and HCO_3^- are strongly correlated ($r = 0.705$, $n = 31$) for the samples of the

Table II. Decadal variations in uranium and $^{234}U/^{238}U$ activity ratios in the Yamuna, Ganga and the Chambal rivers

River/location	Sample date	ΣCat*[a] mg L^{-1}	U μg L^{-1}	$^{234}U/^{238}U$ activity ratio	Ref.
Yamuna/Saharanpur	11/1983	86.0	2.52	1.07 ± 0.03	1
	10/1998	53.4	1.30	1.08 ± 0.03	2
Yamuna/Musoorie	11/1983	43.4	1.72	1.01 ± 0.03	1
	10/1998	70.6	1.07	1.09 ± 0.03	2
Ganga/Rishikesh	11/1983	32.2	2.25	1.04 ± 0.03	1
	10/1998	26.0	1.83	1.01 ± 0.02	2
Chambal/Dholpur	9/1982	50.6	0.88	1.41 ± 0.04	1
	9/1998	64.3	0.56	1.39 ± 0.04	2

1. Sarin et al., 1990. 2. This study.

[a]ΣCat* = (Na* + K + Ca + Mg), where Na* is Na corrected for chloride. Data for the Yamuna and the Ganga from Dalai et al. (2002) and the Chambal from Rengarajan (2004).

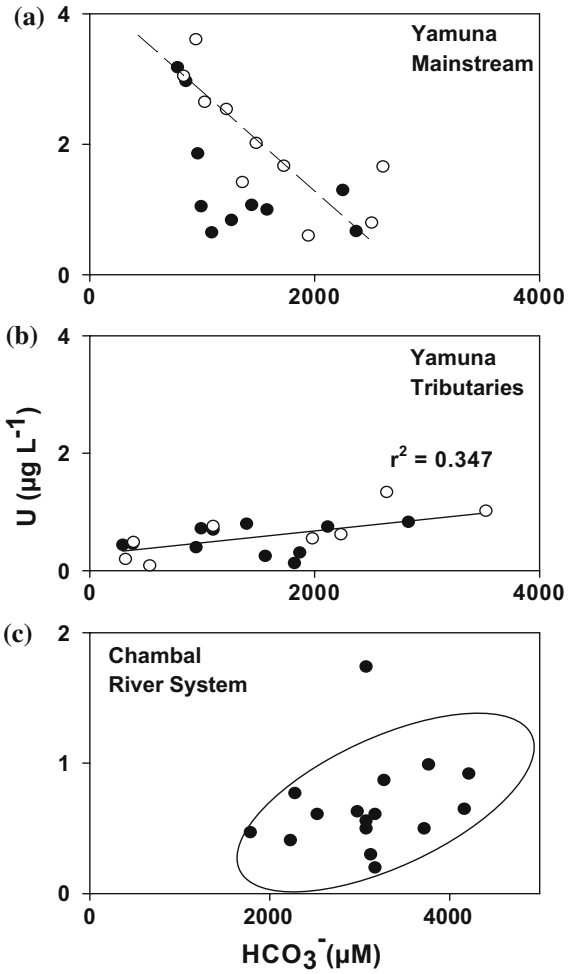

Figure 6. Variations of uranium concentration (µg L^{-1}) against HCO_3^- (µM) in (a) the Yamuna mainstream (b) the Yamuna tributaries and (c) the Chambal river and tributaries. In Figure a and b, filled and open circles are samples during October 1998 and June 1999, respectively. There is an overall positive trend in the Chambal river samples. HCO_3^- data for the Yamuna and the Chambal rivers are from Dalai et al. (2002) and Rengarajan (2004), respectively.

Yamuna system collected during October 1998 whereas they are only weakly correlated in the case of the Chambal.

5.2. SOURCES OF URANIUM TO THE YAMUNA AND THE CHAMBAL RIVERS

In the Yamuna river, the highest uranium concentration is in the sample from Hanuman Chatti (Table I). Sarin et al. (1992a) also had reported high

dissolved uranium (up to 4 μg L^{-1}) in the Bhagirathi, near its source at Gangotri. The lithology of the basins upstream of Hanuman Chatti of the Yamuna and Gangotri of the Bhagirathi is predominantly Higher Himalayan Crystallines (HHC) and hence the high concentration of uranium in these waters has to be derived from HHC. Downstream the Yamuna flows through the Lesser Himalaya where a number of its tributaries merge with it (Figure 1). Potential sources of dissolved uranium in these headwaters of the Yamuna are:

(i) Granites and meta-sediments. Granites and gneisses from the Himalaya typically have ~3 μg g^{-1} uranium with U/Na weight ratio of ~0.3 μg mg^{-1} (Singh et al., 2003). Distribution of U/Na* weight ratios in the Yamuna river water samples are shown in Figure 7. The data, though have a large spread, show that about half of the samples have U/Na* weight ratios < 0.5 μg mg^{-1}, similar to that in granites, indicating that in principle, a significant part of uranium in many of these headwaters can be from granites/gneisses weathering. It is, however, possible that uranium and sodium may not be released to rivers during weathering in the same ratio as their abundances in the rocks, as significant part of uranium in these granites may occur in weathering resistant mineral phases. Singh et al. (2003) addressed this issue in their synthesis on the Bhagirathi river by assuming that U/Na* ratio of small streams which drain predominantly crystallines (0.06 μg mg^{-1}) is representative of U/Na released from granites to streams. This led Singh et al. (2003) to infer that in most of the samples only ~1% to 20% of uranium is of

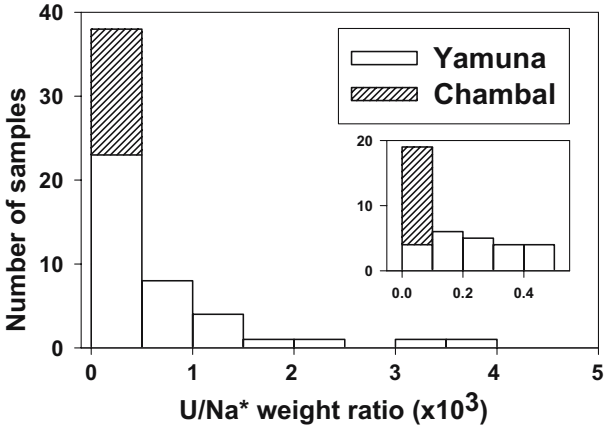

Figure 7. Distribution of U/Na* weight ratios in the Chambal and the Yamuna rivers. The inset shows in an expanded scale the distribution of samples with U/Na* weight ratios between 0.0 and 0.5 μg mg^{-1}. It is seen that U/Na* in the Yamuna river show much wider variation compared to those from the Chambal. Na* data for the Yamuna and the Chambal rivers are from Dalai et al. (2002) and Rengarajan (2004), respectively.

silicate origin. Extending this approach to the Yamuna river mainstream, the uranium fraction from silicates can be estimated to be in the range of ~1% to 20% excluding three samples (RW984, RW99-5 and RW99-2) which have values ~40%. In the tributaries, typically about one-third of uranium is of silicate origin. As in some of the Bhagirathi tributaries, a few of the Yamuna tributaries, which have low uranium (Table I), the silicate contribution can account for most of it. Thus in the Yamuna mainstream and some of its tributaries, particularly those with U/Na* ratio greater than 0.5 μg mg^{-1}, other sources of uranium have to be invoked.

(ii) A significant part of drainage basins of some of the Yamuna tributaries lie in Precambrian carbonates of the Lesser Himalaya/Siwaliks. The U/Ca weight ratio in these rivers are in the range of 6.8–27.2 ng mg^{-1}, which is higher than "mean" U/Ca weight ratio reported for Precambrian carbonates of the Himalaya, 2.9 ng mg^{-1} (Singh et al., 2003). This can be interpreted to suggest that Precambrian carbonates are not a dominant source of uranium to these waters if both Ca and U are released to water congruently from carbonates and if they behave conservatively after their supply to rivers. The behaviour of Ca in some of the rivers from the Himalaya is a topic of debate (Dalai et al., 2003; Jacobson et al., 2002). With the available data, it is difficult to confirm if it is removed by calcite precipitation from the rivers. Many of the tributaries of the Yamuna (e.g. Amlawa, Aglar, Bata, Giri) are supersaturated in calcite (Dalai et al., 2002). If this causes removal of Ca from the waters by calcite precipitation, it would enhance the U/Ca weight ratio in the waters as the partition of uranium into $CaCO_3 << 1$ (Meece and Benninger, 1993). Based on the assumption that all carbonate in their bed sediments is calcite precipitated from rivers, Dalai et al. (2002) have estimated a maximum of 50% of Ca from the Yamuna waters could be removed by precipitation. Even if this removal is considered, it is seen that for most rivers, Precambrian carbonates are not a major source of uranium, unless during weathering of carbonates, uranium is released preferentially over Ca.

(iii) Uranium rich accessory minerals. Saraswat and Mahadevan (1989) and Pachauri (1992) had reported occurrence of uranium mineralization in granites from Badrinath, Gangotri and Yamunotri above Main Central Thrust (MCT) in the Himalaya. This localized U-mineralization can be a potential source of dissolved uranium. Apatites are another uranium rich common accessory mineral in granites. The shale normalized dissolved REE in the Yamuna river samples have MREE enrichment (Rengarajan and Sarin, 2004), which has been attributed to dissolution of apatites present in granites. Thus apatites are a prospective source for uranium to these waters and are easily weathered relative to silicates.

(iv) Organic rich sediments/black shales, which are generally rich in uranium. This could be more important for the rivers draining the Lesser Himalaya. Based on average concentration of uranium in black shales

($\sim$37 μg g^{-1}) from the Lesser Himalaya, Singh et al. (2003) suggested that their weathering can be a prospective source for the high dissolved uranium of the Ganga river water, if their abundances in the drainage basin are in the range of $\sim$2%.

Dalai et al. (2002a) suggested that bulk of the dissolved rhenium and by analogy uranium in the Yamuna and the Ganga-Brahmaputra rivers are derived from weathering of black shale/carbonaceous sediments. These elements are known to be enriched in black shales and are released to rivers as oxyanions during their weathering. Figure 8a and b are scatter plots of rhenium and uranium in the Yamuna system. The data of the Yamuna mainstream (Figure 8a) do not show any discernable relationship; whereas in the tributaries (Figure 8b) there is about an order of magnitude increase in Re for a small change in uranium. The scatter in the U-Re plot is due to the widely different U/Re ratios in the black shales of the region, from 0.07 to 30 μg ng^{-1} (Singh et al., 1999, 2003). The observation that organic rich shales from the Himalaya have high uranium in them and that they are dispersed in the drainage basin, however, makes them a prospective source for dissolved uranium in these rivers (Singh et al., 2003). Furthermore, some of these black shales are associated with phosphates, which are also generally rich in uranium.

In the Chambal river system, all samples except the one from the Mangli (CH-21), have uranium concentration in the range of 0.2–1.0 μg L^{-1} (Table I). Vigier et al. (2005) reported dissolved uranium in the Deccan rivers in the range of 0.11–0.42 μg L^{-1} during monsoon period. Deccan Trap basalts have uranium concentration in the range of 0.1–1.1 μg g^{-1} (Mahoney et al., 2000) with U/Na weight ratios from 0.01 to 0.08 μg mg^{-1}. Data on uranium and U/Na in the Vindhyan system and alluvial tracts of the Chambal river are unavailable. The U/Na* weight ratios for the Chambal river and its tributaries (< 0.08 μg mg^{-1}, Figure 7) overlap with that in the basalts. It would be tempting to interpret the similarity in U/Na ratios as due to supply of uranium to rivers from basalts. However, the possibility that a significant part of Na in the rivers of the Chambal system can be from saline and/or alkaline soils limits the use of U/Na ratio as an indicator of uranium source. If indeed significant component of Na in the Chambal system is from saline/alkaline soils and anthropogenic sources, then analogous to that in the Yamuna, additional sources of uranium have to be invoked to account for its abundance in water.

Groundwaters can be another source of uranium to rivers, the insignificance, however, would depend on their contribution to water discharge and their uranium concentration (Durand et al., 2005). In the samples analysed in this study, the Chambal was sampled during the tail end of monsoon when river stage was high and the Yamuna during post-monsoon when water flow is medium to high. Thus, during these seasons, groundwater discharge in

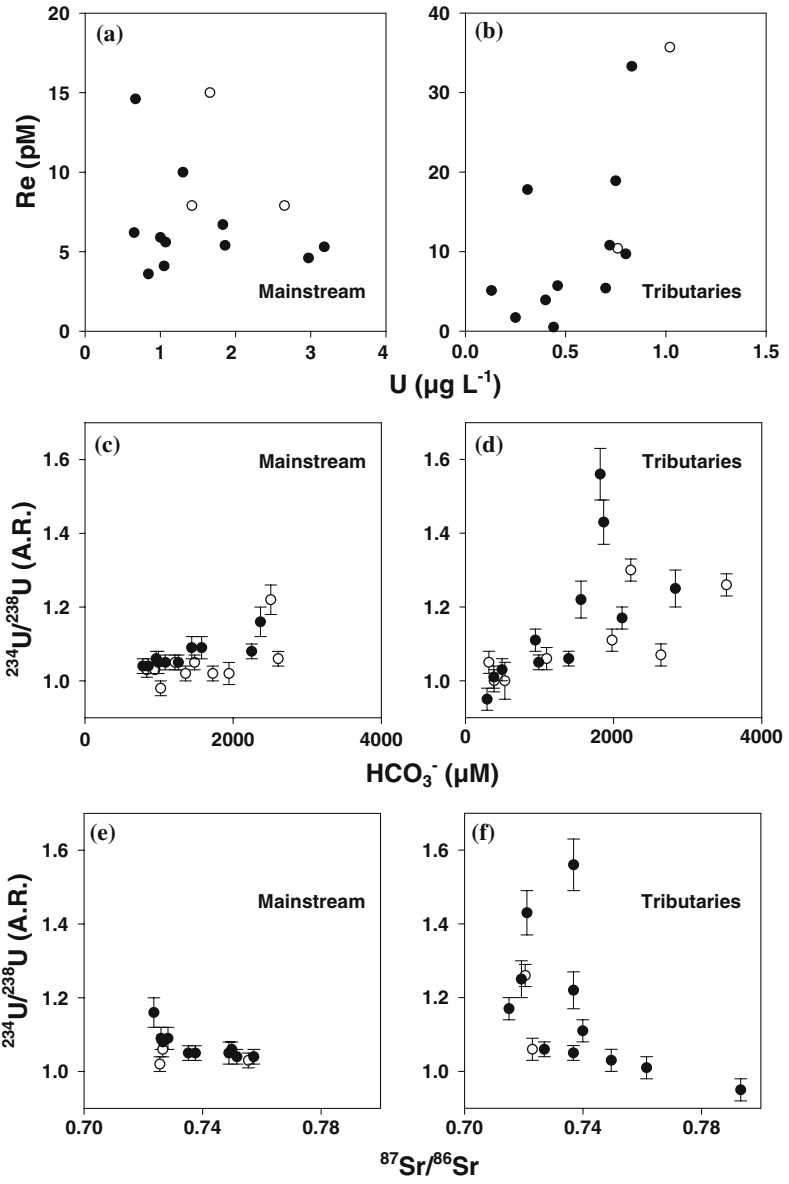

Figure 8. Plots showing Re versus U in the Yamuna mainstream (a) and its tributaries (b). No discernable relation between rhenium and uranium is seen in the mainstream whereas in the tributaries, there is an order of magnitude increase in Re for a small change in uranium. The plots (c) and (d) are $^{234}U/^{238}U$ activity ratio versus HCO_3 in the Yamuna mainstream and its tributaries; and the plots (e) and (f) are $^{234}U/^{238}U$ activity ratio versus $^{87}Sr/^{86}Sr$ in the Yamuna mainstream and its tributaries. Filled and open circles denote samples collected during October 1998 and June 1999, respectively. Re and $^{87}Sr/^{86}Sr$ data from Dalai et al. (2002a, 2003).

these rivers is unlikely to be an important component of surface water flow and hence to the river budget unless uranium in groundwaters is much higher than that in the rivers. In samples collected from the Yamuna during summer, groundwater component could be important, its role, however, is difficult to resolve as glaciers/snow melt also supplies significant amount of water to the river in summer.

Anthropogenic supply of uranium to rivers is reported for many global rivers (Chabaux et al., 2003; Mangini et al., 1979; Zielinski et al., 2000). In the Yamuna, particularly in its upper reaches, this should not be an important source as the area is not densely populated and impacted by intense agricultural practices. The highest uranium concentration as mentioned earlier is in samples near the source of the river, where the environment is nearly pristine. The Yamuna samples from Saharanpur (RW98-33) and its tributaries in the lower reaches: the Giri and the Bata (RW98-2 and RW98-3) have higher NO_3^- concentration than the upstream samples, with values exceeding 30 μM (Dalai et al., 2002). This could be derived from fertilizer use. The Chambal basin, in contrast, is more affected by land use changes and agricultural practices. In these cases, therefore, there is a concern of anthropogenic supply of uranium.

5.3. $^{234}U/^{238}U$ ACTIVITY RATIOS

The $^{234}U/^{238}U$ activity ratios of samples from the Chambal watershed are in the range of 1.15 ± 0.05 to 1.67 ± 0.04 (Table I). The $^{234}U/^{238}U$ activity ratios in the Yamuna watershed are relatively lower (range $= 0.95 \pm 0.03$ to 1.56 ± 0.07, during post-monsoon and 0.98 ± 0.01 to 1.30 ± 0.03, during summer, Table I). Chabaux et al. (2001) interpreted variations in $^{234}U/^{238}U$ activity ratios in the Himalayan rivers in terms of supply from the main structural units: values slightly less than equilibrium (≤1.0) in the TSS basin, marginally in excess of 1.0 in the Higher Himalayan Crystalline series and Lesser Himalayan (HHC-LH) regions and much higher ratios in the Siwaliks area. In this study, the Yamuna mainstream samples have $^{234}U/^{238}U$ activity ratios marginally in excess of 1.0, whereas a few of its tributaries, especially those draining the Lesser Himalaya, the Amlawa (RW98-5), Aglar (RW98-8), Bata (RW98-3) and the Giri (RW98-2) have $^{234}U/^{238}U$ activity ratios distinctly in excess of the equilibrium value, in the range of 1.17 ± 0.03 to 1.56 ± 0.07 (Table I).

The Song river, a tributary of the Ganga, flowing through the Siwaliks has a high $^{234}U/^{238}U$ activity ratio of 1.44 ± 0.04 (Sarin et al., 1992a). Low $^{234}U/^{238}U$ activity ratio in the rivers flowing through HHC-LH basin and high $^{234}U/^{238}U$ activity ratios in rivers flowing through Siwaliks are explained by Chabaux et al. (2001) in terms of differences in water-rock interactions in subsurface environments. The marked ^{234}U excess in some of the rivers

draining Siwaliks has been explained in terms of rates of weathering and uranium release or groundwater inputs with significant uranium isotopic disequilibrium. It is interesting to note that some of the rivers having pronounced $^{234}U/^{238}U$ disequilibrium (the Aglar, Bata and the Giri, Table I) originate as springs and are fed by groundwater in their source regions (Negi, 1991). Data on uranium concentration and $^{234}U/^{238}U$ activity ratio in groundwater and springs of the region are needed to address the issue quantitatively.

A plot of $^{234}U/^{238}U$ activity ratio versus HCO_3^- in the Yamuna system (Figure 8c and d) shows that in the mainstream, except for two samples collected after the confluence of the Bata, the $^{234}U/^{238}U$ activity ratio is nearly uniform at 1.05 ± 0.03 and independent of HCO_3^-. This is unlike the data for the tributaries, which show an increase in $^{234}U/^{238}U$ activity ratio from $\sim$1.0 to $\sim$1.20 with increase in HCO_3^-. The $^{234}U/^{238}U$ activity ratio remains nearly the same with further increase in HCO_3^-. Considering that the HCO_3^- content of Yamuna waters increases downstream primarily due to weathering of limestone and dolomites (Dalai et al., 2002), it is tempting to ascribe the $^{234}U/^{238}U - HCO_3^-$ co-variation to preferential release of ^{234}U from carbonates. Interestingly, the plot of $^{234}U/^{238}U$ activity ratio versus $^{87}Sr/^{86}Sr$ (Figure 8e and f) seems to attest to such an interpretation. The data show that samples with high $^{87}Sr/^{86}Sr$ ratios have low $^{234}U/^{238}U$ activity ratios and vice versa; similar to that reported for tributaries of the Strengbach river (Riotte and Chabaux, 1999). The end member with elevated radiogenic Sr isotope composition can be silicates and calc-silicates of the HHC-LH (Bickle et al., 2001; Dalai et al., 2003; Krishnaswami et al., 1999). The samples with lower $^{87}Sr/^{86}Sr$ isotope ratios, characteristic of tributaries from the lower reaches draining carbonates and other sediments have higher $^{234}U/^{238}U$ activity ratio. Consequently, the trend in Figure 8e and f requires that lithologies contributing to high $^{87}Sr/^{86}Sr$ (HHC-LH silicates and calc-silicates) supply uranium to water with near equilibrium $^{234}U/^{238}U$ activity ratio. A possible scenario for this is uranium mineralized zones in HHC-LH crystallines which can yield high dissolved uranium with near equilibrium $^{234}U/^{238}U$ activity ratio to rivers. The high $^{234}U/^{238}U$ activity ratio in tributaries draining carbonates could be a result of weathering of silicates contained in the carbonates as has been suggested to explain high $^{234}U/^{238}U$ activity ratio in Carboniferous Limestone aquifer of SW England (Bonotto and Andrews, 1993).

The observed $^{234}U/^{238}U$ activity ratios in the Yamuna and the Chambal rivers bracket the range of the Ganga and the Indus (Pande et al., 1994; Sarin et al., 1990, 1992). Sarin et al. (1990) reported a distinct difference in $^{234}U/^{238}U$ activity ratio between the lowland (Chambal, Betwa, Ken and Son) and highland waters (Gontak, Ghaghra and the upper reaches of Ganga) of the Ganga system and attributed the difference to variations in the

lithology of their drainage basins and the type of weathering processes. The near equilibrium value of $^{234}U/^{238}U$ activity ratio in the highland rivers is similar to that observed for many rivers in the upper reaches of the Yamuna system in this study.

$^{234}U/^{238}U$ activity ratio versus 1/U of the Yamuna and the Chambal rivers are plotted to assess the extent of mixing between end members (Figure 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, albeit significant scatter. The scatter may be due to multiple end members, with their own characteristic $^{234}U/^{238}U$ activity ratios and uranium concentrations. The mixing trend of the Yamuna shows that its low concentration end member has high $^{234}U/^{238}U$ activity ratio contrary to that in the Chambal river. The summer samples of the Yamuna river system do not show any discernible mixing trend.

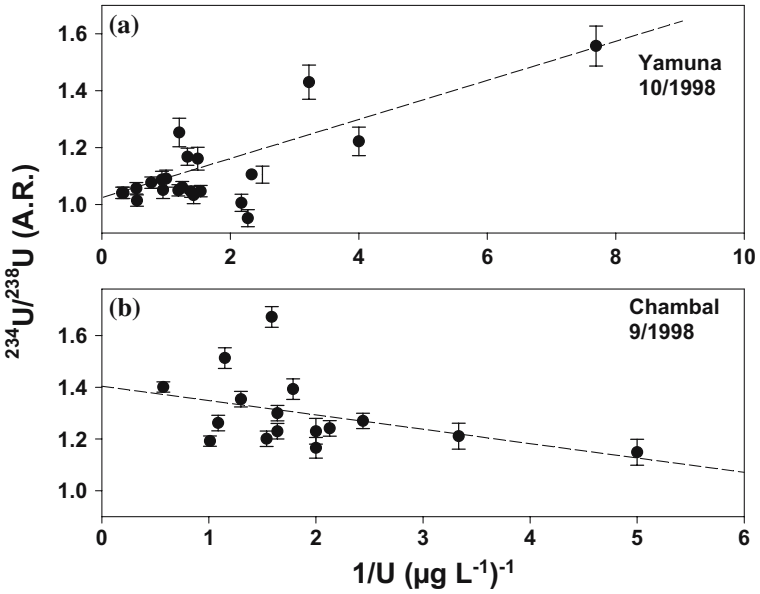

Figure 9. Plot of $^{234}U/^{238}U$ activity ratio vs. reciprocal uranium concentration (μg $L^{-1})^{-1}$, for samples from the Yamuna and the Chambal rivers. The samples were collected during (a) October 1998 and (b) September 1998. The Yamuna samples collected during post-monsoon and the Chambal seem to show an overall mixing trend ($r = 0.778$ for the Yamuna and 0.418 for the Chambal). The end member characteristics in the two river systems are opposite to each other. In the Yamuna, the low uranium end member has a high $^{234}U/^{238}U$ activity ratio whereas in the Chambal, the low uranium end member also has low $^{234}U/^{238}U$ activity ratio.

5.4. URANIUM WEATHERING RATES FROM THE YAMUNA AND THE CHAMBAL RIVERS

Using uranium concentration of 0.80 μg L^{-1} for the Yamuna river at Batamandi (downstream of the Bata river, RW98-4) and 0.41 μg L^{-1} for the Chambal river (upstream of Jawahar Sagar Dam, CH-22) and their corresponding water discharge (Table III), it can be estimated that ~9 and ~12 tons of uranium are transported annually in dissolved form from the Yamuna river at Batamandi (the foothills of the Himalaya) and the Chambal river at Udi respectively. This corresponds to uranium weathering rate of 0.9 kg U km^{-2} y^{-1} for the Yamuna river and 0.09 kg U km^{-2} y^{-1} for the Chambal river. The Yamuna and other Himalayan rivers have uranium weathering rates of ~1–2 kg U km^{-2} y^{-1} (Table III; Sarin et al., 1990), much higher than that of the Chambal and other Peninsular rivers, 0.1–0.5 kg U km^{-2} y^{-1} (Table III) as well as the global average value of ~0.08 kg U km^{-2} y^{-1} (Palmer and Edmond, 1993; Sarin et al., 1990).

The higher uranium weathering rate of the Yamuna river reinforces earlier results from other Himalayan rivers (Bhagirathi-Alaknanda river system) that the uranium fluxes to the Ganga-Brahmaputra is dominated by contribution from weathering of the HHC along with its associated uranium rich accessary minerals and some uranium rich sediments of the Lesser Himalaya (Sarin et al., 1990; Singh et al., 2003). Further, the annual uranium flux from the Ganga-Brahmaputra system to the Bay of Bengal is 1095×10^3 kg (Table III; Sarin et al., 1990). This is ~5 times the annual uranium production by India for nuclear power plants (207×10^3 kg y^{-1}; NEA, 2002). Also this uranium flux is ~15% of the global riverine flux to the ocean (Sarin et al., 1990); disproportionately higher by a factor of ~6 compared to contribution to global water discharge.

6. Conclusions

The study of the dissolved ^{238}U concentration and $^{234}U/^{238}U$ activity ratio in the headwaters of the Yamuna river draining the Himalaya and the Chambal river draining the Deccan Traps and the Vidhyan system in the plains of central India has provided insight into weathering and mobilization of uranium through these two distinct geological and lithological regimes. In general, uranium concentrations in these rivers are higher than the global average dissolved uranium concentration of 0.3 μg L^{-1} in rivers. About 9×10^3 kg and 12×10^3 kg 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. The uranium weathering rate of the Yamuna river is ~10 times higher than that of the Chambal as well as global average value of ~0.08 kg U km^{-2} y^{-1}. The

Table III. Comparison of uranium weathering rates in the Yamuna and the Chambal rivers with other major Indian rivers

River	Area 10^6 km^2	Water flow km^3 y^{-1}	Uranium Conc. μg L^{-1}	Uranium weathering rate		Ref.
				10^6 g y^{-1}	kg km^{-2} y^{-1}	
Himalayan rivers						
Yamuna at Batamandi	0.0096	10.8	0.8	8.6	0.90	1
Yamuna at Allahabad	0.140	93	1.72	160	1.14	3
Bhagirathi	0.0078	8.3	2.45	20	2.63	4
Alaknanda	0.0118	14	1.86	26	2.22	4
Ganga at Rishikesh	0.0196	22.4	2.65	59	3.03	1
Gomti	0.030	8	8.06	61	2.0	3
Narayani	0.0318	49.4	2.7	133	4.2	6
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
Indus	0.97	238	2.21	526	0.54	5
Peninsular rivers						
Chambal at Udi	0.139	30	0.41[a]	12	0.09	1
Chambal at Udi	0.139	30	1.04[b]	31	0.22	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
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

1. This work; 2. Borole et al. (1982); 3. Sarin et al. (1990); 4. Sarin et al. (1992); 5. Pande et al. (1994); 6. Chabaux et al. (2001).

[a]Uranium concentration at CH-22 (upstream of Jawahar Sagar Dam).

[b]Discharge weighted average uranium concentration at Dholpur (Sarin et al., 1990).

uranium weathering rates in the Himalaya is higher than that of the Chambal in the plains of central India and reinforces the importance of the Himalayan rivers in contributing dissolved uranium to oceans.

In the Yamuna main stream, uranium is highest at its source and decreases steadily along its course, from 3.18 μg L^{-1} at Hanuman Chatti and 0.67 μg 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 is derived from the weathering of the HHC and associated accessory minerals. The high concentration of uranium in organic rich sediments of the Lesser Himalaya makes this as a prospective source of dissolved uranium to the rivers of the Yamuna system draining this region.

In the Yamuna drainage basin, the $^{234}U/^{238}U$ activity ratio of the Yamuna mainstream is marginally in excess over radioactive equilibrium value whereas a few of its tributaries in the lower reaches flowing predominantly through the Lesser Himalaya, have high $^{234}U/^{238}U$ activity ratios. There is an overall inverse trend between $^{234}U/^{238}U$ activity ratio and $^{87}Sr/^{86}Sr$ in the Yamuna river system, the samples with lower $^{87}Sr/^{86}Sr$ isotope ratios, characteristic of tributaries from the lower reaches draining carbonates, have higher $^{234}U/^{238}U$ activity ratios.

The Chambal river and tributaries generally have lower uranium than the Yamuna watershed with higher $^{234}U/^{238}U$ activity ratios. The low uranium in the Chambal river system can be due to its low abundance in the Deccan Trap basalts and the Vindhyan system through which it flows.

Studies on the role of groundwater input and fertilizers in contributing to dissolved uranium in these rivers should be a focus of future research on the topic.

Acknowledgements

We thank Drs. T. K. Dalai S. K. Singh and J. R. Trivedi for their help during sample collection. We also thank the two anonymous reviewers for their helpful comments.

References

Bhat S. G. and Krishnaswami S. (1969) Isotopes of uranium and radium in Indian rivers, *Proc. Ind. Acad. Sci. (Earth Planet. Sci.)* **70**, 1–17.

Bickle M. J., Harris N. B. W., Bunbury J. M., Chapman H. J., Fairchild I. J. and Ahmad T. (2001) Controls on the $^{87}Sr/^{86}Sr$ ratio of carbonates in the Garhwal Himalaya, headwaters of the Ganges, *J. Geol.* **109**, 737–753.

Bonotto D. M. and Andrews J. N. (1993) The mechanism of $^{234}U/^{238}U$ activity ratio enhancement in karstic limestone groundwater, *Chem. Geol. (Isot. Geosci. Sect.)* **103**, 193–206.

Borole D. V., Krishnaswami S. and Somayajulu B. L. K. (1982) Uranium isotopes in rivers, estuaries and adjacent coastal sediments of western India: Their weathering, transport and oceanic budget, *Geochim. Cosmochim. Acta* **46**, 125–137.

CBPCWP (1982) *Basin-sub-basin inventory of water pollution. The Ganga Basin Part I The Yamuna sub-basin*. Central Board for the Prevention and Control of Water Pollution (CBPCWP), New Delhi, 114 pp.

Chabaux F., Riotte J., Clauer N. and France-Lanord C. (2001) Isotopic tracing of the dissolved U fluxes of Himalayan rivers: implications for present and past U budgets of the Ganges-Brahmaputra system, *Geochim. Cosmochim. Acta* **65**, 3201–3217.

Chabaux F., Riotte J. and Dequincey O. (2003) U–Th–Ra fractionation during weathering and river transport, *Rev. Mineral. Geochem.* **52**, 533–576.

Dalai T. K., Krishnaswami S. and Sarin M. M. (2002) Major ion chemistry in the headwaters of the Yamuna river system: Chemical weathering, its temperature dependence and CO_2 consumption in the Himalaya, *Geochim. Cosmochim. Acta* **66**, 3397–3416.

Dalai T. K., Singh S. K., Trivedi J. R. and Krishnaswami S. (2002a) Dissolved rhenium in the Yamuna River system and the Ganga in the Himalaya: Role of black shale weathering on the budgets of Re, Os and U in rivers and CO_2 in the atmosphere, *Geochim. Cosmochim. Acta* **66**, 29–43.

Dalai T. K., Krishnaswami S. and Kumar A. (2003) Sr and $^{87}Sr/^{86}Sr$ in the Yamuna river system in the Himalaya: sources, fluxes and controls on Sr isotopic composition, *Geochim. Cosmochim. Acta* **67**, 2931–2948.

Devi L. (1992) *Climatic Characteristics and Water Balance (A study of Uttar Pradesh)*. Concept Publishing Company, New Delhi, 207 pp.

Durand S., Chabaux F., Rihs S., Duringer P. and Elsass P. (2005) U isotope ratios as tracers of groundwater inputs into surface waters: Example of the upper Rhine hydrosystem, *Chem. Geol.* **220**, 1–19.

Gansser A. (1964) *Geology of the Himalaya*. Interscience, London, 289 pp.

Ghosh D. B. (1976) The nature of Narmada-Son lineament. In *Geological Survey of India*, Vol. 34, pp. 119–132. Miscellaneous Publications, "Tectonics and metallogeny of South and east Asia".

Herczeg A. L., Simpson H. J., Anderson R. F., Trier R. M., Mathieu G. G. and Deck B. L. (1988) Uranium and radium mobility in groundwaters and brines within the Delaware Basin, southeastern New Mexico, USA, *Chem. Geol. (Isot. Geosci. Sect.)* **72**, 181–196.

Jacobson A. D., Blum J. D. and Walter L. M. (2002) Reconciling the elemental and Sr isotope composition of Himalayan weathering fluxes: Insights from the carbonate geochemistry of stream waters, *Geochim. Cosmochim. Acta* **66**, 3417–3429.

Jha P. K., Subramanian V. and Sitaswad R. (1988) Chemical and sediment mass transfer in the Yamuna river – a tributary of the Ganges system, *J. Hydrol.* **104**, 237–246.

Krishnan M. S. (1982) *Geology of India and Burma*. CBS Publishers & Distributors, New Delhi, 536 pp.

Krishnaswami S. and Sarin M. M. (1976) The simultaneous determination of Th, Pu, Ra isotopes, ^{210}Pb, ^{55}Fe, ^{32}Si and ^{14}C in marine suspended phases, *Anal. Chim. Acta* **83**, 143–156.

Krishnaswami S., Trivedi J. R., Sarin M. M., Ramesh R. and Sharma K. K. (1992) Strontium isotope and rubidium in the Ganga-Brahmaputra river system: Weathering in the Himalaya, fluxes to the Bay of Bengal and contribution to the evolution of oceanic $^{87}Sr/^{86}Sr$, *Earth Planet. Sci. Lett.* **109**, 243–253.

Krishnaswami S., Singh S. K. and Dalai T. K. (1999) Silicate weathering in the Himalaya: Role in contributing to major ions and radiogenic Sr to the Bay of Bengal. In *Ocean*

Science – Trends and Future Directions (ed. B. L. K. Somayajulu), pp. 23–51. Ind. National Sci. Academy & Akademia Books International, New Delhi.

Langmuir D. (1978) Uranium solution-mineral equilibria at low temperatures with application to sedimentary ore deposits, *Geochim. Cosmochim. Acta* **42**, 547–569.

Mahoney J. J., Sheth H. C., Chandrasekharam D. and Peng Z. X. (2000) Geochemistry of flood basalts of the Toranmal Section, northern Deccan Traps, India: Implications for regional Deccan stratigraphy, *J. Petrol.* **41**, 1099–1120.

Mangini A., Sonntag C., Bertsch G. and Müller E. (1979) Evidence for a higher, natural U-content on world rivers, *Nature* **79**, 337–339.

Meece D. E. and Benninger L. K. (1993) The coprecipitation of Pu and other radionuclides with $CaCO_3$, *Geochim. Cosmochim. Acta* **57**, 1447–1458.

NEA (2002) *Uranium 2001. Resources Production and Demand.* 19th edn. Nuclear Energy Agency and Organization for Economic Co-Operation and Development, Paris, France, 350 pp.

Negi S. S. (1991) *Himalayan Rivers, Lakes and Glaciers*. Indus Publishing Co., New Delhi.

Pachauri A. K. (1992). Plate tectonics and metallogeny in the Himalaya, In *Himalayan Orogen and Global Tectonics, International Lithosphere Programme, Publication No. 197* (ed. Sinha, A. K.). New Delhi: Oxford and IBH Publishing, pp. 267–288.

Palmer M. R. and Edmond J. M. (1993) Uranium in river water, *Geochim. Cosmochim. Acta* **57**, 4947–4955.

Pande K., Sarin M. M., Trivedi J. R., Krishnaswami S. and Sharma K. K. (1994) The Indus river system (India-Pakistan): Major ion chemistry, uranium and strontium isotopes, *Chem. Geol.* **116**, 245–259.

Rao K. L. (1975) *India's Water Wealth*. Orient Longman Ltd., New Delhi, 255 pp.

Rengarajan R. (2004) Radium isotopes and rare earth elements in Indian rivers and the Bay of Bengal, Ph. D. thesis, Mohan Lal Sukhadia University, Udaipur, 245 pp.

Rengarajan R. and Sarin M. M. (2004) Distribution of rare earth elements in the Yamuna and Chambal rivers, India. *Geochem. J.* **38**, 551–569.

Rengarajan R., Sarin M. M. and Krishnaswami S. (2003) Uranium in the Arabian Sea: Role of denitrification in controlling its distribution, *Oceanol. Acta* **26**, 687–693.

Riotte J. and Chabaux F. (1999) $^{234}U/^{238}U$ activity ratios in freshwaters as tracers of hydrological processes: The Strengbach watershed (Vosges, France), *Geochim. Cosmochim. Acta* **63**, 1263–1275.

Saraswat A. C. and Mahadevan T. M. (1989) On the genetic aspects of uranium mineralisation in the Himalaya, Proc. Tech. Comm. Meet. on "Metallogenesis of Uranium Ore Deposits", International Atomic Energy Agency, Vienna, IAEA-TC-542/23, pp. 369–397.

Sarin M. M., Krishnaswami S., Dilli K., Somayajulu B. L. K. and Moore W. S. (1989) Major ion chemistry of the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal, *Geochim. Cosmochim. Acta* **53**, 997–1009.

Sarin M. M., Krishnaswami S., Somayajulu B. L. K. and Moore W. S. (1990) Chemistry of uranium, thorium and radium isotopes in the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal, *Geochim. Cosmochim. Acta* **54**, 1387–1396.

Sarin M. M., Bhushan R., Rengarajan R. and Yadav D. N. (1992) Simultaneous determination of ^{238}U series nuclides in waters of Arabian Sea and Bay of Bengal, *Indian J. Mar. Sci.* **21**, 121–127.

Sarin M. M., Krishnaswami S., Sharma K. K. and Trivedi J. R. (1992) Uranium isotopes and radium in the Bhagirathi-Alaknanda river system: Evidence for high uranium mobilization in the Himalaya, *Curr. Sci.* **62**, 801–805.

Singh S. K., Trivedi J. R. and Krishnaswami S. (1999) Re-Os isotope systematics in black shales from the Lesser Himalaya: Their chronology and role in the $^{187}Os/^{188}Os$ evolution of seawater, *Geochim. Cosmochim. Acta* **63**, 2381–2392.

Singh S. K., Dalai T. K. and Krishnaswami S. (2003) ^{238}U series isotopes and ^{232}Th in carbonates and black shales from the Lesser Himalaya: Implications to dissolved uranium abundances in Ganga-Indus source waters, *J. Environ. Radioact.* **67**, 69–90.

Valdiya K. S. (1980) *Geology of the Kumaun Lesser Himalayas*. Wadia Inst. Himalayan Geology, Dehradun, 291 pp.

Valdiya, K. S.,Bhatia, S. B.and Gaur, V. K. (eds.) (1982) *Geology of Vindhyanchal*. Hindustan Publishing Corporation, Delhi, 231 pp.

Vigier N., Bourdon B., Lewin E., Dupré B., Turner S., Chakrapani G. J., van Calsteren P. and Allègre C. J. (2005) Mobility of U-series nuclides during basalt weathering: An example from the Deccan Traps (India), *Chem. Geol.* **219**, 69–91.

Yadav D. (1995) Chemical and isotopic studies in coastal areas of the Arabian Sea and saline lakes of Rajasthan (India), Ph.D. thesis, M. S. University, Baroda, 140 pp.

Zielinski R. A., Simmons K. R. and Orem W. H. (2000) Use of ^{234}U and ^{238}U isotopes to identify fertilizer-derived uranium in Florida Everglades, *Appl. Geochem.* **15**, 369–383.