Chapter 2

Materials and Methods

The primary goals of this thesis, as detailed in the Introduction, are to determine (i) the sources of sediments to the Ganga basin in the plain in terms of various sub-basins (ii) spatial variability in physical and chemical erosion among the Ganga sub-basins (iii) chemical and silicate erosion in the Ganga drainage based on elemental composition of water and sediments and (iv) the budget of Sr and ^{87}Sr/^{86}Sr in the Ganga and its relation to the geochemistry of dissolved Ca. Addressing these goals require sampling of water, sediment and other relevant samples from the Ganga basin and knowledge of basin lithology and hydrology. This chapter provides a description of these details, viz lithology of the basin, the sampling locations, their collection and analytical methods. The accuracy and precision of various measurements are also given in this chapter.

2.1 Study Area

This work, as mentioned in the Introduction chapter, is focused on studies of dissolved and particulate components of the Ganga river system. The Ganga River, known as the Bhagirathi in the Himalaya, originates from the Gangotri glacier at "Gaumukh" in the Higher Himalaya. At Devprayag, the Alaknanda joins the Bhagirathi and forms the Ganga (Fig-2.1a). The head waters of the Alaknanda, the Saraswati and the Dhauli, emerge from the Bhagirathi Kharak (east of the Gangotri glacier) and the Bamak glaciers. At Haridwar, the Ganga descends to the plains after cutting across the Siwalik ranges. The Ganga receives many tributaries, the Ramganga, the Gomti, the Ghaghra, the Gandak and the Kosi from the north and the Yamuna and the Son from the south (Fig-2.1b). The Gomti and the Son are two major tributaries of the Ganga which have non-Himalayan sources.

The Gomti is a rain fed river with its entire drainage in the Ganga plain. It originates from the reservoir Madho-Tanda (Fig-2.1b; Miankot, elevation ~200 m, 28° 34′ N and 80° 07′ E) in the Pilibhit district, Uttar Pradesh located ~ 50 km south of the foot hills of the Himalaya. It drains the interfluve sediments between the Ganga and the Ghaghra, through an area of ~30×10^3 km^2, prior to joining the Ganga at Udyar Ghat near Ghazipur, ~30 km downstream of Varanasi (Fig-2.1b). The annual water discharge of the Gomti is 7.4 km^3, with most of its flow during the southwest monsoon. The river drainage of the Gomti has a gentle slope, in the range of 550 and 100 mm km^{-1} with a maximum relief of ~25 m (Singh et al., 2005a; Singh et al., 2005b).

The Yamuna is the largest tributary of the Ganga in terms of drainage area ~366 x10^3 km^2 and accounts for ~40 % of the Ganga basin. It originates from the Yamunotri glacier in the Himalaya and descends to the Ganga plain at Dak Pathar, after merging with a number of tributaries in the Himalaya (Dalai et al., 2002). The annual water discharge of the Yamuna at Tajewala (Fig-2.1b), near the foot hills of the Himalaya is 10.8 km^3 yr^{-1}, about 12% of its discharge at Allahabad, 93 km^3 yr^{-1} (Rao, 1975). Nearly 75% of the discharge of the Yamuna occurs during June-Sept, the south west monsoon period. The Chambal, Sind, Betwa and the Ken are the major tributaries of the Yamuna, all of which originate in and flow almost entirely through peninsular India. All these tributaries join the Yamuna in the Gangetic plain before its confluence with the Ganga at Allahabad (Fig-2.1b). Of the total drainage area of the Yamuna, ~3% is in the Himalaya, 63% in the peninsular basin and 34% in the Ganga plain. In estimating this, the sum of the areas of the Chambal, Sind, Betwa and the Ken are taken to be equal the peninsular drainage. The headwater basins of the Yamuna tributaries in the peninsular drainage have a slope of ~750 mm km^{-1}. Drainage basins of both the Gomti and the Yamuna, particularly in the plain, are endoreic with micro-depressions or level topography with poor drainage. Rain and flood waters often get trapped in these basins eventually subject to drying during summer. This results in the deposition of various salts, such as sodium carbonate, sodium bicarbonate, sodium chloride and sodium sulphate in the basin (Agarwal and Gupta, 1968; Bhargava et al., 1981; Pal et al., 2003). Some of these salts make their way to rivers and also to groundwater during subsequent wetting cycles in monsoon. The salinization of soils has been further aggravated with the development of canal systems in the Gangetic plain for irrigation.

The Son is another tributary of the Ganga with its drainage predominantly in peninsular India. A part of its basin prior to its confluence with the Ganga is in the Ganga plain. The Son originates from the Amarkantak in the Bundelkhand plateau and merges with the Ganga ~25 km upstream Patna (Fig-2.1b). The Son is also a rainfed river with annual discharge of $\sim32\times10^9$ m^3 and drainage area of $\sim71\times10^3$ km^2 with $\sim10\times10^3$ km^2 in the plain (estimated using global mapper). The headwaters of the Son are in the mountainous region of the Indian craton and Vindhyan having a slope of ~1500 mm km^{-1}, its outflow in the Gangetic plain, however, has a much gentler slope, ~100 mm km^{-1}. The Son is also a seasonal river with most of its discharge during monsoon. Its drainage receives an annual rainfall of ~1300 mm yr^{-1} (http://www.tropmet.res.in). Its runoff is ~450 mm yr^{-1}.

The Kosi (Sapta Kosi), Gandak (Narayani) and the Ghaghra (Karnali) are major rivers of the Ganga system, all of them originating from glaciers and snow-fed lakes of the Nepal Himalaya. The Kosi river system consists of the Arun, the Sunkosi and the Tamakosi rivers (Fig-2.1a). Flowing through a narrow gorge and called the Kosi after it enters into the Indian territory. The Kosi has the second largest drainage area ($\sim75\times10^3$ km^2; Table-2.1) among the tributaries of the Ganga after the Yamuna. It is joined by the tributaries, the Bagmati and the Kamala before it merges in to the Ganga. The Gandaki river system in central Nepal consists of the Kaligandaki, Budhigandaki, Marsyandi, Trishuli and Seti rivers. The Kaligandaki and the Trishuli are the main tributaries of this system. The Kaligandaki converges with the Trishuli and is called the Narayani which goes on to meet the Ganges as the Gandak near Hazipur. The Ghaghra river system originates from the western Nepal. It consists of the Kali, Karnali, Seti and the Bheri rivers and has the highest water discharge ($\sim95\times10^9$ $m^{3)}$ among the tributaries of the Ganga system (Table-2.1). The Ghaghra merges with the Ganga near Revilganj. Among these three basins, the precipitation over the Gandak drainage in the Higher Himalaya is much higher compared to those over the Ghaghra and the Kosi headwaters. It also has the highest relief of >3 km as compared to that of the Ghaghra (2.6 km) and the Kosi (2.8 km) among the Himalayan tributaries of the Ganga (Bookhagen and Burbank, 2006).

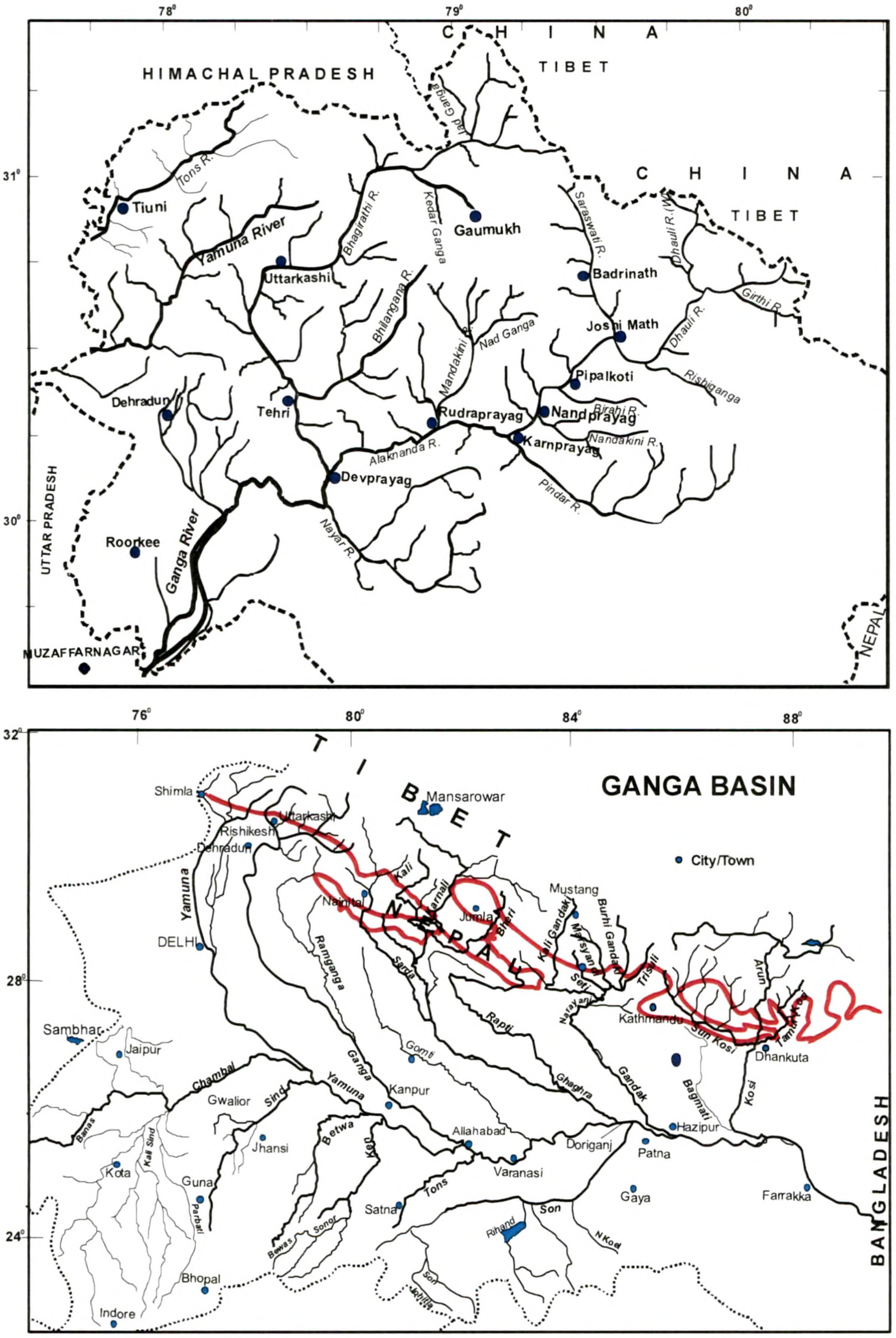


Fig-2.1a & 1b: Map of the Ganga basin. (a): the head water basin of the Ganga in the Himalaya (b): the Ganga basin, with its major tributaries in the Himalaya and the plains. The red line is MCT.

The Gandak and the Kosi rivers have an average gradient of 5 km in 200 km whereas the Ghaghra has a marginally lower gradient of 5 km in 300 km (S-N distance) across the Himalaya. Table-2.1 gives the discharge and drainage area of the Ganga and some of its tributaries at locations prior to their confluence with the Ganga in the plains. The total drainage area of the Ganga basin is ~935×10^3 km^2 with a discharge $380\text{x}10^9$ m^3 yr^{-1} at Farakka, near the Indo-Bangladesh border (Table-2.1).

Table 2.1: Drainage Area and Discharge of major rivers of the Ganga System

River	Location	Area		Discharge	
		Total	Himalaya	Total	Himalaya
		10^3 km^2		10^9 m^3 yr^{-1}	
Bhagirathi	Devprayag	7.8	7.8	8.3	8.3
Alaknanda	Devprayag	11.8	11.8	14.1	14.1
Ganga	Rishikesh	21.7	21.7	23.9	23.9
Ramganga*		32.5	2.5	15.6	9.8
Yamuna	Allahabad	366	9.8	93.0	10.8
Tons*		16.9	nil	5.9	nil
Gomti*	Sighauna	30.5	nil	7.4	nil
Ghaghra*	Revilganj	128	57.6	94.4	63.4
Gandak	Hazipur	46.3	31.8	52.2	49.4
Kosi*	Dumariaghat	74.5	51.4	62.0	48.2
Son*	Koilawar	71.3	nil	31.8	nil
Ganga	Farakka	935	176	380	206

Data from[*Galy*, 1999; *http://www.grdc.sr.unh.edu*, 2004; *Rao*, 1975]
*Before confluence with the Ganga mainstream

The rainfall and runoff among the different regions of the Ganga basin show significant heterogeneity with the highest runoff in excess of a meter yr^{-1} in the Himalayan drainage (Donold,1992) and the lowest of ~0.3 m yr^{-1} over the Gangetic Plains and the peninsular regions (Rao,1975). The southwest monsoon (June-September) is the major source of water to the Ganga system; however snowmelt and groundwater also contribute water to the rivers draining the Himalaya (Bahadur, 1997). Melt water from the Himalayan glaciers contribute

~15% of the Ganga river discharge at Haridwar (Das Gupta, 1975). The Ganga divides into two distributaries before it enters the Bangladesh. It joins the Brahmaputra in Bangladesh and discharges into the Bay of Bengal through many distributaries.

2.2 Geological setting

The Ganga catchment is spread over the Himalaya in the north, peninsular India in the south and the Gangetic plain between them. The head waters of the Ganga, its tributaries the Ghaghra, Gandak and the Kosi have a significant part of their drainage in the Himalaya. The tributaries of the Yamuna (the Chambal, Sind, Betwa and the Ken; Fig-2.1b) and the Son flow mainly through peninsular India. The rivers Gomti and the Ganga down stream of Haridwar drain the Ganga plain.

The Himalaya in the Ganga basin is made of four major lithological units, the Tethyan Sedimentary Series (TSS), the Higher Himalaya (HH), the Lesser Himalaya (LH) and the Siwalik (Gansser, 1964; Valdiya, 1980; Sarin et al., 1989; Bickle et al., 2001). The lithology of each of these units over the entire Himalayan range, from east to west, is roughly the same (Gansser, 1964; Le Fort, 1975; Valdiya, 1980). The head waters of the Alaknanda, Ghaghra, Gandak and the Kosi lie in the Tethyan Sedimentary Series (TSS). The TSS is composed of carbonates and clastic sedimentary rocks (Oliver et al., 2003). The HH consists of ortho- and paragneisses, migmatites and metamorphosed carbonates and calc-silicates. Granites, gneisses and leuco-granites which form the Higher Himalayan Crystallines (HHC) are exposed widely in this region. South of the HH, and separated by the Main Central Thrust (MCT) is the Lesser Himalaya (LH). The lithologies of the LH are meta-sedimentary rocks which include limestones, dolomitic carbonates, shales, slates, quartzites, evaporites and calc-silicates. The LH is divided into two sedimentary sequences, the outer and inner belts, separated by the Lesser Himalayan Crystallines (LHC) consisting of granites and gneisses (Valdiya, 1980). The Siwaliks is the southernmost unit of the Himalaya formed by the uplift of sediments deposited in its foreland basin during the Mio-Pliocene (Valdiya, 1980). It consists mostly of sandstones.

The Peninsular drainage: The major lithologies exposed in this drainage are the Bundelkhand crystallines (granites), the Vindhyan sediments (carbonates, shales and sandstones) and the Deccan basalts (Krishnan, 1982; Singh et al., 2008). Besides these lithologies, saline and alkaline soils are dispersed to varying degrees in the recent alluvium of this basin including the Chambal drainage around Gwalior (Agarwal and Gupta, 1968; Bhargava and Bhattacharjee, 1982; Sarin et al., 1989; Tamgadge et al., 1996; Rengarajan et al., 2008). The tributaries of the Yamuna (Chambal, Sind, Betwa and Ken) and the Son though drain peninsular India, they flow through different lithologies. The Yamuna tributaries (Chambal, Sind, Betwa) drain the Deccan Traps and the Vindhyans whereas the Son lies mainly in the Vindhyan-Bundelkhand plateau. The latter region is made of crystalline igneous and metamorphic rocks of the Archean shield and limestones, shales and sandstones of the Vindhyans (Krishnan, 1982). Southern tributaries of the Son drain the sedimentary sequences of the Gondwana comprising of sandstone, shales and carbonates (Krishnan, 1982).

The Ganga plain: is a major alluvial tract that has evolved through time (Singh, 1996). It is formed by the accumulation of detritus from the source regions of the Ganga and its tributaries, the Higher and the Lesser Himalaya (Singh, 1996; Singh et al., 2008; Rai et al, 2008) and consists of beds of clay, sand and gravel (Sinha et al., 2005). These alluvial sediments also contain impure calcareous matter in the form of irregular concretions in clays or as independent layers, locally known as "kankar" (Agarwal et al., 1992; Singh et al., 2004, Sinha et al., 2006). These kankars are formed from river water/groundwater during their drying cycles and are dispersed in sediments of the plain (Agarwal et al., 1992; Srivastava, 2001; Sinha et al., 2006). Besides these kankar carbonates, detrital carbonate brought from the Himalaya is also present in these alluvial sediments. The carbonates are predominantly calcium carbonate, though magnesium carbonate is also reported in some of them (Agarwal et al., 1992; Singh et al., 2004; Sinha et al., 2006). The abundance of calcareous matter in the plain varies significantly, with values as high as 30% (Wadia, 1981; Gupta and Subramanian, 1994). At places these carbonates form large deposits which are mined locally (Kumar, 2005). A significant part of the soils in the Gomti and the Yamuna drainage in the Ganga plain is impregnated with alkaline and saline salts formed locally due to the endoreic nature of the basins and excessive use of river and groundwater for irrigation (Agarwal and Gupta, 1968; Bhargava and Bhattacharjee, 1982; Tamgade et al., 1996; Pal et al., 2003). The abundance of these soils varies significantly within and among the basins. For example, in the Ganga plain high content is reported (Singh et al., 2004) in the stretch between Kanpur to Ghazipur (Ganga), Delhi to Allahabad (Yamuna) and Madho-Tanda to Ghazipur (Gomti). In general, the abundance of these alkaline/saline soils is more towards the western basin of the Ganga due to the semi-arid climate and basin characteristics. The soils, as mentioned earlier, contain many sodium salts (Agarwal and Gupta, 1968; Bhargava et al., 1981; Bhargava and Bhattacharjee, 1982; Datta et al., 2002, Singh et al., 2004).

2.3 Climatic features of the Ganga Basin:

The Ganga catchment and its sub-basins, covering the northern India and Nepal (Fig-2.1a & 2.1b) experience tropical monsoon climate with varying intensities (Devi, 1992) induced by the altitude and mountain barriers. The temperature in the Ganga catchment reaches its minimum in January and the maximum in the month of June. The temperature decreases with the onset of southwest monsoon in June. In the Ganga basin, the cold period extends from December to February with the coldest in January when air temperature dips below 10°C. The air temperatures starts rising from March onwards and persists up to mid June with May being the hottest month in the basin (Assessment and development study of river basin Series ABSORBS/7/1982-83). In the Ganga plain, at many locations, the daily mean temperature exceeds to 40°C in May causing extensive evaporation. The maximum evaporation takes place during March to July in the entire basin (Fig-2.2). The southwest monsoon sets in the

Ganga basin during June-July and continues for about 3-4 months. This is the major source of water for the Ganga basin and is reflected in its monthly water discharge pattern (Fig-2.3) for the four locations (Rishikesh, Allahabad, Patna and Azamabad). The spatial and temporal variation in water discharge of the Ganga river are regulated by its tributaries which in turn are controlled by rain fall in their basin.

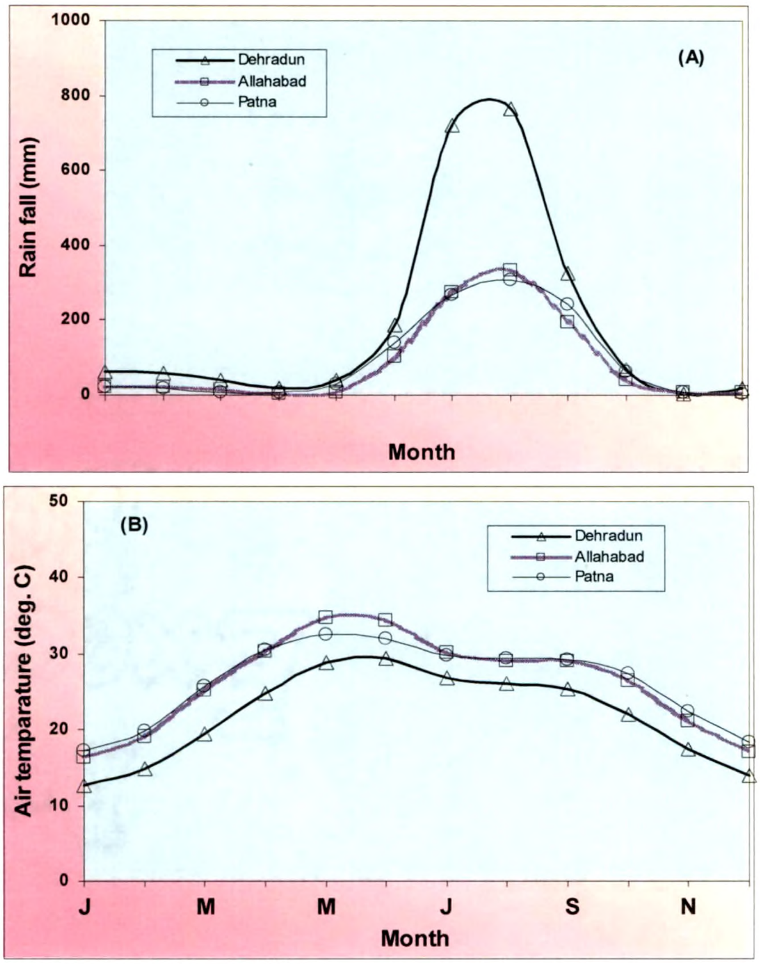


Fig-2.2: Monthly variation of (A) Rainfall; the maximum rainfall is restricted to Jun-Sept, southwest monsoon. (B) Mean air temperature at the different location in the Ganga basin. (Data Source: Assessment and development study of river basin Series ABSORBS/7/1982-83)

The geographical distribution of rain fall (Fig-2.4; averaged over 10 years) clearly shows a negative gradient form east to west in the plains. Rainfall contours over the Ganga drainage for Jan 1998 -May 2007 (Fig-2.4) (http://disc2.nascom.nasa.gov/Giovanni/tovas/TRMM_V6.3B43.shtml) show that belts of higher rainfall are observed close to and paralleling the Main Central Thrust (MCT) particularly over the Gandak sub-basin and in the Son and Ken headwaters in peninsular India and lower rainfall in the plains and over catchments of the southern tributaries. High precipitation is also observed over the Lesser Himalayan catchment of the Ganga sub-basin around Rishikesh. This variability in precipitation among different regions of the Himalaya and the plain, results in significant regional differences in runoff and in contribution to the water budget of the Ganga. Thus the Himalayan basin of the Ganga has a runoff of about 1m yr^{-1} and accounts for ~54% of its water discharge, in comparison the peninsular rivers contribute ~22% of water discharge with a runoff of ~0.3 m yr^{-1} (Galy, 1999; Rao, 1975).

Annual rainfall in the Gomti basin, based on data for the decade (1997-2006), average ~1025 mm (http://www.tropmet.res.in/; http://disc2.nascom.nasa.gov/Giovanni/tovas/TRMM_V6.3B43.shtml;Fig-2.4) whereas its runoff is only 240 mm yr^{-1}. Thus, about 75 % of rainfall in the Gomti drainage is either returned to the atmosphere through evaporation/evapotranspiration and/or stored as groundwater. Rainfall in the drainage basin of the Yamuna shows significant spatial variation (Fig-2.4). Its headwaters in the Himalaya receive ~1300 mm yr^{-1} rainfall which decreases to ~700 mm yr^{-1} around Delhi in the Ganga plain. The peninsular drainage of the Yamuna receives an annual rainfall of ~800 mm (http://www.tropmet.res.in, TRMM). The runoff of the Yamuna in the Himalayan region is ~1100 mm yr^{-1} whereas in the peninsular drainage it is much lower, ~250 mm yr^{-1}.

2.4 Sampling

For this work, samples of water, sediments and particulate matter from the entire stretch of the Ganga in India, from Gangotri near its source to Rajmahal near its outflow and from the major tributaries of the Ganga in the Himalaya and the plains were collected. The sampling work was done during three field campaigns, May 2003, May 2004 and October 2006.

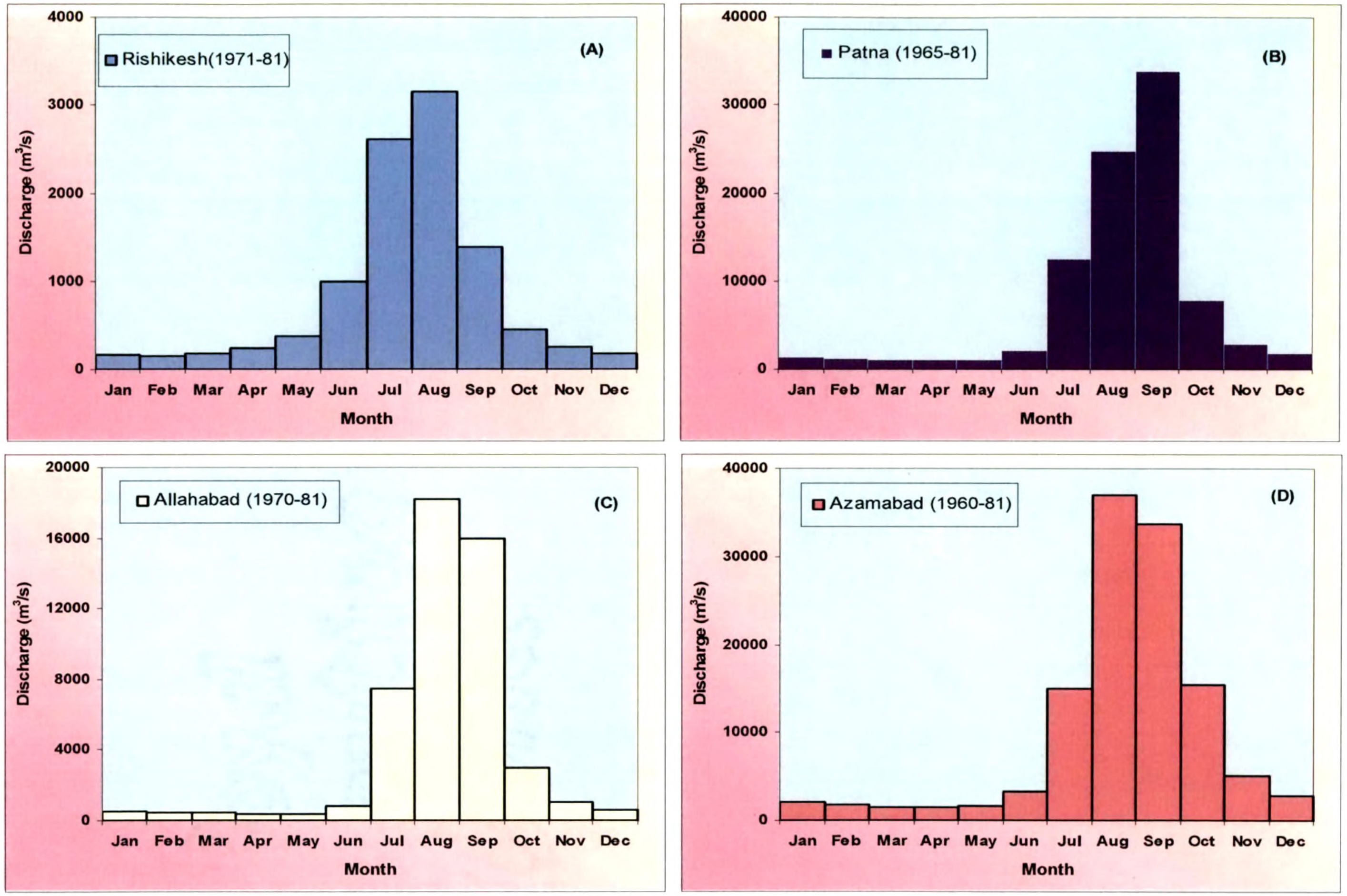


Fig-2.3 (A, B, C & D): Monthly variation of water discharge of the Ganga river at different locations along its course.
(Data Source: Assessment and development study of river basin Series ABSORBS/7/1982-83)

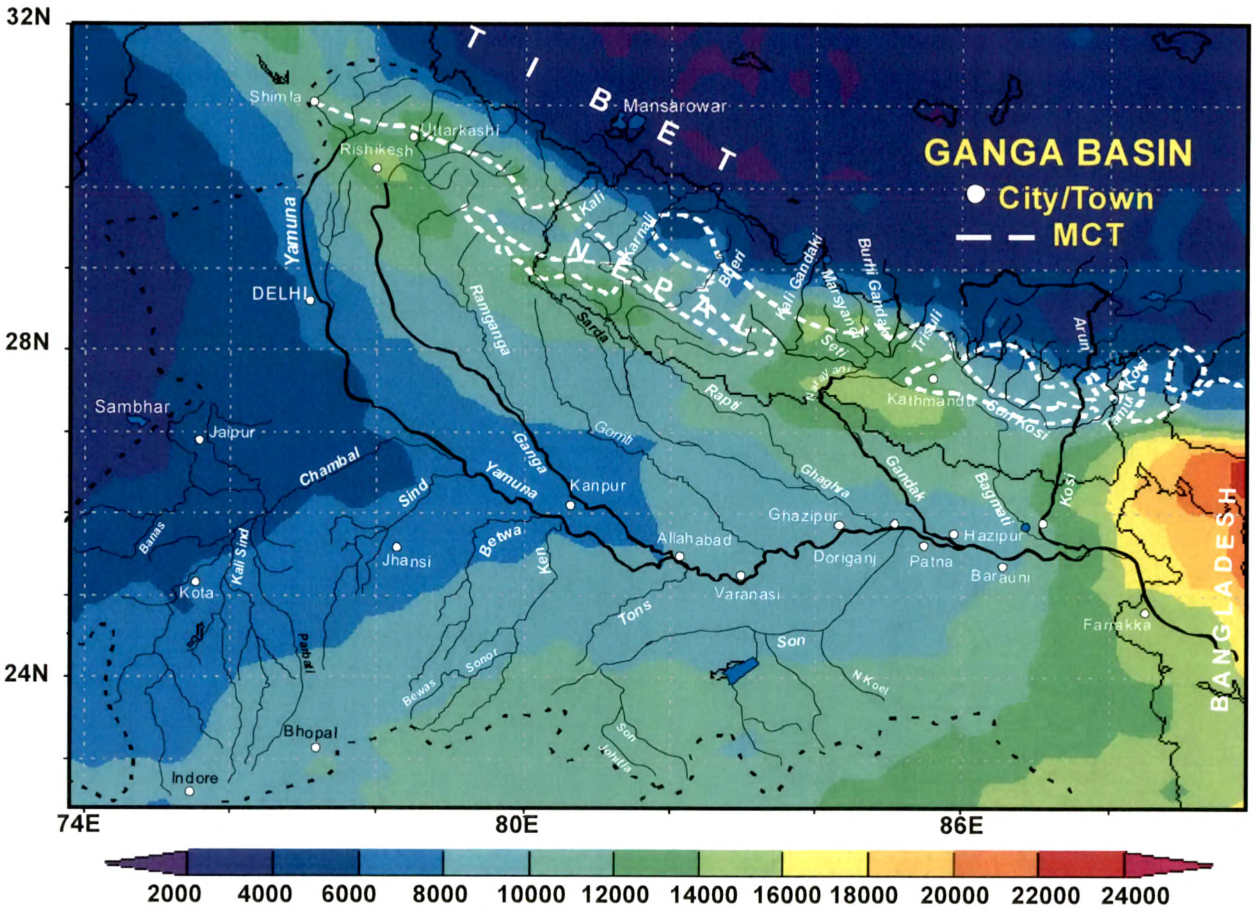


Fig-2.4: Precipitation over the Ganga drainage for the period January 1998 to May 2007, from TRMM (expressed in mm). The precipitation over the Gandak drainage in the Higher Himalaya is much higher compared to those over the Ghaghra and the Kosi head waters. The region of higher rainfall in the Gandak drainage coincides with the high relief. The Main Central Thrust (MCT) is marked as dashed line.

Table - 2.2: Sample locations of river sediments

Sample code	River	Date d/m/y	Location	Latitude N	Longitude E	Altitude m	Drainage Lithology
Ganga Mainstream							
RS03-3	Bhagirathi	02.05. 03	Gangotri	30° 60'	78° 56'	2968	HH
RS03-7	Bhagirathi	03.05. 03	Uttarkashi	30° 44'	78° 27'	1192	HH
RS03-1	Ganga	01.05. 03	Rishikesh	30° 31'	78° 21'	335	LH, LH
BR05-1	Ganga	25.05.05	Kanpur				GP,SW, LH, HH
BR352, 351**	Ganga	14.05. 04	Allahabad	25° 26'	81° 53'		GP,SW, LH, HH, P
BR06-12-2	Ganga	20.10.06	Allahabad	25° 30'	81° 52'		GP,SW, LH, HH, P
BR382, 383**	Ganga	17.05. 04	Varanasi	25° 18'	84° 00'		GP,SW, LH, HH, P
BR06-14-2	Ganga	21.10.06	Varanasi	25° 18'	83° 01'		GP,SW, LH, HH, P
BR06-10-1	Ganga	19.10.06	Ghazipur	25° 32'	83° 12'		GP,SW, LH, HH, P
BR06-802	Ganga	19.10.06	Doriganj	25° 44'	84° 49'		GP,SW, LH, HH, P
BR306	Ganga	07.05. 04	Patna	25° 37'	85°09'		GP,SW, LH, HH, P
BR06-303	Ganga	16.10.06	Patna	25° 37'	85° 09'		GP,SW, LH, HH, P
BR315, 314**	Ganga	08.05. 04	Barauni	25° 23'	86° 00'		GP,SW, LH, HH, P
BR06-404	Ganga	17.10.06	Barauni	25° 22'	86° 00'		GP,SW, LH, HH, P
BR324, 325**	Ganga	09.05. 04	Rajmahal	25° 04'	87° 50'		GP,SW, LH, HH, P
BR06-101	Ganga	15.10.06	Rajmahal	25° 03'	87° 50'		GP,SW, LH, HH, P
Alaknanda							
RS03-28	Alaknanda	05.05.03	Birhai, Bef. Confl[a]	30° 25'	79° 23'	1037	LH, HH
RS03-27	Birahi Ganga	05.05. 03	Birahi			1039	LH, HH
RS03-31	Pindar	05.05. 03	Pindar Valley	30° 05'	79° 28'	1034	LH, HH
Bhagirathi Tributaries							
RS03-9	Syansu Gad	03.05. 03		30° 29'	78° 24'	838	LH, HH
RS03-12	Bhilangna	03.05. 03	Ghanshyali				LH, HH
Tributaries in Plain							
BR348	Yamuna	15.05. 04	Allahabad	25° 25'	81° 50'		GP,SW, LH, HH, P
BR06-13-2	Yamuna	20.10.06	Allahabad	25° 25'	81° 50'		GP,SW, LH, HH, P

BR365, 364**	Rapti	15.05. 04	Gorakhpur	26° 44'	82° 21'	GP,SW, LH, HH
BR378	Gomti	16.05. 04	Before Confl.	25° 30'	83° 08'	GP
BR06-11-3	Gomti	19.10.06	Ghazipur	25° 30'	83° 08'	GP
BR355, 356**	Ghaghra	15.05. 04	Ayodhya	26° 49'	82° 12'	GP,SW, LH, HH
BR371, 372**	Ghaghra	15.05. 04	Doharighat			GP,SW, LH, HH
BR343, 344**	Ghaghra	12.05. 04	Revelganj	25° 49'	84° 35'	GP,SW, LH, HH
BR06-905	Ghaghra	19.10.06	Revilganj	25° 49'	84° 36'	GP,SW, LH, HH
BR06-205	Son	16.10.06	Koilawar	25° 34'	84° 48'	P
BR336**, 335**	Gandak	11.05. 04	Barauli	26° 22'	84° 45'	GP,SW, LH, HH
BR310	Gandak	07.05. 04	Hazipur	25° 41'	85° 11'	GP,SW, LH, HH
BR06-701	Gandak	18.10.06	Hazipur	25° 41'	85° 11'	GP,SW, LH, HH
BR330, 331**	Kosi	10.05. 04	Dumarighat	25° 32'	86° 43'	GP,SW, LH, HH
BR06-502	Kosi	18.10.06	Dumarighat	25° 33'	86° 43'	GP,SW, LH, HH
BR06-603	Baghmati	18.10.06	Dumarighat	25° 33'	86° 43'	GP

* Major lithologies in the drainage basin upstream of sampling site.
HH: Higher Himalaya, LH: Lesser Himalaya, SW: Siwaliks, GP: Ganga plain, P: Peninsular.

** From these location two samples were collected, one representative of bank sediments and the other samples richer in clay collected from sand bars or depositing from still water condition within a few of meters from the bank.

[a] bef. confl.: before confluence with mainstream

Table 2.3: Sampling details of the Ganga River and its tributaries

Sample	River	Date	Location	Elevation	pH	Temp.	Cond.	CSI
Bhagirathi system								
RW03-5	Bhagirathi (Gangotri)	02.05.2003	N 30^0 59.642' E 78^0 56.477'	2968	-	-	-	
RW03-8	Bhagirathi (Uttarkashi)	03.05.2003	N 30^0 43.755' E 78^0 26.777'	1192	-	-	-	
RW03-9	Syansu Gad	03.05.2003	N 30^{0}29.373' E 78^0 23.745'	838	-	-	-	
RW03-10	Bhilangana (Ghaushyali)	03.05.2003	-	-	-	-	-	
RW03-3	Bhagirathi (DevPrayag)	01.05.2003	N 30^0 08.729' E 78^0 35.866'	448	8.6	17.5	-	0.09
RW03-6	Glacier melt (Higher Himalaya)	02.05.2003	N 30^0 59.853' E 78^0 41.720'	2641	-	-	-	
Alaknanda system								
RW03-4	Alaknanda (DevPrayag)	01.05.2003	N 30^0 08.730' E 78^0 35.872'	455	8.1	17.5	-	-0.23
RW03-11	Alaknanda (Rudrapryayag)	04.05.2003	N 30^{0}17.280' E 78^0 58.744'	629	-	-	-	
RW03-12	Mandakini (Rudrapryayag)	04.05.2003	N 30^{0}17.280' E 78^0 58.744'	629	-	-	-	
RW03-13	Birhi Ganga (Trib.)	04.05.2003	N 30^{0}23.823' E 79^0 23.935'	1077	-	-	-	
RW03-14	Birahi Ganga (Birhi)	05.05.2003	N 30^{0}24.488' E 79^0 23.281'	1045	-	-	-	
RW03-15	Alaknanda (Birhi, before confl.)	05.05.2003	N 30^{0}24.542' E 79^0 23.291'	1037	-	-	-	
RW03-16	Pindar river (Pindar Valley)	05.05.2003	N 30^{0}05.290' E 79^0 27.845'	1150	-	-	-	
Ganga in Plain(2004)								
RW03-2	Ganga (Rishikesh, upstream)	01.05.2003	N 30^0 30.865' E 78^0 20.806'	335	8.1-8.6	17.9	-	0.05
BR-388	Ganga (Varanasi)	17.05.2004	N 25^0 17.840' E 84^0 00.400'	75	8.3	32.4	565	0.83
BR-309	Ganga (Patna)	07.05.2004	N 25^0 37.400' E 85^0 09.050'	45	8.1	29.0	432	0.62
BR-318	Ganga (Rajmahal)	09.05.2004	N 25^0 03.660' E 87^0 50.420'	28	8.1	30.9	322	0.44
Tributaries in Plain(2004)								
BR-346	Yamuna (Allahabad)	14.05.2004	N 25^0 25.160' E 81^0 50.190'	-	8.2	30.4	701	0.76
BR-375	Gomati (Ghazipur)	16.05.2004	N 25^0 30.350' E 83^0 08.360'	68	8.6	34.0	495	1.13
BR-342	Ghagra (Revilganj)	12.05.2004	N 25^0 49.170' E 84^0 35.090'	56	8.2	30.4	300	0.54
BR-354	Ghagra (Faizabad)	15.05.2004	N 26^0 48.770' E 82^0 12.150'	98	8.2	29.5	299	0.59
BR-363	Rapti (Gorakhpur)	15.05.2005	N 26^0 44.200' E 82^0 20.710'	81	8.3	31.8	376	0.83
BR-311	Gandak (Hazipur)	07.05.2004	N 25^0 41.290' E 85^0 11.300'	45	8.0	30.4	251	0.20
BR-334	Gandak (Barauli)	11.05.2004	N 26^0 21.600' E 84^0 44.710'	67	8.1	31.7	267	0.35

Sample	River	Date	Location	Elevation	pH	Temp.	Cond.	CSI
BR-327	Kosi (Dumarighat)	10.05.2004	N25° 32.400' E 86^0 43.270'	38	7.9	31.4	183	-0.14
Ganga in Plain(2006)								
BR06-12-1	Ganga (Allahabad)	20.10.2006	N25° 30.474' E81° 51.759'					
BR06-14-1	Ganga (Varanasi)	21.10.2006	N25° 17.827' E83° 00.600'					
BR06-10-1	Ganga (Ghazipur)	19.10.2006	N25° 32.050' E83° 11.909'					
BR06-801	Ganga (Doriganj)	19.10.2006	N25° 43.670' E84° 49.455'					
BR06-301	Ganga (Patna)	16.10.2006	N25° 37.435' E85° 09.209'					
BR06-401	Ganga (Barauni)	17.10.2006	N25° 22.478' E86° 00.090'					
BR06-104	Ganga (Rajmahal)	15.10.2006	N25° 03.409' E87° 50.229'					
Tributaries in plain 2006								
BR06-13-1	Yamuna (Allahabad)	20.10.2006	N25° 25.332' E81° 50.255'					
BR06-11-1	Gomti (Ghazipur)	19.10.2006	N25° 30.283' E83° 08.448'					
BR06-901	Ghaghara (Revilganj)	19.10.2006	N25° 48.783' E84° 35.807'					
BR06-705	Gandak (Hazipur)	18.10.2006	N25° 41.326' E85° 11.485'					
BR06-201	Son (Koilawar)	16.10.2006	N25° 33.805' E84° 47.555'					
BR06-501	Kosi (Dhumarighat)	18.10.2006	N25° 32.704' E86° 43.138'					
BR06-601	Bagmati (Dhumarighat)	18.10.2006	N25° 32.570' E86° 43.240'					
Miscellaneous samples								
RW03-20	Seepage water	08.05.2003	N 30^{0}46.261' E 77^0 49.625'	2185	-	-	-	
RW03-21	Seepage water	08.05.2003	N 30^{0}45.809' E 77^0 48.921'	2373	-	-	-	
RW03-22	Seepage water	08.05.2003	N 30^{0}45.379' E 77^0 48.875'	2466	-	-	-	
MW03-1	Drip water	30.04.2003	N 30^0 21.611' E 78^0 80.404'	750	7.3	22.1	-	
MW03-2	Drip water	30.04.2003	N 30^0 21.611' E 78^0 80.404'	750	7.8	-	-	
MW03-3	Drip water	30.04.2003	N 30^0 21.611' E 78^0 80.404'	750	8.1	22.3	-	
RW03-7	GANG NANI (Hot spring)	02.05.2003	No GPS reading	-	-	-	-	
RW03-17	Drip water (Sahashra Dhara)	07.05.2003	N 30^{0}23.147' E 79^0 07.718'	862	-	-	-	
RW03-18	Sulphurous water (Sahashra Dhara)	07.05.2003	N 30^{0}23.123' E 79^0 07.734'	856	-	-	-	
RW03-19	Stream water (Kempty Fall)	07.05.2003	N 30^{0}29.207' E 79^0 02.093'	1380	-	-	-	
RW03-1	Bandal (sherki)	30.04.2003	N 30^0 21.163' E 78^0 08.400'	732	7.4	21.7	-	

In addition, time series water sampling for the Yamuna at Allahabad and the Ganga after the confluence with Yamuna at Allahabad at biweekly intervals over a period of 10 months was also done during 2004-2005. Further, a few other specific samples, mainly from seepage, drip and spring waters from the Himalayan basin of the Ganga, precipitated carbonates from locations adjacent to drip water and a few ground water samples close to the river banks were also collected. The details of sampling are discussed below. The sampling locations are listed in the Tables-2.2 and 2.3.

2.4.1 River and Groundwater

The parameters measured in the dissolved phase of river and ground waters are major ions, silica, $^{87}Sr/^{86}Sr$ and Sr. The sampling locations (latitude and longitude) were determined mainly using global positioning system. At some locations during the 2003 sampling GPS was unable to track the satellites and hence these locations are based on maps. The sampling was done with the help of boats or from bridges from mid channel of the rivers to avoid anthropogenic and local influences. For major ions and Sr isotopes, samples were collected using clean polyethylene containers.

The water was filtered at the sampling site through 0.2 µm Nucleopore filters and stored in two precleaned polyethylene bottles of 500ml capacity. The samples were brought to the laboratory within a week; one of the bottles was acidified with high purity HNO_3 to pH~2 for the analysis of Na, K, Ca, Mg, Sr, and Sr isotopes. The second bottle was stored un-acidified for analysis of anions (Cl, F, NO_3 and SO_4). Another aliquot of unfiltered river water was collected and stored in ~120 ml bottles for alkalinity measurements.

In addition, shallow ground water samples were collected from wells at ~200m away from the banks of the Yamuna and the Ganga at Allahabad. In addition to the above river water samples, a set of time series water samples was collected at biweekly intervals over a period of ~10 months from the Yamuna (at Yamuna bridge, Allahabad) and the Ganga (Chhatanag, Allahabad) after the confluence with the Yamuna. The samples were collected in 5 liter bottles and kept as such at Allahabad. At the end of the sampling period, two aliquots, one of one liter and the other of 120 ml from each biweekly sample were gently transferred to polypropylene bottles at site. The particulate matter settled at the bottom of 5L bottle was separated by decanting the supernatant water. All the water and particulate matter samples were brought to the laboratory. The water samples in 1 liter bottle were filtered with 0.2 µm Nucleopore filters, split into two aliquots; one was acidified as discussed above. The samples were analysed as detailed later.

2.4.2. Sediments and Suspended Particulates

Sediment samples from the Ganga mainstream and its major tributaries in both the Himalaya and the plain were collected from their banks within a few meters of water. In addition, sediment samples richer in fine fraction were also collected, generally from sandbars exposed in the mid-channel of the rivers. The sampling spanned the entire stretch of the Ganga, from its source at Gangotri to near its outflow at Farakka (Figs-2.1a, b). The sampling was done during May 2003 (summer) from the Himalayan sector and during May 2004 (summer) and October 2006 (monsoon/post monsoon) from the plain. A single sample of the Ganga sediments was collected from Kanpur in May 2005. The repeat sampling in the plain was done to assess the temporal variability in the chemical and isotopic composition of sediments along the Ganga mainstream and the role of tributaries in contributing to this variability. During sampling, wherever possible, 5-6 samples were collected from an area of ~ 500 m × 500 m and were mixed and homogenized at site to yield a representative sample of sediment from that location. Sediments samples (~1kg) after collection were stored in polythene bags and were taken to laboratory. Suspended matter samples were recovered from ~10 liters of water by settling (~2 weeks). This water sampling was done during October 2006, when the suspended matter concentration is generally high due to monsoon. After settling, the clear supernatant water was decanted and the slurry containing suspended matter was transferred to a beaker and dried in an oven. The dried material was powdered using agate mortar and pestle and used for various analyses.

2.4.3 Other samples

In addition to river and ground water samples, drip and spring waters from the upper catchment of the Ganga in the Himalaya, freshly precipitated carbonates from the regions near drip water, and gastropods and calcium carbonate nodules, locally called *kankars* (Sarin et al., 1989; Pal, 1994, 2003; Agarwal et al., 1992; Singh, 2005; Sinha et al., 2006) were also collected as a part of this study. The drip waters are either from caves or from fissures (seepage) exposed on surface. Near to these drip/seepage waters there were precipitated carbonates, these were also sampled for this study. The gastropods were sampled from the Ganga river and the kankar (impure carbonates) was collected from the bank of the Ganga at Allahabad (after its confluence with Yamuna).The sample was collected from a section ~1-2 m below the sediment surface.

2.5 Analytical Techniques

The analytical techniques used depended on the type of samples being analysed and the parameters being measured. Among the various analytical techniques used in this study, significant efforts were put in establishing chemical procedures for extraction and purification of Sr and Nd from riverine suspended and particulate phases and their isotopic analysis by Thermal Ionization Mass Spectrometry (TIMS). This was done as a part of setting up of a new mass spectrometric facility at PRL, Ahmedabad. Nd extraction procedures and its mass spectrometry were established for the first time in our laboratory and are based on those available in literature (Richard et al., 1976; Alibert, et al.,1983). These chemical procedures and associated mass spectrometric analyses are described in some detail in this section, the methods used for the determination of elemental abundances in water and sediments are mentioned only briefly as they are based on available procedures in our laboratory (Sarin et al., 1989; Dalai, 2001; Das, 2005).

2.5.1 Water Samples

(a) pH, temperature and electrical conductivity:

pH and electrical conductivity (EC) of river waters were measured at site using a multi-purpose kit (Model: Multiline 7000). The pH probe was calibrated with freshly prepared buffer solutions of pH 4.0 and 9.2, and the EC probe with 0.01 M KCl solution prior to making the measurements. The precision of pH measurements is better than 0.1 units and that of EC measurement is better than 10 µS cm^{-1}. Temperature of river waters was measured by a portable thermometer (MA line), with precision better than 0.1 °C.

(b) Major ions and dissolved silica:

Alkalinity measurements were done on unfiltered water samples generally within about two weeks of collection by acid titration with dilute HCl of known strength (~0.01M) using an auto-titrator (Metrohm 702 SM Titrino) with a glass electrode. Prior to measurements the samples were kept undisturbed for several days to settle the particulates. A known aliquot of supernatant water was pipetted for alkalinity measurements. In the time series samples, the alkalinity measurements were made at the end of sampling, therefore in some cases the delay between collection and measurement were several months. The measurement was based on fixed end point method corresponding to two end points at pH values of 8.3 and 4.3 for CO_3^{2-} and total carbonate species (HCO_3^- and CO_3^{2-}). Cl, F, NO_3 and SO_4 were determined by ion chromatography (Dionex series 2000i/SP) in filtered, un-acidified samples (Dalai, 2001; Rastogi, 2005).

The system was calibrated using standards prepared from analytical grade salts (NaF, NaCl, Na_2SO_4 and KNO_3). The separation of ions (F, Cl, NO_3 and SO_4) was done on AS14A column using an appropriate eluent. In some cases samples were suitably diluted with distilled water to make the concentrations of the ions within the range of measurement.

Si measurements were done using a spectrophotometer (Model Beckman 26) based on the Mo-blue method (Strickland and Parson, 1972; Das 2005) at wavelength of 810 nm. The working Si-standard was prepared by dissolving Na_2SiF_6 in double distilled water. The analyses were done in filtered, un-acidified aliquots. In one sample, Si measurement was checked in both the acidified and un-acidified splits; they yielded Si concentration within the analytical precision of ~2%.

Among the cations, Na and K measurements were done in filtered un-acidified samples using flame-AAS (Perkin Elmer Model 4000). The calibration was done using Merck® standard solutions. The accuracy of measurement was checked by measuring solutions of known concentrations prepared from analytical grade salts (NaCl and KCl). Ca and Mg measurements were done in filtered, acidified splits by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Jobin Yvon, Model 38S). The measurements were done by sequential scanning of the emission line at wavelengths of 279.806 nm (Mg) and 422.673 nm (for Ca). Ca and Mg standards were made by dissolving pure anhydrous $CaCO_3$ and Mg metal in acids. Ca and Mg were also measured at flame-AAS (Perkin Elmer Model 4000). The two measurements were consistent within ±5%. In some of the time series water samples (un-acidified), the major ions (Na, K, Ca, Mg, Cl, and SO_4) were measured by ion chromatography with analytical precision better than 2% (Table 2.4).

The reproducibility of major ion measurements was checked by repeat analyses. The results expressed as coefficient of variation is given in Table-2.4. Based on replicate analyses, the coefficients of variation were calculated using the formula.

$$CV(\%) = \left(\frac{1}{2n} \sum \left(\frac{d_i}{x_i} \right)^2 \right)^{\frac{1}{2}} \times 100 \qquad \text{.......................................} \ (2.1)$$

where d_i is difference between the duplicates with mean x_i and n is the total sets of duplicates. Reproducibility of measurements for dissolved silica and major ions were better than 2.5% except F (4.3%) and NO_3 (3.5%).

Two numbers are given for the alkalis and alkaline earth elements in Table-2.4. For Na, K and Mg, the first column is based on ion chromatograph, and the second AAS. For Ca it is based on ion chromatograph and ICP-AES and for Sr, AAS and TIMS. Silica data is based on spectrophotometric analysis. For anions, it is based on ion chromatograph, except for alkalinity which was measured by titration. The accuracy of measurements was checked by Merck standards of known concentrations.

Table-2.4: Coefficient of Variation for major ions and silica in river waters

Ion/Species	**Coefficient of Variation (%)**	
Na^+	1.0	1.6
K^+	1.4	1.0
Mg^+	1.3	0.5
Ca	1.6	2.6
Sr	3.4	0.4
F	4.3	-
Cl	2.2	-
SO_4	1.5	-
NO_3	3.5	-
HCO_3	0.4	-
SiO_2	0.4	-

(c) Sr and ^{87}Sr/^{86}Sr isotopes in water samples:

Sr concentration in water samples was measured in the filtered, acidified samples (May 2004) using graphite furnace AAS. Calibration of the instrument was done with Merck standard solutions. In some of the water samples (October 2006), Sr concentration was determined by isotope dilution (using ^{84}Sr tracer) by thermal ionization mass spectrometry (TIMS). For Sr isotope measurements, typically about 100-150 ml of filtered, acidified river water was taken in cleaned FEP beakers and evaporated to near dryness. The volume of water used for Sr isotope analysis was decided based on Sr concentration in water such that at least 5 μg of Sr was available for isotope measurements. To the residue, about ~1 ml of HNO_3 (Seastar chemicals®) was added to oxidize organic matter and dried completely. The residue was taken in 1.5 ml 2N HCl. The solution was centrifuged and from the clear solution Sr was separated by ion exchange chromatography using Dowex 50X8 (200-400 mesh) in 2N HCl medium (Dalai, 2001; Singh et al., 2006).

In a few water samples, Sr was separated using Eichrom® Sr specific resin (50-100μm; Horwitz, et al., 1992; Pin and Bassin, 1992; Pin et al., 1994; Rai and Singh, 2007). The Sr specific resin was conditioned with 3N HNO_3. In this method 4 -10 ml of water was dried; the residue was taken in 3N HNO_3 medium and loaded on ~200 μl of resin contained in 10 ml capacity columns. The Sr from the resin was eluted with milli Q water. The pure Sr fraction was dried, dissolved in a few μl of 2N HCl and loaded with H_3PO_4 on degassed and oxidized high purity Ta or Re filaments. The Sr isotope measurements were carried out on TIMS in multi collector mode. Several repeat measurements were made to check the reproducibility of results.

The accuracy of measurements was checked by analyzing USGS standard (G-2) solution. The measured ^{87}Sr/^{86}Sr is 0.709785±0.000008 (n=1) with Sr concentration 460 ± 8 ppm. This compares well with the reported value (USGS certificate of analysis for reference material G-2) of 709785±0.000058 (n=3) and Sr concentration 478±2 ppm. The precision for Sr measurements by graphite furnace AAS and TIMS are 3.4 and 0.4% respectively.

2.5.2 Sediments

(a) Major elements

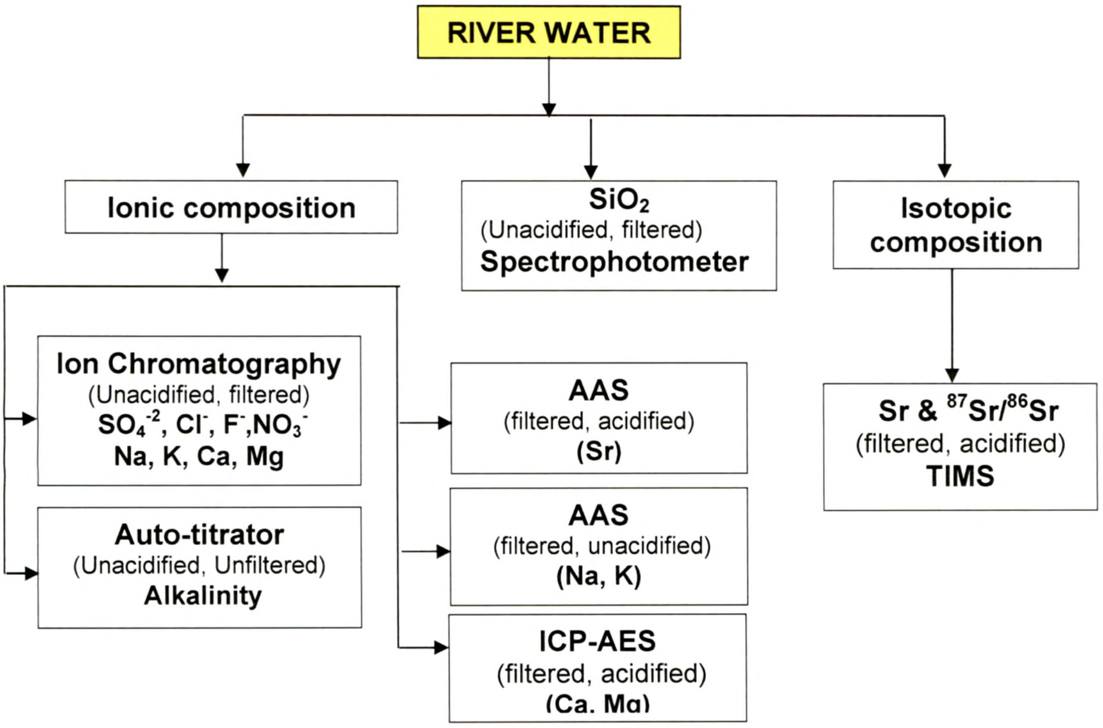
The sediments stored in plastic bags were brought to the laboratory for analysis. In the laboratory, a fraction of the sediments (~250g) was transferred to clean glass beakers and dried at ~50°C for 2~3 days. These dried sediments were powdered using an agate ball mill and sieved through nylon sieves of 100 µm size. The sieved samples were stored in plastic containers. Care was taken to avoid any metal contact during powdering and sieving. A known weight of finely powdered (≤100 µm) sediments was taken in quartz crucibles and combusted at ~600 °C to oxidize organic matter. About 0.5 g of ashed samples were taken in PTFE dishes and digested with HF to remove silica. The residues were brought to solution by repeatedly treating with HCl-HNO_3 mixture. The solutions were made to 50 ml in 0.2N HNO_3. Few samples were digested in duplicate to check the overall precision of analyses. Along with the samples, USGS reference standards W-1 and G-2 (for Sr and $^{87}Sr/^{86}Sr$) were also processed to check the accuracy of analyses.

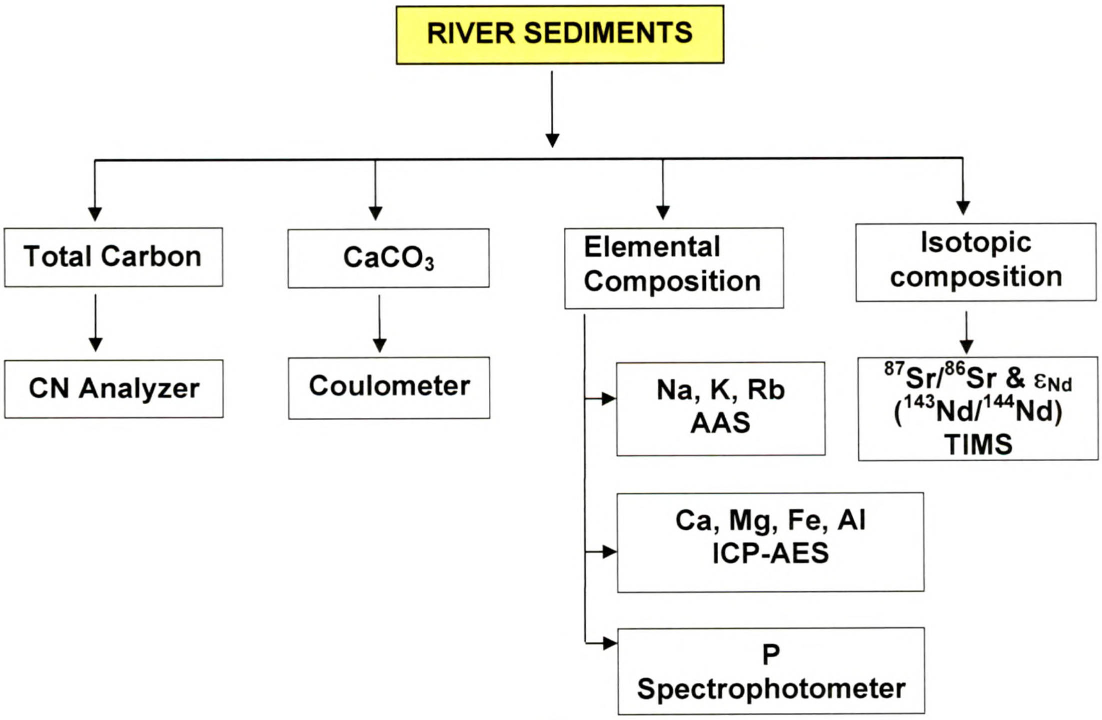
Table 2.5: Results of elemental analyses in USGS reference material W-1

Element	**Technique**	**Measured**	**SD**	**Reported**[+]	**SD**
		(wt%)		(wt%)	
Ca	ICP-AES	7.98	0.26	7.86	0.09
Mg	ICP-AES	4.02	0.08	3.99	0.08
Na	AAS	1.68	0.07	1.60	0.04
K	AAS	0.55	0.03	0.53	0.02
Fe	ICP-AES	7.76	0.26	7.71	0.16
Al	ICP-AES	7.75	0.26	7.88	0.14
P (ppm)	UV-VIS Spectrophoto.	581	-	580	40
Rb (ppm)	AAS	22	2	21	0.3

[+] USGS certificate of analysis; Potts et al., 1992

SCHEMES OF ANALYSES





Na, K and Rb were measured in the solution by Flame-AAS (Multi element standards (Merck) were used for calibration and were checked by internal lab standard prepared from their respective salts). For measurements using AAS, all samples were suitably diluted to bring them into linear range of absorbance-concentration relation. Other major elements (Ca, Mg, Fe and Al) were measured using ICP-AES. P was measured by molybdenum blue method (wavelength 885 nm) using a spectrophotometer (Strickland and Parson, 1972; Das, 2005). The precision of measurements based on the repeat measurements for various elements are presented in Table-2.5 and given in the Fig-2.5. The measured values in USGS standard W1 show excellent agreement with those reported in literature (Potts et al., 1992).

(b) $CaCO_3$ and organic carbon

The carbonate content in river sediments was measured using a coulometer (UIC Coulometer; Model 5012). The instrument was calibrated with Na_2CO_3 solution prepared from analytical grade reagent. CO_2 was liberated from solution/sediments by treating the samples with 40% H_3PO_4 at 85°C for 10 minutes in an extraction cell. About 100 mg of dry sample powder was taken for analyses.

Table 2.6: Results of repeat analyses of major elements in sediments

Sample ID	**Ca** %	**Mg** %	**Na** %	**K** %	**Fe** %	**Al** %	**P** (ppm)	**Rb** (ppm)
BR-306	2.27	0.84	1.09	1.51	2.17	3.91	682	86
BR-306(D)	2.33	0.85	1.11	1.54	2.17	3.92	714	87
BR-330	0.71	0.43	1.37	2.02	1.79	4.76	377	114
BR-330(D)	0.69	0.41	1.32	2.02	1.82	5.00	373	114
BR-365	1.85	0.41	0.63	1.22	1.37	2.70	355	63
BR-365(D)	1.88	0.42	0.64	1.21	1.39	2.69	355	64

BR-344	3.18	2.34	0.36	3.68	6.45	10.94	249
BR-344(D)	3.15	2.30	0.35	3.71	6.68	11.08	250
BR-383	1.78	2.15	0.24	2.83	7.80	11.62	200
BR-383(D)	1.72	2.03	0.24	2.82	8.21	11.80	203
BR06-205	0.46	0.23	0.41	1.90	0.62	2.17	82
BR06-205(D)	0.50	0.26	0.38	1.91	0.63	2.14	80
BR06-701	5.79	1.13	0.91	1.51	2.02	3.99	87
BR06-701(D)	5.57	1.14	0.90	1.50	1.86	3.86	85
BR06-SL1	1.31	1.56	0.74	2.90	4.49	8.15	196
BR06-SL1(D)	1.40	1.57	0.75	2.90	4.30	8.14	198
BR06-SL6	1.16	1.43	0.83	3.03	4.41	8.33	220
BR06-SL6(D)	1.20	1.41	0.80	3.00	4.11	8.05	216

Table 2.7: Coefficient of variation for different elements in sediments⁺

Element	**Technique**	**Coefficient of Variation (%)**
Ca	ICP-AES	2.9
Mg	ICP-AES	3.5
Na	AAS	2.3
K	AAS	0.7
Fe	ICP-AES	3.2
Al	ICP-AES	1.7
P	Spectrophoto.	1.9
Rb	AAS	1.0

+ based on nine pairs of repeat measurements except P, for which it is based on three pairs.

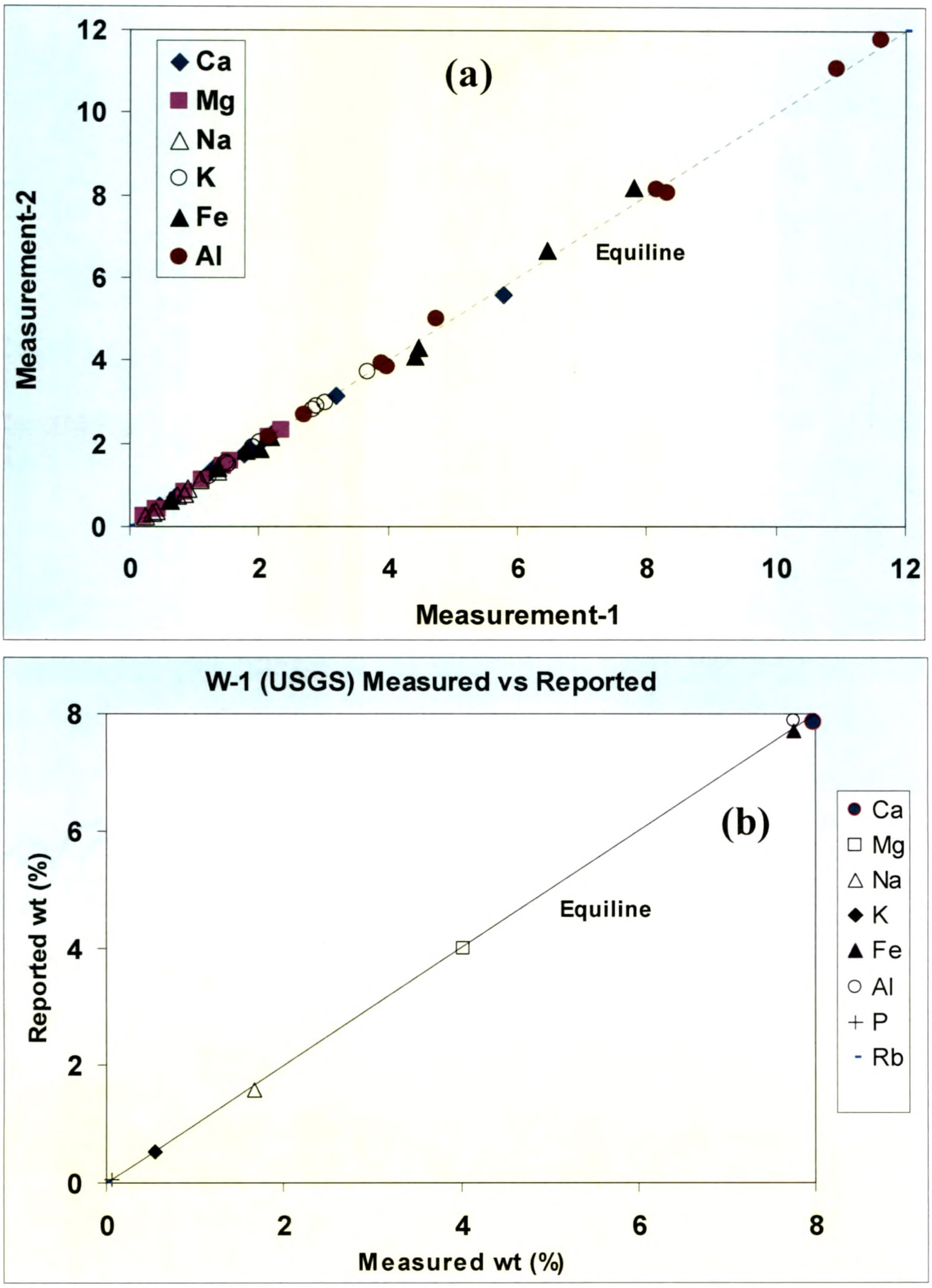


Fig 2.5: Results of (a) repeat measurements (wt. %) of different elements in sediment samples. The repeat measurements show excellent agreement (b) measured concentration of various elements in USGS rock standard W1 plotted against those reported in literature (Potts et al., 1992).

The CO_2 liberated from the sediment sample was purified through a column of silica gel and anhydrous $MgClO_4$. The purified CO_2 was measured in the coulometer titration cell.The precision of inorganic carbon (IC) measurements based on replicate analyses and standard solutions over wide range of concentration (<0.1% to 5.6%) of IC was ~ 2.5% (Table-2.8). Total carbon (TC) was measured using FISONS NA1500 CN elemental analyzer (Fisons Inc., Italy; Sarin et al., 1997). For this, 10-30 mg of dried sediment sample was packed in aluminum cups and was introduced into the combustion tube of an auto sampler for carbon and nitrogen analysis.

Table-2.8: Replicate measurements of inorganic carbon (IC)and total carbon (TC) in river sediments

Sample ID	**IC (%)**		**TC (%)**	
	Meas (1)	Meas (2)	Meas (1)	Meas (2)
RS03-27	5.61	5.65	7.23	-
RS03-31	1.21	-	1.29	1.26
BR-306	0.65	0.64	0.67	-
BR-330	0.03	0.03	0.08	-
BR-343	0.91	0.91	1.08	-
BR-348	0.50	-	0.61	0.63
BR-371	0.99	0.98	1.18	-
BR-378	0.34	0.34	0.49	-
BR-382	0.22	0.23	0.32	-
SLG-10	0.61	-	0.68	0.70
SLG-16	0.18	0.17	0.66	-
SLY-14	1.12	-	1.82	1.84
SLY-15	1.15	1.16	1.88	1.91
SLG-17	0.18	-	0.60	0.62

A three-point calibration line was made using the Deer River Shale containing 2.53 wt.% carbon as the reference material (Krom and Berner, 1983; Sarin et al., 1997; Bhushan et al., 2001). C_{org} content is calculated by the difference between total carbon and carbonate carbon contents in the sample (Verardo et al. 1990).

C_{org} = TC - IC……………………(2.2)

where TC is the total carbon and IC is the inorganic carbon (from carbonates). The analytical precision for measurements of $CaCO_3$ and total carbon are 2.1% and 1.6% respectively (Table-2.8).

(c) Isotopic Measurements: Mass Spectrometry

Sr, and Nd isotopes were measured in different samples (river water, sediments and carbonates) using a new generation solid source mass spectrometer (Micromass Isoprobe-T) set up at the Physical Research Laboratory (PRL), Ahmedabad. The mass spectrometer was procured at PRL during the course of this thesis work. Part of my work involved working with Dr. Sunil K. Singh to establish procedures for the extraction of Sr and Nd from various samples and measurement of their isotopic composition using the mass spectrometer. There was considerable expertise for Sr isotope measurements at PRL whereas the Nd measurements were made for the first time at PRL as a part of this work. The Nd separation from matrix and its measurement procedure is adapted from literature (Alibert et al., 1983; Richard et al., 1976) and is discussed briefly in section (d).

The Sr and Nd isotope measurements were made in static multi collector mode. Mass fractionation corrections for Sr and Nd were made by normalizing $^{86}Sr/^{88}Sr$ to 0.1194 and $^{146}Nd/^{144}Nd$ to 0.7219 respectively. Internal precision for both these ratio measurements were better than 10 ppm ($1\sigma_\mu$). During the course of the study, SRM987 Sr and JNdi Nd standards were repeatedly measured, these yielded $^{86}Sr/^{88}Sr$ values of 0.710230±0.000013 (1σ, n = 72) for $^{86}Sr/^{88}Sr$ and 0.512105±0.000006 (1σ, n =9) for $^{143}Nd/^{144}Nd$ respectively, (Fig-2.6) well within the recommended values. Several repeat measurements of Sr isotopes of the Arabian Sea water and in a coral sample from the Bay of Bengal were also made to check the precision and accuracy of Sr measurements (Table-2.9).

(d) Sr and Nd isotopes in sediments:

The Sr and Nd concentration and isotopic measurements were carried out in the *silicate* fraction of total sediments and their < 4 μm size separates. The < 4 μm fraction was separated from bulk (total) sediments by settling in water.

The abundance of < 4 μm fraction in sediments from the higher reaches (i.e., upstream of Rishikesh, Fig-2.1a) was very low and hence in many of these samples only bulk sediment analyses could be made. In the laboratory, the dried sediment samples were powdered (≤ 100μm) and used for analysis. The major element concentrations were made in total sediments whereas the Sr and Nd isotope measurements were made in their silicate fraction. For isotopic measurements, a known weight of powdered sample (~ 1 gram) was leached using 0.6 N HCl with intermittent ultrasonic treatment at 80°C to remove carbonates. The slurry was centrifuged; the residues washed with water, dried and ashed at ~ 600°C to oxidize organic matter.

A known weight (about 100 mg) of the carbonate and organic matter free sediments were transferred to 7 ml Savillex® vials and brought to complete solution using ultra-pure HF and HNO_3 (Seastar Chemicals®) in presence of ^{84}Sr and ^{150}Nd tracers. Sr and REEs were separated from the solution following standard ion exchange procedure (Singh and France-Lanord, 2002; Singh et al., 2008). From the REE fraction, Nd was separated using HDEHP coated Teflon powder (Richards et al., 1976; Alibert, 1983; Singh et al., 2008). The purified Nd was loaded on the outer Tantalum filament of the triple filament assembly. Sr and Nd concentrations and their $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ were measured using Isoprobe-T Thermal Ionization Mass Spectrometer (TIMS). Nd isotopes systematics in sediments is expressed in ε_{Nd} units (Faure, 1986). To check on the precision and accuracy of $^{87}Sr/^{86}Sr$ analyses sea water and coral samples were analysed. The results are given in Table-2.9. The samples Sea water-1, 2,

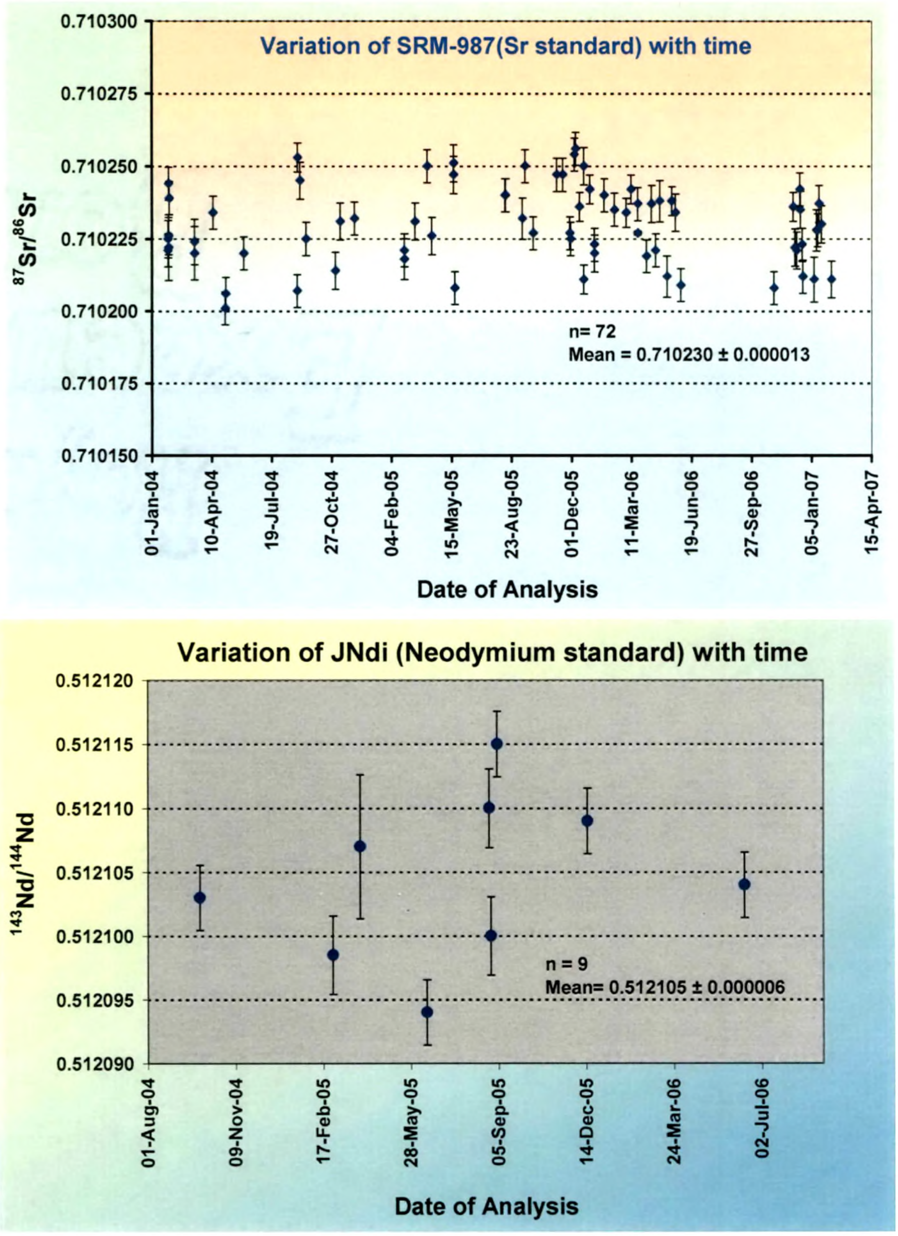


Fig-2.6: Temporal variation in ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd measured in standards.

3 and 4 are all aliquots of the same seawater sample processed separately. The sample Sea water-1R is re-run of the same Sr load of Sea water-1. Three coral samples from the Bay of Bengal were powdered and processed for Sr. The data show good reproducibility. Several Sr and Nd total procedural

blanks were measured along with the samples; average blank for larger (~100 ml) water and sediment sampling was 1.8 ±0.77 ng; (n=11) whereas for Nd it was ~300 pg. For these determinations of Sr procedural blanks, 100 ml Milli-Q water was used in place of river water and processed with the same quantity of reagents as used for the samples.

Table- 2.9: ^{87}Sr/^{86}Sr in Arabian Sea water and corals

Date of Run	Sample	^{87}Sr/^{86}Sr	±($1\sigma_\mu$)
17-Feb-04	Sea Water-1	0.709140	0.000006
26-Feb-04	Sea Water-1R	0.709150	0.000008
17-Feb-04	Sea Water-2	0.709129	0.000009
23-Feb-04	Sea Water-3	0.709172	0.000008
24-Feb-04	Sea Water-4	0.709154	0.000008
	Mean	0.709149	
	SD (N=5)	0.000016	
03-Jan-07	Coral SM-1	0.709154	0.000007
03-Jan-07	Coral SM-3	0.709150	0.000007
03-Jan-07	Coral SM-4	0.709151	0.000007
	Mean	0.709152	
	SD (n=3)	0.000002	

Sr blanks for the Sr specific resin used for smaller volume water samples range from 300 pg to 600 pg. ^{87}Sr/^{86}Sr was measured in three blanks which yielded value of ~0.7118 ± 0.0002 (n =3). These Sr blanks are about three orders of magnitude lower than typical total Sr and Nd analysed and hence no corrections were made for blanks.