Chapter-4

Sr, $^{87}Sr/^{86}Sr$ and major ions in the Ganga River System: Chemical weathering in the Ganga plain and peninsular sub-basins and dissolved Ca and Sr budgets

4.1 Introduction:

This chapter presents results on the chemical and Sr isotope composition of water from the Ganga and its tributaries and their application to determine chemical weathering in plain, peninsular and Himalayan sub-basins of the Ganga and better understand Sr geochemistry in these rivers. The suggestion that silicate weathering in young organic belts such as the Himalaya is a key driver of climate change over million year time scales (Raymo and Ruddiman, 1992; Raymo et al., 1994; Ruddiman, 1997; Kump et al., 2000; Huh, 2003) led to a number of studies on the chemical and isotopic composition of the Ganga and the Brahmaputra (Sarin et al.,1989, 1992; Palmer and Edmond 1992; Krishnaswami et al.,1992, 1999; Edmond and Huh, 1997; Galy and France-Lanord, 1999; Dalai et al., 2002; Singh and France-Lanord, 2002; Bickle et al., 2003, 2005; Singh et al., 2005, 2006; Rai and Singh, 2007). Between these two rivers, the Ganga is relatively more investigated with many of the studies focusing on the Himalayan sub-basin of the Ganga drainage and a few others covering almost the entire stretch of the Ganga river system, from its origin in the Himalaya to its outflow to the Bay of Bengal (e.g. Sarin et al., 1989; Galy and France-Lanord, 1999; Krishnaswami et al., 1999). The latter studies yielded chemical and silicate erosion rates integrated over the entire Ganga basin spread over the Himalaya, the Ganga plain and the peninsular India. In spite of all these studies, there is only very limited information on the significance of chemical erosion in the plain and peninsular sub-basins of the Ganga, which account for ~80% of its drainage, in contributing to the flux of various elements transported by the Ganga to the Bay of Bengal. The available inferences (Galy and France-Lanord, 1999) seem to indicate that chemical erosion in the Ganga plain is much less than that in the Himalaya. One of the objectives of this thesis is to address this issue, i.e., to evaluate chemical erosion rates in the Ganga plain and peninsular sub-basins of the Ganga and their impact on its water chemistry and overall chemical erosion rate in the Ganga basin. Sr isotope studies of the G-B river system have been motivated by two major considerations (i) to assess the role of the G-B system and chemical weathering in the Himalaya in contributing to Sr isotope evolution of oceans since the Cenozoic (Krishnaswami et al., 1992, 1999; Raymo and Ruddiman, 1992; Richter et al., 1992; Ruddiman, 1997; Galy et al., 1999) and (ii) to explore the potential of Sr isotopes as a proxy of silicate weathering. It is known that the Sr isotope composition of the Ganga and the Brahmaputra are highly radiogenic compared to other global rivers (Fig-4.1; Palmer and Edmond, 1989; 1992; Krishnaswami et. al 1992, 1999; Edmond 1992; Galy et al., 1999; Singh et al., 1998, 2006; Bickle et al., 2003; Rai and Singh, 2007). It is suggested that the source of radiogenic Sr to these rivers is weathering of silicates of the Higher and Lesser Himalaya, which would make the Sr isotopic composition a good proxy for silicate weathering in their basins (Edmond 1992; Krishnaswami et. al., 1992, 1999; Raymo and Ruddiman, 1992; Singh et al., 1998; Krishnaswami and Singh, 1998; Galy et al., 1999; Bickle et al., 2003). This hypothesis, however, was questioned following the observations of highly radiogenic carbonates and vein calcites disseminated in the Himalaya (Palmer and Edmond., 1992; Harris et al., 1998; Jacobson and Blum, 2000; Bickle et al., 2003, 2005; Tipper et al., 2006). Recent studies of Bickle et al. (2005) based on detailed sampling of head waters of the Ganga and modeling concludes that the primary source of radiogenic Sr to these rivers is silicates. The application of Sr isotope as a proxy of silicate weathering is further hampered by difficulties associated with balancing the budget of Sr in rivers in terms of its supply from silicates and carbonates (Krishnaswami and Singh, 1998; Dalai et al., 2003). These attempts, based on Sr/Ca ratio and $^{87}Sr/^{86}Sr$ of the Ganga and Yamuna head waters, Pre-Cambrian carbonates and silicates observed that the Sr budget in these rivers could not be balanced if Ca in these waters behave conservatively. This led to suggest that in addition to carbonates and silicates there must be the other source(s) of Sr, low in both $^{87}Sr/^{86}Sr$ and Ca/Sr to account for its budget in these waters. A few other studies (Jacobson et al., 2002; Dalai et al., 2003; Bickle et al., 2005; Tipper et al., 2006), however, indicate that there could be removal of dissolved Ca via calcite precipitation and hence carbonate fraction of Sr derived from Ca abundance in river water could be an underestimate. Indeed, Jacobson et al. (2002) based on synthesis of available data on Sr, Ca/Sr, $^{87}Sr/^{86}Sr$ and modeling showed that precipitation of calcium carbonate in the Himalayan streams is an ongoing process and that about ~70% Ca in water can be lost due to calcite precipitation.

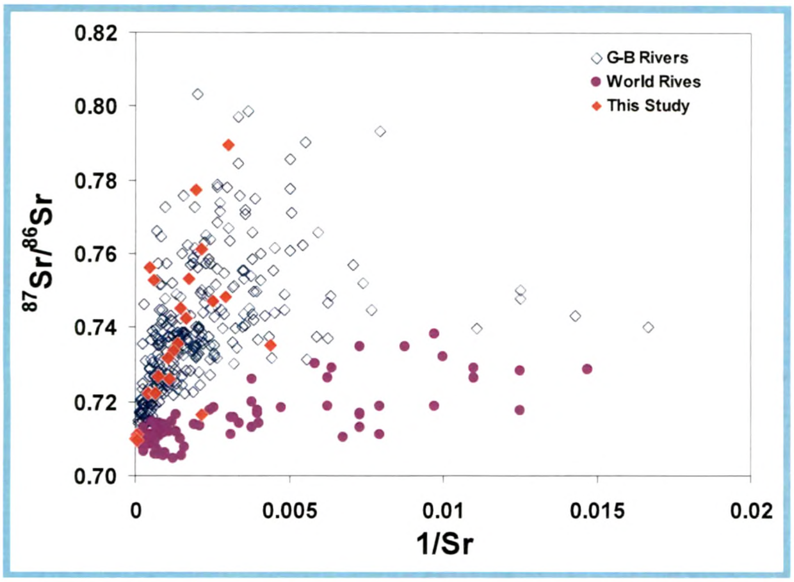


Fig-4.1: $^{87}Sr/^{86}Sr$ vs 1/Sr (Sr in ppb) plot of the G-B and global rivers. It is evident that in general the G-B rivers are more abundant in Sr with highly radiogenic $^{87}Sr/^{86}Sr$ relative to other global rivers.

Dalai et al. (2003) based on their studies of the Yamuna waters and sediments though hinted at the possibility that up to ~50% of Ca supplied to these waters could be lost by precipitation, they were uncertain if such removal is indeed occurring. Bickle et al. (2005) based on abundances of major ions, Sr and $^{87}Sr/^{86}Sr$ observed that ~50% of Sr in the Ganga headwaters is of silicate origin, the balance being contributed by carbonate weathering. More importantly, they concluded that the silicate sources provide ~ 70% of ^{87}Sr flux which regulates the seawater $^{87}Sr/^{86}Sr$ isotope composition.

In this work, a comprehensive study of major ions, Sr and $^{87}Sr/^{86}Sr$ have been carried out in water and sediments of the Ganga river collected from its entire stretch, from near its source at Gangotri to its mouth at Farakka and its tributaries. These measurements, as mentioned earlier have been carried out to determine chemical erosion in the Ganga plain and peninsular region and learn about Sr geochemistry in the Ganga system. Among the tributaries the Gomti, the Son and the Yamuna drain the plain and peninsular regions of the Ganga basin. The Gomti and the Son have their entire drainage in the Ganga plain and/or peninsular region (chapter-2; Fig-2.1). The Yamuna, though originates in the Himalaya, also has most of its drainage (~ 97 %) in the Ganga plain and peninsular region (Rao, 1975). The studies of these rivers therefore, can yield information on chemical erosion in the plain and peninsular regions of the Ganga basin and its comparison with erosion in Himalayan sub-basin of the Ganga. Further, the abundances of Mg-Ca-Sr in these rivers and their $^{87}Sr/^{86}Sr$ ratio along with those in a few other samples such as dripping and seepage waters from caves and fissures and precipitated carbonates have been used to learn more about the geochemistry of Ca-Sr in these waters, particularly calcite precipitation from them and its impact on dissolved Sr budget. The results of chemical erosion of the various sub-basins are presented first followed by Sr isotope and its investigations.

4.2 Results and Discussion:

The details of the river water sampling locations and the temperature and pH of the waters are presented in chapter-2 (Table-2.3). The results of major ions, silica, TDS, Sr and $^{87}Sr/^{86}Sr$ composition of the Ganga mainstream and its tributaries are given in Table-4.1. The results of analyses of seepage water, hot springs and other miscellaneous water samples are also presented in this Table-4.1.

4.2.1 General Observations:

Temperature of waters collected during the two summer field trips (May, 2003 and 2004) range from 17 to 34 °C. The range does not include the headwaters in the Himalaya as they were not measured. The pH shows a range of 7.3-8.6 suggestive of mild alkaline nature of the rivers sampled. The major ion data show good balance between total cations (TZ^+) and anions (TZ^-), the regression line through the data has a slope of 0.971 ± 0.004 and $r^2 = 0.999$. Of the 50 samples analysed, 45 show normalized inorganic charge balance (NICB = $(TZ^+-TZ^-)/TZ^-$) with an average deviation of 2.9±2.3%. This leads to conclude that the ions measured by and large account for the charge balance. Five samples however, have significant excess of anions ($TZ^- > TZ^+$ range 11- 23.3%). Analytical uncertainties associated with measurements is unlikely to be a cause for these considering the accuracy and precision of analyses as estimated from standards and repeats (presented in chapter-2, section 2.5.1) and the good charge balance observed for the other 45 samples. Therefore other reasons have to be invoked to explain this observation; one could be the presence of other cations in these waters, (e.g. $NH4^+$) which were not measured.

Total dissolved solids (TDS) show significant spatial and temporal variations along the course of the Ganga river (Fig-4.2). TDS for the May 2003 samples (head waters of the Ganga), vary from 49 to 153 mg ℓ^{-1}, lower than the values of 159 to 574 mg ℓ^{-1} in the Ganga and its tributaries in the plains (collected in summer 2004). For the October 2006 samples from the plains, TDS varies from 114 to 390 mg ℓ^{-1} showing the effect of dilution due to monsoon discharge. This effect is not prominent in case of the Gomti river (Fig-4.2). The lowest value of TDS (49 mg ℓ^{-1}) was measured in a small stream from the Higher Himalaya, (RW03-6). Water samples collected from a spring in the Higher Himalaya at Gang Nani (RW03-7) and those from the Shahashradhara and the Kempty fall in the Lesser Himalaya (RW03-19) show high TDS values 798 to 2422 mg ℓ^{-1} (Table-4.1). The discharge of such springs and seepage waters with high TDS into rivers can influence major ion budget of rivers in and around their confluence. The importance of spring water on the major and minor element budgets of the head waters of the Ganga system has been brought out in some of the earlier work (Evans et al., 2001; Bickle et al., 2003). The molar abundances of major cations in the Ganga headwaters decrease as Ca>Mg>Na>K (Table-4.1), consistent with that reported earlier (Sarin et al., 1989; 1992) in the region. Ca together with Mg account for ~85% of TZ^+, in upper reaches of the Ganga which decreases to ~75% for the Ganga mainstream and its tributaries in the plains.

Table-4.1: Dissolved major ions (μM), Sr (nM), TDS (mg/L) and $^{87}Sr/^{86}Sr$ in the Ganga river and its tributaries

Sample	River	Na	Na*	K	Mg	Ca	Cl	NO_3	F	SO_4	HCO_3	SiO_2	Sr	TDS	NICB $(TZ^+-TZ^-)/TZ^-$	$^{87}Sr/^{86}Sr$
Head Waters																
Bhagirathi system																
RW03-5	Bhagirathi (Gangotri)	90	78	43	86	245	12	0	39	353	188	127	468	69	-16.0	0.76101
RW03-8	Bhagirathi (Uttarkashi)	107	65	45	120	361	42	0	15	156	818	99	685	94	-6.2	0.74512
RW03-9	Syansu Gad	323	248	29	128	418	75	0	6	111	1261	240	1724	133	-7.6	0.75268
RW03-10	Bhilangana (Ghanshyali)	90	61	41	53	279	29	0	18	106	778	104	342	81	-23.3	0.74828
RW03-3	Bhagirathi (Devprayag)	130	97	42	137	347	33	0	21	184	811	121	571	98	-7.5	0.75330
RW03-6	Glacier melt (Higher Him.)	65	58	51	33	154	7	0	9	185	183	158	228	49	-14.0	0.73504
Alaknanda system																
RW03-4	Alaknanda (Devprayag)	91	71	40	165	403	20	0	10	150	1066	95	822	110	-9.2	0.73368
RW03-11	Alaknanda (Rudrapryayag)	79	56	43	166	460	23	0	9	145	1087	85	970	112	-2.5	0.73158
RW03-12	Mandakini (Rudrapryayag)	96	70	35	41	277	26	0	12	72	626	116	400	69	-5.0	0.74709
RW03-13	Birahi Ganga (Trib.)	27	18	40	166	340	9	0	3	52	1032	130	331	96	-6.0	0.78955
RW03-14	Birahi Ganga (Birahi)	121	90	62	321	541	31	0	25	145	1607	93	514	153	-2.3	0.77738
RW03-15	Alaknanda (Birahi bef. confl.)	95	74	36	190	451	21	0	11	218	978	87	1404	113	-2.2	0.72662
RW03-16	Pindar river (Pindar Valley)	58	39	41	168	481	19	0	9	96	1229	84	616	116	-3.6	0.74231
Ganga mainstream (2004)																
RW03-2	Ganga (Rishikesh, upstream)	106	77	41	164	419	29	0	13	175	973	107	731	108	-3.8	0.73572
BR-388	Ganga (Varanasi)	2380	1418	179	922	814	962	0	22	257	4631	321	3937	477	-1.6	0.71859
BR-309	Ganga (Patna)	1354	891	116	722	903	463	0	18	166	3986	275	3070	381	-1.6	0.72184
BR-318	Ganga (Rajmahal)	800	542	156	510	784	258	0	14	172	2865	197	2157	280	1.8	0.72673
Tributaries merging in Plain(2004)																
BR-346	Yamuna (Allahabad)	3575	2082	136	1104	794	1493	0	27	335	5300	325	5889	574	0.2	0.71467
BR-375	Gomti (Ghazipur)	1354	954	127	894	872	400	17	22	252	4193		3173	388	-2.4	0.72759
BR-342	Ghaghra (Revilganj)	446	374	102	569	762	72	0	13	163	2932	172	1952	266	-4.0	0.73125
BR-354	Ghaghra (Faizabad)	322	264	194	524	848	58	0	11	153	2944	176	1815	269	-1.8	0.73282
BR-363	Rapti (Gorakhpur)	565	450	166	703	950	115	0	13	136	3737	197	2157	331	-2.4	0.73009
BR-311	Gandak (Hazipur)	217	106	83	356	714	111	0	8	253	2182	146	3675	216	-13.1	0.73675

BR-334	Gandak (Barauli)	245	121	18	403	795	124	0	8	274	2211	157	1552	223	-8.0	0.73707
BR-327	Kosi (Dumarighat)	283	214	81	187	544	69	0	15	125	1578	174	742	157	-4.5	0.74806
Ganga in Plain(2006)																
BR06-12-1	Ganga (Allahabad)	829	529	164	528	685	300	24	7	238	2606	17	1655	261	0.2	0.72969
BR06-14-1	Ganga (Varanasi)	966	519	102	415	658	447	19	6	165	2424	61	2078	247	-0.3	0.71575
BR06-10-1	Ganga (Ghazipur)	876	456	94	367	632	420	15	6	156	2276	24	2033	229	-2.0	0.715532
BR06-801	Ganga (Doriganj)	422	294	79	369	800	128	9	5	132	2513	49	1530	228	-2.7	0.72447
BR06-301	Ganga (Patna)	495	332	75	376	725	164	9	6	124	2343	50	1561	217	0.1	0.72198
BR06-401	Ganga (Barauni)	407	277	78	364	754	131	8	5	137	2294	61	1447	213	0.3	0.72402
BR06-104	Ganga (Rajmahal)	334	240	75	273	709	94	4	5	96	2111	75	1122	192	-1.5	0.72707
Tributaries merging in Plain (2006)																
BR06-13-1	Yamuna (Allahabad)	1275	579	85	443	673	696	50	6	181	2572	129	2717	280	-2.6	0.71239
BR06-11-1	Gomti (Ghazipur)	1399	1075	130	848	859	324	7	10	200	4286	92	2717	390	-1.6	0.72714
BR06-901	Ghaghara (Revilganj)	256	212	74	384	867	43	11	4	131	2555	102	1373	230	-1.5	0.73002
BR06-705	Gandak (Hazipur)	138	99	82	308	712	39	11	3	187	1911	91	1064	184	-3.3	0.73526
BR06-201	Son (Koilawar)	431	315	43	253	537	116	11	8	50	1833	161	944	170	-0.6	0.72504
BR06-501	Kosi (Dhumarighat)	173	158	69	166	421	15	7	5	67	1252	114	467	118	0.2	0.75732
BR06-601	Bagmati (Dhumarighat)	224	176	70	155	542	48	8	5	51	1551	94	588	141	-1.5	0.74397
Miscelanious water samples																
RW03-20	Seepage water (Lokhandi)	77	47	13	429	1323	30	0	2	70	3513	151	1598	297	-2.5	0.72204
RW03-21	Seepage water (Lokhandi)	58	27	46	550	692	31	0	8	1228	413	135	913	196	-11.0	0.72615
RW03-22	Seepage water (Lokhandi)	17		6	1268	1104		0	4	534	3575	96	468	351	2.0	0.71626
MW03-1	Drip water	123	123	62	4379	5414						195	7454	339		0.71576
MW03-2	Drip water	26	26	15	2119	1815						152	1336	134		0.71517
MW03-3	Drip water	25	25	20	2026	1416						143	1236	115		0.71577
RW03-7	Gangnani (Hot spring)	10874	8688	547	312	1516	2186	30	382	368	11364	1603	2295	1248	2.6	0.75615
RW03-17	Drip water (S. Dhara)	62	35	38	2108	3687	27	0	97	3979	3348	145	16461	798	2.3	0.71093
RW03-18	Sulphurous water (S. Dhara)	339	297	61	4234	13773	42	0	66	15365	4420	203	84715	2422	3.3	0.70977
RW03-19	Stream water (Kempty Fall)	76	40	28	2979	4304	36	0	41	5734	2844	159	28607	982	1.9	0.70950
RW03-1	Bandal (sherki)	91	91	43	918	1009					2883	141	2443			0.72209

It is evident from the ternary plot (Fig-4.3a) that many of the river water samples analysed are closer to the Ca apex with some of the Ganga mainstream and tributaries in the plain heading towards (Na+K) apex. The drip, seepage and fall water samples fall along the Ca-Mg mixing line, the exception being the Gangnani sample which is dominated by Na (Table-4.1).

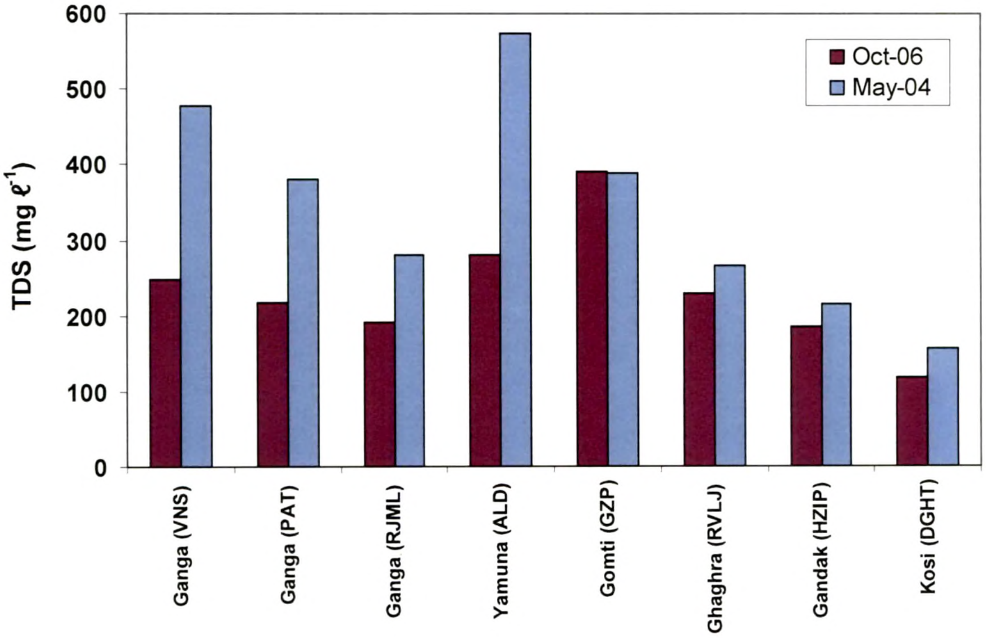
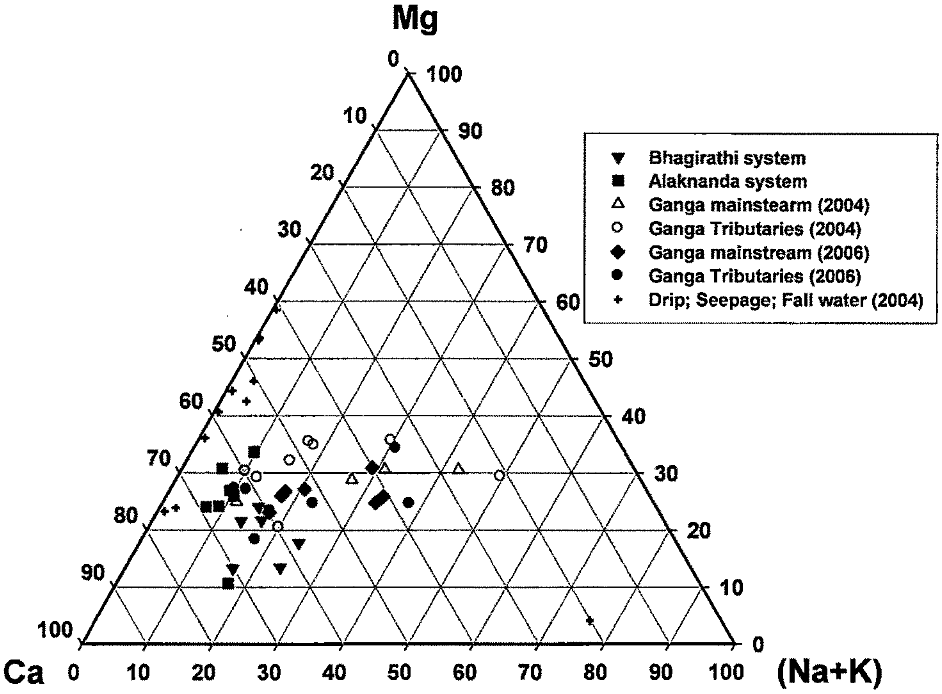
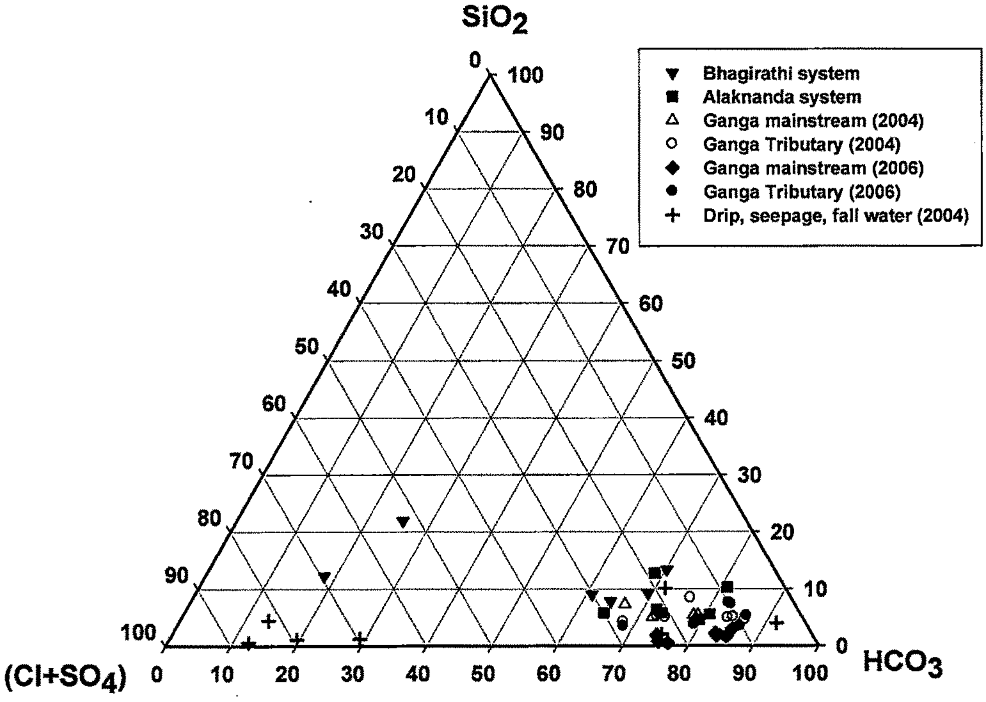


Fig-4.2: Variation in TDS of the Ganga river and its tributaries during two sampling periods, May 2004 and October 2006.

Ca and Mg can be derived from silicates, carbonates and evaporites (gypsum) and minor phases such as apatite. The apportionment of contributions from these various sources is important to estimate silicate and carbonate erosion in the basin and their impact on the draw-down of atmospheric CO_2. Fig-4.4 is a comparison of Ca, Mg and Na abundances along the course of the Ganga mainstream with those reported by Sarin et al. (1989) at the same locations for samples collected in March 1982. It is seen from the figure that the abundances of all these elements are higher in May 2004 compared to March 1982 samples. This difference can be a result of multiple factors such as reduced water flow in May compared to March, enhanced ground water input, interannual variation in major ion abundances or a combination of these.



(a) Ternary plot of cations (µE)



(b)Ternary plot of anions (µE)

Fig-4.3a &b: Ternary plots of major cations (a) and anions (b) in the Ganga head waters, mainstream and tributaries measured during different field campaigns. The data of miscellaneous water samples are also plotted (Table-4.1).

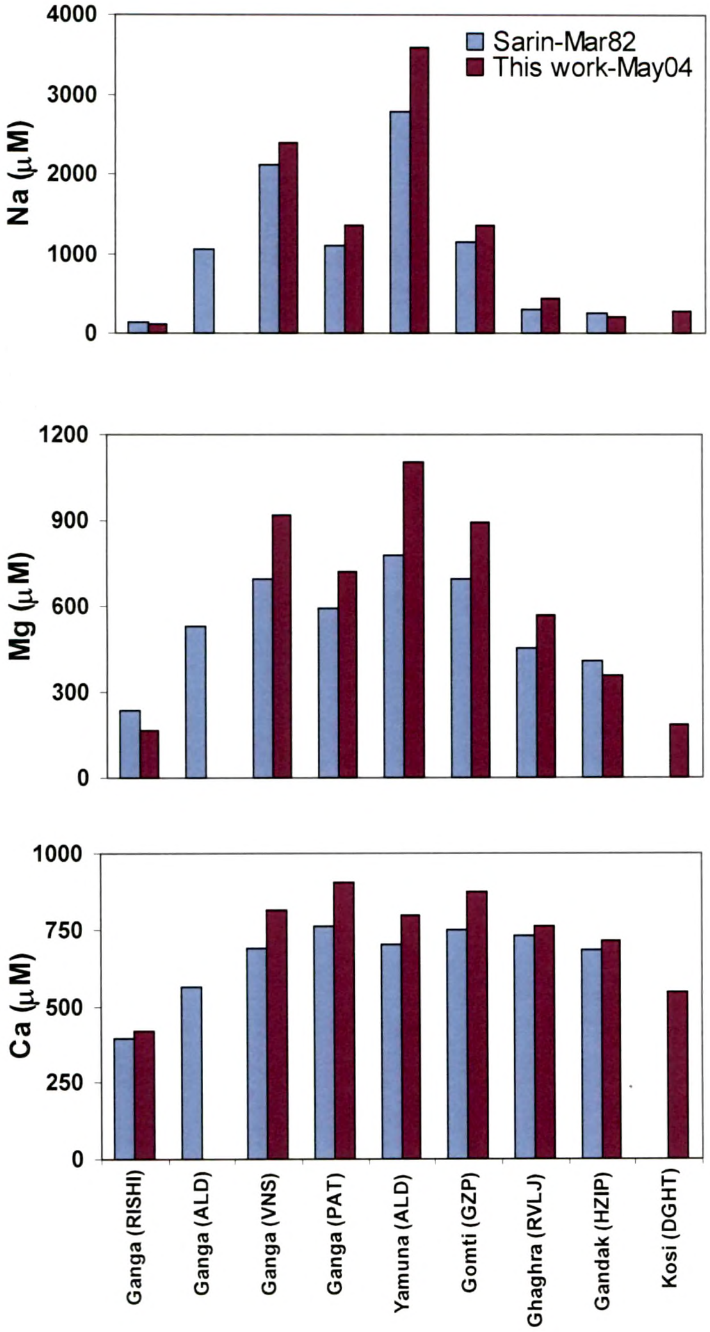


Fig-4.4: Comparison of Ca, Mg and Na abundances in the Ganga mainstream measured in this study with those reported for the sample collected during 1982/83 from the same locations by Sarin et al., (1989). The codes in parentheses refer to sample locations. RISHI= Rishikesh; ALD=Allahabad; VNS=Varanasi; PAT= Patna; GZP= Ghazipur; RVLJ= Revilganj; HZIP= Hazipur; DGHT= Dumarighat.

Among anions, HCO_3 is generally the most abundant, contributing ~ 70 % of TZ^- in the source region and ~80% in the plains (Fig-4.3b). The anion abundances decrease as $HCO_3 > SO_4 > Cl > F > NO_3$ in the headwaters. In the anion ternary plot (Fig-4.3b), the spring, seepage and Kempty Fall samples tend towards the ($Cl+SO_4$) apex in contrast to the river samples which cluster around the HCO_3 apex. This observation brings out the importance of evaporites (gypsum and halite) and sulfuric acid weathering in regulating the major ion composition of these spring, seepage and water fall samples. Among the river waters, two samples from the upper reaches of the Bhagirathi plot away from the HCO_3 apex (Fig-4.3b). These two samples (RW03-5 & RW03-6) have high SO_4 and $SO_4/Ca > 1$ indicating the supply of SO_4 by pyrite oxidation. Sarin et al. (1992) also observed $SO_4/Ca > 1$ in the Bhagirathi sample from the Gangotri. Fig-4.5 is a plot of (Ca+Mg) vs (HCO_3+SO_4) in the water samples. The plot shows that the data of the Bhagirathi, Alaknanda and other samples collected during Oct 2006 all lie close to, but above the equiline. In contrast, the data of samples collected during summer of 2004 from the Ganga plain lie far away from the equiline, showing definite excess of (HCO_3+SO_4). This trend, as discussed later is a result of contribution of Na salts from alkaline/saline soils.

There is no detectable NO_3 throughout the Ganga in summer, however the monsoon samples from the plain show an average NO_3 concentration of 14 μM, with a range between 4 and 50 μM (Table-4.1). The highest NO_3 concentration is found in the Yamuna (50 μM) whereas in the mainstream Ganga the Allahabad sample, before the confluence of the Yamuna, has the highest concentration, 24 μM. The source of NO_3 can be atmospheric deposition and/or of industrial waste from units near Allahabad or from fertilizers used in agricultural fields of this region. The presence of measurable NO_3 brings out the role anthropogenic sources may have on the supply of nutrients to the Ganga river. Fluoride concentration along the entire stretch of the Ganga, from Gangotri to Rajmahal, in summer ranges from 3 to 39 μM with an average of 15 μM (May 2003, 2004). This value decreases to ~6 μM in samples from the plain collected during October 2006 attributable to dilution by rains. Fluoride can be introduced in rivers from precipitation (Madhavan and Subramanian, 2001) and through weathering of fluorite and/or fluor-apatite, the latter is known to be disseminated in the Himalaya (Jain et al., 2000; Catlos et al., 2007).

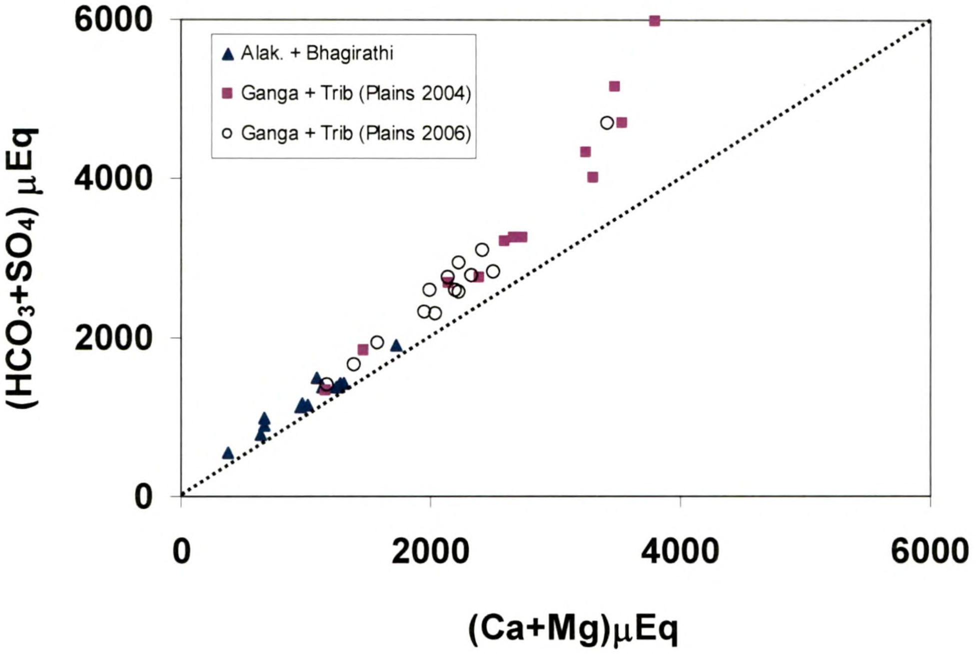


Fig-4.5: Scatter plot of (Ca+Mg) and (Alkalinity + SO_4). The dashed line represents 1:1 ratio. Deviation from the equiline, particularly in samples collected during May 2004 indicates the contribution of (HCO_3+SO_4) as Na salts from alkaline/saline soils in the Ganga plain.

Dissolved Si in the Ganga headwaters (Bhagirathi and Alaknanda) has a range of 84 µM to 240 µM (Table-4.1) with an average of ~120 µM. Si concentrations in the Ganga main stream in plain show significant variation between May 2004 and October 2006, with the later samples having much lower values (Table-4.1). Among the samples analysed highest Si concentration (325 µM) was observed in the Yamuna sample at Allahabad during May 2004. The high Si abundance in Yamuna water can result from weathering of Deccan Basalts. Rengarajan et al. (2008) in their study of the Chambal, the major tributary of the Yamuna, draining the Deccan basalts reported high Si, with values ranging from 157 to 607 µM. Si/(Na*+K) molar ratio has been used as a proxy to investigate intensity of silicate weathering in river basins (Stallard, 1980; Stallard and Edmond, 1983; Sarin et al.,1989). The ratio is ~1.0 to 1.4 in the Ganga head waters, and drops to quite low values in the plain. This drop is a result of Na addition to water thereby rendering Si/(Na*+K) ratio a less reliable proxy to learn about silicate weathering (see later discussion).

4.2.2 Water Chemistry of the Gomti, Yamuna and the Son and its impact on the chemistry of the Ganga Mainstream in the plain

The chemistry of the rivers draining these three regions is discussed together as they are used to derive chemical erosion in the plain and peninsular sub-basins of the Ganga drainage. The major ion chemistry of the Gomti waters sampled during both May and October is nearly the same (Table-4.2) with high abundances of Na, Mg and Ca and highest TDS among all the October samples (Table-4.1). The major ion composition of the Gomti measured in this study is very similar to that reported by Sarin et al. (1989) in samples of March and November 1982/83, from Dhobni, a few kms upstream of Ghazipur. The moderately high concentrations of Mg (~870 ± 25 μM) and Ca (~860 ± 10 μM) in samples (Table-4.2) suggest that carbonate weathering is prevalent in the Gomti basin. Further, the similar or higher concentrations of Mg and Ca in the Gomti, relative to that in the Ghaghra and the Gandak, the Himalayan tributaries of the Ganga (Table-4.1), suggest that the role of carbonates in contributing to the major ion chemistry of all these three rivers is roughly similar. Some of the earlier work (Singh et al., 2005b) on particulate and dissolved phases of the Gomti has hinted at the possibility of precipitated carbonates (kankar) as a potential source of Ca to the Gomti river. The Sr isotope composition of the Gomti water and sediment also attests to the dominant role of carbonates in determining its water chemistry. The $^{87}Sr/^{86}Sr$ of the Gomti water, 0.7271 – 0.7276 (Table-4.2) is far less radiogenic compared to the $^{87}Sr/^{86}Sr$ of silicate fraction of its bed sediments (0.79276, Table-3.1 chapter-3, Singh et al., 2008). The lower $^{87}Sr/^{86}Sr$ of water relative to bed sediment silicates, most likely results from mixing of Sr derived from radiogenic silicates and unradiogenic carbonates.

The chemistry of the Yamuna waters (Allahabad) is unique with the May sample having the highest TDS, Na, Mg, Cl and Sr among the samples analyzed (Table-4.2). The cations (equivalent units) in this sample decrease as Na > Mg > Ca > K, unlike the Himalayan tributaries which generally have Ca > Mg > Na > K (Table-4.1). The data of Sarin et al., (1989) also show high Na in the Yamuna at Allahabad during both March/ November 1982-83. Na abundance in both the Gomti and Yamuna (Allahabad) rivers are quite high among the rivers of the Ganga system and range between 1275 to 3575 μM (Table-4.2). In general, Na^+ is a significant contributor to cation charge in samples with TZ^+ >3000 μEq. There is a significant excess of Na over Cl in these samples (Tables-4.1, 4.2) suggesting that sources in addition to halite dissolution supply Na to them. Charge balance considerations show that in some of these samples, $Na^+ > (Cl^- + 2SO_4^{2-})$ requiring part of Na^+ in them to be associated with HCO_3^-.

Table-4.2 Major ions (μM), TDS (mg ℓ^{-1}), Sr (nM) and $^{87}Sr/^{86}Sr$ in the Gomti, Son and the Yamuna Rivers

River (Location)	Na	K	Mg	Ca	Cl	NO_3	SO_4	HCO_3	SiO_2	TDS	Sr	$^{87}Sr/^{86}Sr$
Gomti (Ghazipur)												
May-04	1354	127	894	872	400	17	252	4193	-	388	3173	0.72759
Oct-06	1399	130	848	859	324	7	200	4286	92	390	2717	0.72714
Son (Koilawar)												
Oct-06	431	43	253	537	116	11	50	1833	161	170	944	0.72504
Yamuna (Batamandi)*												
Jun-99	306	49	661	967	73	6	556	2508	193	285	2044	-
Oct-98	255	52	497	1019	60	35	333	2369	211	254	1802	0.72356
Yamuna (Allahabad)												
May-04	3575	136	1104	794	1493	0	335	5300	325	574	5889	0.71467
Oct-06	1275	85	443	673	696	50	181	2575	129	280	2717	0.71239

* at foot-hills of the Himalaya. Data from Dalai et al., (2002)

Silicate weathering in the basin by carbonic acid can contribute to this association. Alternatively, in the Yamuna, Gomti and the Ganga (samples downstream of Allahabad), saline and alkaline soils occurring in their basins

(Agarwal and Gupta, 1968; Bhargava and Bhattacharjee 1982; Sarin et al.,1989; Datta et al.,2002; Singh et al.,2004; Singh et al.,2005b) can supply Na as Na_2SO_4, $NaHCO_3$ and Na_2CO_3. These soils lie in the semi-arid alluvial regions of Uttar Pradesh, (south west Ganga basin) parts of Haryana and Bihar. In Uttar Pradesh, the salt affected zone occurs between the intervluves of Ganga-Yamuna and Ganga-Ghaghra rivers (Fig-4.6). Saline/alkaline soils are frequent in patches (Agrawal and Gupta 1968) in low lying areas of the state where water logging conditions prevail.

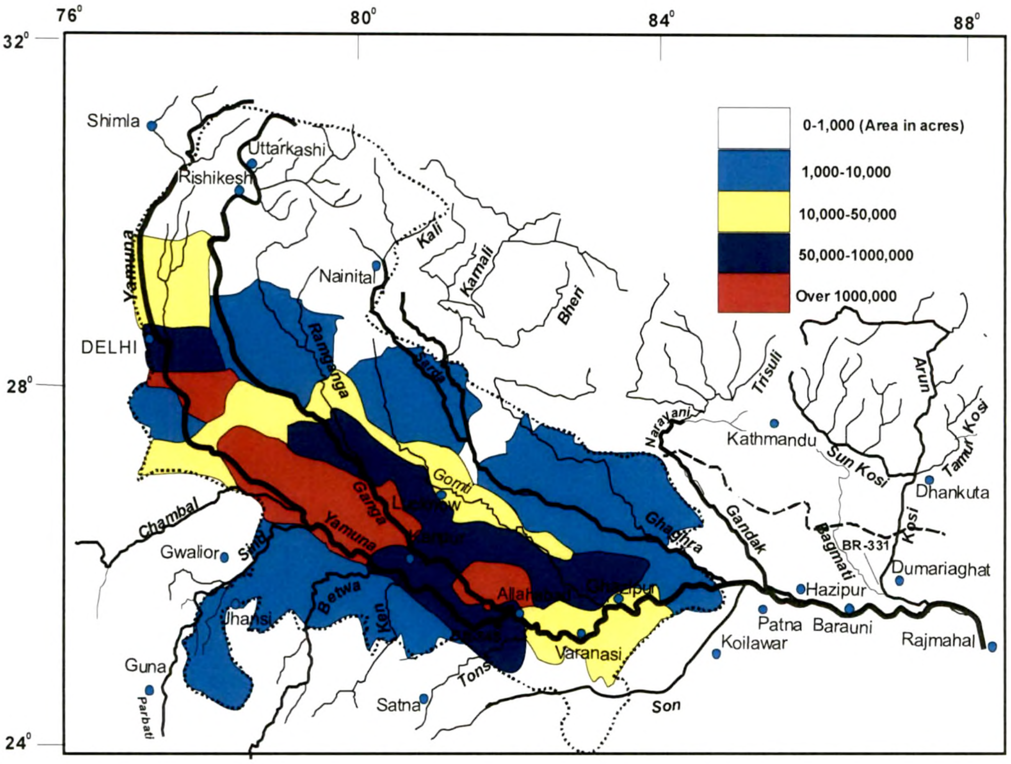


Fig-4.6: Arial distribution of salt affected (usar) soils in different parts of Uttar Pradesh (after Agarwal and Gupta, 1968)

Table-4.3: Chemical composition of water extract of salt affected surface soils from the Ganga plain (mE: milli equivalents)

Location	Ca	Mg	K	Na	CO_3	HCO_3	Cl	SO_4
Kasimabad (Hardoi, UP)	3.5	1.0	1.5	145.0	90.0	51.0	8.0	0.0
Malihabad (Lucknow, UP)	8.0	3.0	0.8	155.9	142.0	13.0	14.0	0.0
Kasimabad (Hardoi, UP)	2.0	0.5		27.1	0.0	18.0	10.0	0.0
Ghatampur (Kanpur, UP)	3.5	3.0	0.3	10.1	0.0	6.0	11.0	0.0
Shikarpur (Azamgarh, UP)	1.6	1.0		4.6		1.2		
Gaura (Azamgarh, UP)	1.0	-	-	115.6	2.8	9.0	1.8	111.6

Source: Agarwal and Gupta (1968) and references therein

Table-4.4: Salt Composition of surface soils from the Ganga plains

Location	Total soluble Salt (%)	Na_2CO_3 (%)	$NaHCO_3$ (%)	NaCl (%)	Na_2SO_4 (%)
Saline Soils					
Ghazipur (UP)	4.690			1.500	2.790
Western Yamuna Canal (UP)	3.087	0.904	-	1.142	1.093
Barauli (Farrukhbad,UP)	1.494	0.087	-	0.116	1.318
Chinhat (Lucknow, UP)	0.261	0.197	-	0.048	0.046
Cherat (Agra, UP)	0.095	0.813	-	0.071	0.063
Ganga Khadir (Aligarh, UP)	0.200	0.007	0.131	0.021	0.014
Ganga Khadir (Meerut, UP)	0.303	-	0.249	0.015	
Yamuna Khadir (Aligarh, UP)	0.710	-	0.083	0.156	0.484
Saline -Alkali Soil					
Bicjpuri , Etah (UP)		0.030	0.042	0.007	-
Bicjpuri , Etah (UP)		0.065	0.057	0.014	-

Source: Agarwal and Gupta (1968) and references therein

In the central part of the Indo-Gangetic plain, these soils are called *Usar (meaning sterile or barren) or Reh* with hard surface devoid of vegetation and are characterized by white/grayish white or ash coloured salt encrustations during dry periods. The surfaces of these soils are quite impermeable causing poor or impeded drainage resulting in water stagnation. Analyses of these soils for their Na salts and water soluble extracts are available (Tables-4.3, 4.4) which shows considerable variation. This constrains the estimation of their contribution to the solute budget of the Ganga, particularly Na, SO_4 and alkalinity downstream of Allahabad. *Kankar* (impure calcium carbonate nodule) frequently occur at depths in these soils (Kumar et al., 1996).

The role of these soils on the Na budget of the Son, Yamuna, Gomti and the Ganga downstream Allahabad is also evident from the SiO_2/Na^{**} ratios in them (Na^{**} is Na corrected for both rain and evaporite input, $Na^{**}= Na_r - Cl_r$) During May 2003, the (SiO_2/Na^{**}) in the Ganga headwaters is ~1.4 (Table-4.1), similar to the values reported by Sarin et al. (1989). This value decreases to ≤ 0.4 and ≤ 0.3 in the Ganga downstream of Allahabad during May 2004 and October 2006 respectively. The (SiO_2/Na^{**}) is lowest, ≤ 0.2, in the Gomti and the Yamuna (Allahabad). Such low (SiO_2/Na^{**}) ratios, ≤ 0.4, is difficult to be explained in terms of weathering of common silicate minerals

(Stallard, 1995; Drever, 2002), making it necessary to invoke supply of Na from sources in addition to silicate weathering to interpret the data. Sodium salts contained in alkaline and saline soils of the drainage basins is very likely to be this additional source. Such a source can add Na to water with little (or no) SiO_2 and thus bring down the SiO_2/Na^{**} in water. Further, the supply of such non-chloride Na salts from the alkaline/saline soils can contribute to errors in the estimation of silicate derived Na in water and thus constrain the use of Na^{**} as a proxy to determine silicate weathering rates in these river basins. The silicate erosion rates and associated CO_2 consumption rates of the Ganga basin calculated based on Na^{**} in the Ganga waters downstream Allahabad in some of the earlier studies (e.g. Krishnswami et al.,1999; Galy and France-Lanord, 1999) can be an overestimate if part of Na^{**} is derived from alkaline/saline soils (Rengarajan et al., 2008).

The high Ca and Mg concentration in the Yamuna are attributable to weathering of plagioclase and mafic minerals of Deccan basalts (Das et al., 2005) and carbonates of the Vindhyan in the basins of its peninsular tributaries. Indeed, the studies of Rengarajan et al. (2008) on the Chambal, the major tributary of the Yamuna, draining the Deccan Traps and Vindhyan show high Mg and Ca abundances even in samples collected during monsoon.

The abundances of major ions, except Ca, in the Yamuna decrease by factors of ~ 2 to 3 in the October samples due to dilution by monsoon discharge. Ca abundance in the Yamuna and the Ganga mainstream shows marginal decrease (~10% - 20%) in the October samples relative to summer samples from the same locations. The trends in Ca, Mg and Na variation along the Ganga mainstream in October is roughly similar to that observed during summer of 2004, except as mentioned above, their concentrations are lower in the October samples due to dilution by south-west monsoon rains.

In comparison to both the Yamuna and the Gomti, the abundances of Ca, Mg and Na in the Son are generally lower (Table-4.2). This can result from a number of factors that include higher rainfall and runoff in its drainage, lesser exposure of carbonates and the less weatherability of the Archean granites and sand stones of the Gondwana and the Vindhyan in the Son basin. The drainage of the Son in the Ganga plain also contains alkaline/saline soils (Singh et al., 2004) which can contribute to the Na budget of the Son river.

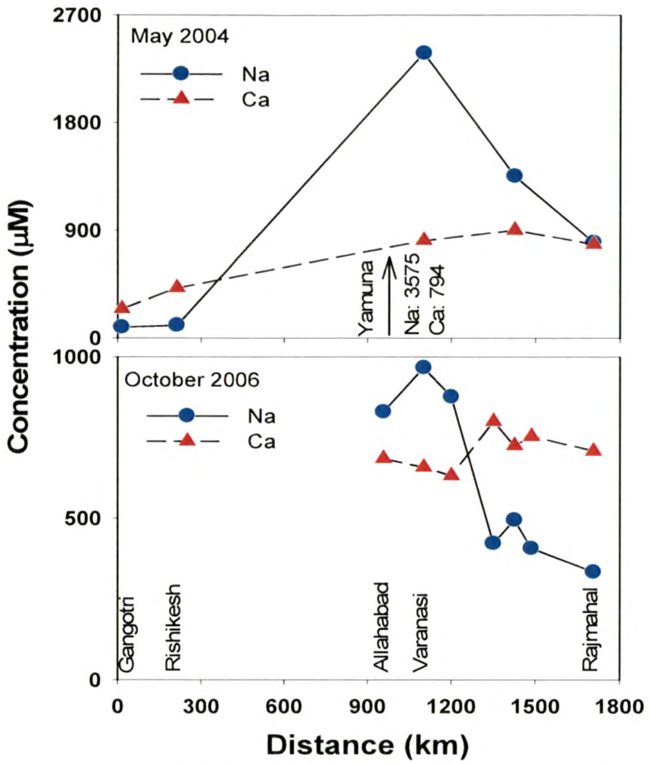
The impact of mixing of the Yamuna waters with the Ganga is clearly evident from the sharp increase in the concentration of Na and to a lesser extent in Mg, Ca and TDS in the Ganga waters at Allahabad / Varanasi (Table-4.1, Fig-4.7) during May. In October, such trends could not be looked for as the sampling was done only downstream of Allahabad. The data, however, show that among the samples analysed Na is highest in Varanasi (Fig.4.7). In the May samples, maximum increase is for Na, from 106 μM at Rishikesh to 2380 μM at Varanasi (Table-4.1, Fig-4.7). Fig-4.8 is a plot of Na vs Cl for the May and October samples of the Ganga mainstream in the plain. Also included in the plot are data for the Ganga at Rishikesh (or the Ghaghra at Revilganj) and the Yamuna at Allahabad. It is seen from the plot that during both the seasons the data show a strong linear trend, attributable to two component mixing, the low Na and Cl Himalayan end member (Rishikesh/Ghaghra) with the high Na and Cl Yamuna at Allahabad. This trend demonstrates the important role of Yamuna waters in determining the Na abundance of the Ganga downstream of its confluence. The best fit lines for the data in Fig-4.8 show that they plot well above the halite line, due to Na excess over chloride. The high Na in the Yamuna, as mentioned earlier, is dominated by contribution from alkaline/saline soils.

During the same period, Ca also increases from 419 μM at Rishikesh to 814 μM at Varanasi whereas the change in Mg is from 164 to 922 μm, double that of Ca. This increase, analogous to that of Na, is a result of mixing of Ca and Mg rich Yamuna (Table-4.1) with the Ganga and due to chemical weathering in the plain between Rishikesh and Varanasi. Downstream of Varanasi, Ca in the Ganga varies within a narrow range of 784 to 903 μM, similar to those of its tributaries, the Ghaghra and the Gandak, ~750 μM (Table-4.5). The concentration of Ca in the October samples, in both the Ganga mainstream and the Ghaghra and the Gandak are marginally lower relative to the May value. The near uniform abundance of Ca in the Ganga and its tributaries from the Himalaya, plain and peninsular India is intriguing and may be a influenced by calcite saturation. Indeed, calcite saturation index (CSI) calculated for the mainstream and tributary waters for the 2004 samples shows that all samples (except Kosi waters at Dumarighat and the Alaknanda in its upper reaches) are supersaturated in calcite and hence are prone to removal of Ca from the dissolved phase via its precipitation.

Table-4.5: Ca, Mg abundance and Ca/Mg in the Ganga system

Location **Ganga Mainstream**		**Distance** **(From Rishikesh)**	**Ca**	**Mg**	**Ca/Mg**
RISHI	2004	0	419	164	2.55
	2006				
ALD	2004	782			
	2006		685	528	1.30
VNS	2004	974	814	922	0.88
	2006		658	415	1.59
PAT	2004	1280	903	722	1.25
	2006		725	376	1.93
BRNI	2004	1375			
	2006		754	364	2.07
RJML	2004	1640	784	510	1.54
	2006		709	273	2.59
Ganga Tributaries					
YAMUNA	2004	784	794	1104	0.72
(Allahabad)	2006		673	443	1.52
GOMTI	2004	1016	872	894	0.98
(Ghazipur)	2006		859	848	1.01
GHAGHRA	2004	1224	762	569	1.34
(Revilganj)	2006		867	384	2.26
GANDAK	2004	1281	714	356	2.01
(Hazipur)	2006		712	308	2.31
KOSI	2004	1550	544	187	2.91
(Dumarighat)	2006		421	166	2.53

Further evidence of Ca removal comes from the relations of Ca/Mg with Ca and CSI (Figs-4.9 and 4.10).These scatter diagrams show that Ca/Mg decreases with increase in both Ca and CSI. This can be explained in terms of preferential loss of Ca during precipitation of $CaCO_3$. From Varanasi to Rajmahal, Mg decreases from 922 to 510 µM (Table-4.5), primarily because of mixing with relatively Mg poor waters of the Ghaghra, Gandak and the Kosi. Among these three Himalayan tributaries the Kosi has the lowest Ca and Mg consistent with low aerial coverage of the Lesser Himalayan carbonates in its basin (Quade et al., 2003).



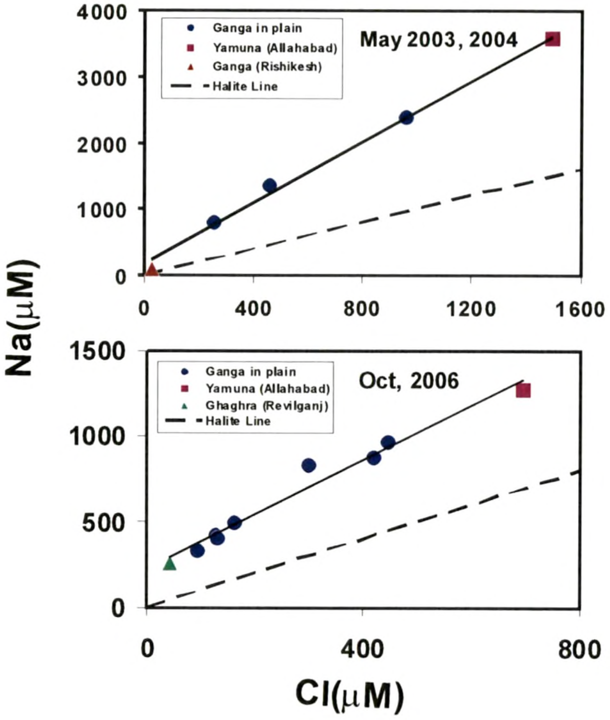


Fig-4.7: (Left) Variations in Na and Ca concentrations of the Ganga mainstream from its source to its outflow at Rajmahal. In the May samples Na in the Ganga increases sharply at Varanasi after confluence with the Yamuna, highlighting the importance of the Yamuna in contributing to Na (and other major ions) to the Ganga mainstream. Ca concentrations also show similar trend along the Ganga mainstream however magnitude of variations is much less, this may be an affect of calcite supersaturation which maintain Ca concentration around ~800 µM.

Fig-4.8: (Right) Variation of Na with Cl of the Ganga mainstream. The data seem to be a result of two end member mixing, the high concentration member (Yamuna) and the low concentration member characterized by the Himalayan tributaries.

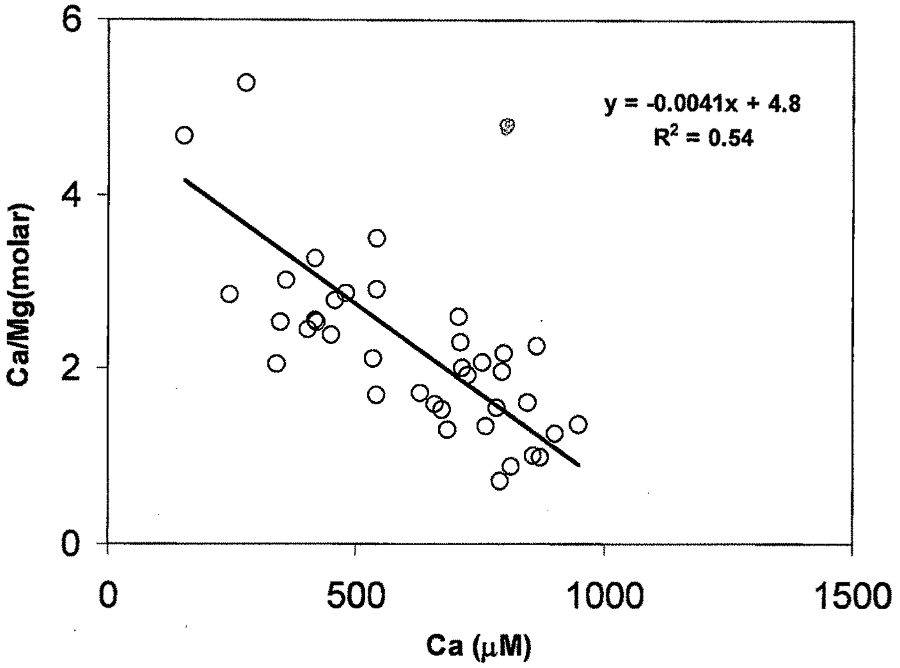


Fig-4.9: Variation of Ca/Mg with Ca in the Ganga river and its tributaries.

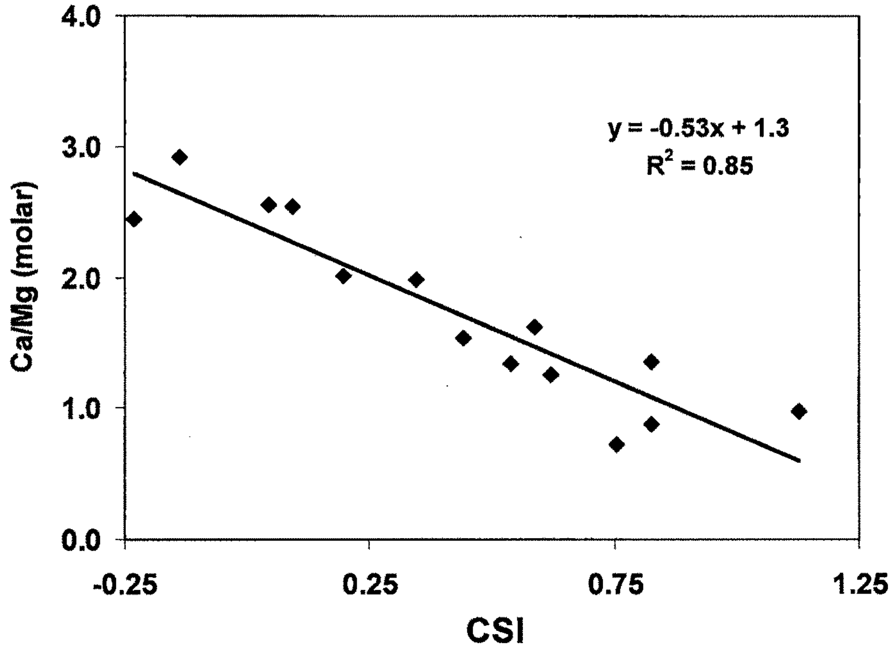


Fig-4.10: Plot between Ca/Mg and Calcium saturation Index (CSI) of water samples from the Ganga and its tributaries. The decrease in Ca/Mg with Ca and CSI can be a result of Ca removal via calcite precipitation.

4.3 Chemical Erosion in the Plain, Peninsular and the Himalayan Sub-Basins of the Ganga

Dissolved major ions in rivers are derived primarily from two sources atmospheric deposition and chemical weathering of various lithologies of the basin (Holland, 1978; Meybeck, 1979; Stallard and Edmond, 1983; Stallard, 1995; Meybeck, 2005). In this study, the atmospheric contribution to Ganga water chemistry is evaluated separately for the Ganga headwaters in the Himalaya and for the Ganga and its tributaries in the plain. The calculation assumes that all chloride in river water samples with lowest Cl is of atmospheric origin. For the head waters, the average of three river samples with the lowest chloride yield a value of (10 ± 2) μM for contribution from precipitation (Table-4.1). For the Ganga and its tributaries in the plain, the average chloride of the samples BR06-901, -705, and -501, (32 ±15) μM, is taken as typical contribution from rain. This value takes into consideration the effect of evapotranspiration as it is based on measured river water concentration. The rain water contribution to chloride is calculated to range from ~13% to 49% in the remaining Ganga headwater samples (Table-4.1) and 2 to 67 % for rivers in the plain. The atmospheric contributions for Na, Mg and Ca are calculated from representative (element/Cl) ratios in precipitation (Table-4.6). For Na this averages ~6% for the head waters and ≤ 11% for all these elements for rivers in the plain. Chloride in excess of atmospheric input in rivers has to be derived from other sources, such as hot springs and evaporites. Hot springs are known to be an important source for excess chloride (over atmospheric contribution) for the Ganga head waters (Evans et al., 2001; Bickle et al., 2003). In the plain and peninsular sub-basins of the Ganga, evaporites in the form of alkaline and saline salts in soils could be relatively more important (Singh et al., 2004, 2008) especially in the drainage basins of the Yamuna, the Gomti and the Ganga downstream of Kanpur.

The Chemical Erosion Rates of cations $(\mathrm{CER})_{\mathrm{cat}}$ have been calculated based on atmospheric contribution corrected major ion and Sr abundances in rivers and their annual water discharge [$(\mathrm{CER})_{\mathrm{cat}} = \Sigma(\mathrm{x}_i^*) \times \mathrm{Q}$, where x_i^* is Na, K, Mg and Ca abundances in river water corrected for rain input and evapotranspiration and Q is the runoff].

Table-4.6: Chemical composition of Rain water, ice and snow in the Himalaya and plain regions.

Sample	Na	K	Ca	Mg	Cl	NO_3	SO_4	Reference
Rain 1 (Dehradun)	0.2	0.8	0.7	0.4	3.2	-	4.5	Dalai et al., 2002
Rain 2 (Dehradun)	0.2	0.8	1.3	0.7	3.8	-	4.8	Dalai et al., 2002
Chhota Shigri (snow)	14	7	6	4	21	8	2	Nijampurkar et al., (1993)
Chhota Shigri (ice)	8	3	2.6	1.4	11	7	1.8	Nijampurkar et al., (1993)
Dokriani Bamak (snow)	10	3.4	4.2	2.4	19	3.4	6.8	Sarin and Rao (2002)
Himalaya (weighted average)	10	2.2	22	6.1	7.4	5.3	6.2	Galy & France-Lanord, 1999
Himalaya	**7.0**	**3.0**	**6.0**	**2.5**	**11.0**	**6.0**	**4.0**	
Roorkee	38.5	14.7	145.1	23.3	59.4	33.4	22.6	Hameed et al., 2006
Dayalbagh (suburban)	54.8	7.7	42	13.2	23.7	17.6	14.2	Saxena et al., (1996)
Gopalpura (Near Agra)	19.4	2.5	67.2	39.2	30.6	42.6	7.7	Satsangi et al., (1998)
Plain (weighted average)	35	6.6	34	9	29	4.8	19	Galy & France-Lanord, 1999
Rain water (Plain)	**37**	**8**	**72**	**21**	**36**	**25**	**16**	

Table-4.7: Major ion and Sr fluxes from the basins of the Ganga and its tributaries

River	Location	Date	Discharge 10^{12} ℓ	Area 10^3 km^2	Basin#	Flux (10^4 tons yr^{-1})							
						Na*	Na**	K*	Mg*	Ca*	Sr	$(\Sigma Flux)_{cat}$	$(\Sigma Flux)^*_{cat}$
Ganga	Rishikesh	May-03	23.9	21.7	H	5.5±1.8	4.2±1.8	3.8±1.1	9±3	40±12	0.15±0.05	58±12	57±12
Ghaghra	Revilganj	Oct-06	94.4	128	H+P	48±17	46±17	27±8	84±26	307±98	1.13±0.34	466±103	464±103
Ghaghra&	Kotilaghat	Nov-94	63.4	57.6	H	28±9	25±9	11±3	66±20	226±68	0.72±0.22	331±71	328±71
Ghaghra			31	70.4	P	20±19	21±19	16±9	18±33	81±119	0.41±0.40	135±126	136±126
Gandak	Hazipur	Oct-06	52.2	46.3	H+ P	13±6	12±5	17±5	37±12	137±45	0.49±0.15	204±47	203±47
Gandak&	Narayanghat	Jun-93	49.4	31.8	H	12±4	6.1±4	9.8±2.9	29±9	118±35	0.41±0.12	169±37	163±37
Gandak			2.8	14.5	P	0.2±6.8	5.9±6.8	7.2±5.9	8±15	19±57	0.08±0.19	34±60	40±60
Gomti	Ghazipur	Oct-06	7.4	30.5	P	23±7	18±7	3.8±1.1	15±5	24±8	0.18±0.05	66±12	61±12
Chambal&	Dholpur	Sep-82	30	129	Pe	39±12	21±13	6.2±1.9	23±7	93±30	0.6±0.18	161±33	143±34
Betwa&	Hamirpur	Nov-83	10	46	Pe	34±11	27±11	2.2±0.7	14±4	38±12	0.3±0.09	88±17	81±17
Yamuna	Allahabad	Oct-06	93	366	H+Pe+P	266±82	124±93	31±9	97±30	230±76	2.2±0.66	624±116	482±124
Yamuna	Batamandi	Oct-98	10.8	9.8	H	6.2±1.9	4.8±1.9	2.2±0.7	13±4	44±13	0.17±0.05	66±14	64±14
Yamuna			82.2	356	Pe+P	259±82	119±93	29±9	84±30	189±77	2±0.66	561±117	421±125
Yamuna				124	P	94±29	74±30	15±5	61±19	97±31	0.72±0.22	267±47	247±47
Yamuna				232	Pe	165±87	45±98	13±10	23±36	90±83	1.33±0.70	291±126	171±133
Son	Koilawar	Oct-06	31.8	71.3	Pe+P	29±10	23±10	5.3±1.6	18±6	61±21	0.26±0.08	113±24	107±24
Kosi	Dumarighat	Oct-06	62	74.5	H+P	20±8	20±8	17±5	23±8	91±32	0.25±0.08	151±34	151±34
Ganga	Rajmahal	Oct-06	380	935	H+Pe+P	262±89	210±90	111±33	237±76	996±329	3.73±1.12	1607±351	1554±351

* Corrected for rain input and evapotranspiration

** Corrected for rain input and halite ($Na^{**} = Na_{riv} - Cl_{riv}$)

&: Data from Galy and France-Lanord (1999) and Sarin et al. (1999)

$(\Sigma Flux)^*_{cat} = (\Sigma Flux)_{cat}$ corrected for Na from halite

#: H: Himalayan, P: Ganga plain, Pe: peninsular drainage

Table-4.8: Major ion and cation Erosion rates in plain, peninsular and Himalayan sub-basins

River	Location	Date	Discharge	Area	Basin[#]	Erosion Rate (tons km^{-2} yr^{-1})							
			10^{12} ℓ	10^3 km^2		Na*	Na**	K*	Mg*	Ca*	Sr	(CER)$_{cat}$	(CER)*$_{cat}$
Ganga	Rishikesh	May-03	23.9	21.7	H	2.5± 0.8	1.9 ± 0.8	1.8 ± 0.5	4.1 ± 1.2	18 ± 6	0.07± 0.02	27± 6	26 ± 6
Ghaghra	Revilganj	Oct-06	94.4	128	H+P	3.8 ± 1.3	3.6 ± 1.3	2.1 ± 0.6	6.6 ± 2.0	24 ± 8	0.09 ± 0.03	36 ± 8	36 ± 8
Ghaghra[&]	Kotilaghat	Nov-94	63.4	57.6	H	4.9 ± 1.5	4.3 ± 1.6	1.9 ± 0.6	11.5 ± 3.4	39 ± 12	0.13 ± 0.04	57 ± 12	57± 12
Ghaghra			31	70.4	P	2.8 ± 2.7	3.0 ± 2.7	2.3 ± 1.2	2.6 ± 4.6	12 ± 17	0.06 ± 0.06	19 ± 18	19 ± 18
Gandak	Hazipur	Oct-06	52.2	46.3	H+ P	2.8 ± 1.3	2.6 ± 1.1	3.7 ± 1.1	8.0 ± 2.6	30 ± 10	0.11 ± 0.03	44 ± 10	44 ± 10
Gandak[&]	Narayanghat	Jun-93	49.4	31.8	H	3.8 ± 1.2	1.9 ± 1.4	3.1 ± 0.9	9.1 ± 2.7	37 ± 11	0.13 ± 0.04	53 ± 12	51± 12
Gandak			2.8	14.5	P	0.1 ± 4.7	4.1 ± 4.7	5.0 ± 4.1	5.5 ± 10.1	13 ± 40	0.06 ± 0.13	24 ± 41	28 ± 41
Gomti	Ghazipur	Oct-06	7.4	30.5	P	7.5 ± 2.3	5.9 ± 2.4	1.2 ± 0.4	4.9 ± 1.5	8 ± 3	0.06 ± 0.02	22 ± 4	20 ± 4
Chambal[&]	Dholpur	Sep-82	30	129	Pe	3.0 ± 1.0	1.6 ± 1.0	0.5 ± 0.1	1.8 ± 0.6	7 ± 2	0.05 ± 0.01	12 ± 3	11 ± 3
Betwa[&]	Hamirpur	Nov-83	10	46	Pe	7.4 ± 2.3	5.9 ± 2.3	0.5 ± 0.1	3.0 ± 0.9	8 ± 3	0.07 ± 0.02	19 ± 4	18 ± 4
Yamuna	Allahabad	Oct-06	93	366	H+Pe+P	7.3 ± 2.3	3.4 ± 2.5	0.8 ± 0.3	2.7± 0.8	6 ± 2	0.06 ± 0.02	17 ± 3	13 ± 3
Yamuna	Batamandi	Oct-98	10.8	9.8	H	6.4 ± 2.0	4.5 ± 2	2.2 ± 0.7	13.3 ± 4.0	45 ± 14	0.17 ± 0.05	67 ± 14	65 ± 14
Yamuna			82.2	356	Pe+P	7.3 ± 2.3	3.3 ± 2.6	0.8 ± 0.3	2.4 ± 0.9	5 ± 2	0.06 ± 0.02	16 ± 3	12 ± 4
Yamuna				124	P	7.6 ± 2.4	6.0 ± 1.8	1.2 ± 0.4	4.9 ± 1.5	8 ± 3	0.06 ± 0.02	22 ± 4	20 ± 4
Yamuna				232	Pe	7.1 ± 3.8	1.9 ± 4.2	0.6 ± 0.4	1.0 ± 1.5	4 ± 4	0.06 ± 0.03	13 ± 5	7± 6
Son	Koilawar	Oct-06	31.8	71.3	Pe+P	4.1 ± 1.3	3.2 ± 1.4	0.7 ± 0.2	2.5 ± 0.8	9 ± 3	0.04 ± 0.01	16 ± 3	15 ± 3
Kosi	Dumarighat	Oct-06	62	74.5	H+P	2.7 ± 1.0	2.7 ± 1.0	2.3 ± 0.7	3.1 ± 1.0	12 ± 4	0.03 ± 0.01	20 ± 5	20 ± 5
Ganga	Rajmahal	Oct-06	380	935	H+Pe+P	2.8 ± 1.0	2.2 ± 1.0	1.2 ± 0.4	2.5 ± 0.8	11 ± 4	0.04 ± 0.01	17 ± 4	17 ±4

* Corrected for rain input and evapotranspiration

** Corrected for rain input and halite ($Na^{**} = Na_{riv} - Cl_{riv}$)

[&]: Data from Galy and France-Lanord (1999) and Sarin et al. (1999)

(CER)*$_{cat}$ = (CER)$_{cat}$ corrected for Na from halite

[#]: H: Himalayan, P: Ganga plain, Pe: Peninsular drainage

Table-4.9: Cation Erosion Fluxes and rates from the Ganga sub-basins*

Sub-basin	River	Date	Location	Water discharge	Drainage Area	$(\Sigma Flux)_{cat}$	$(\Sigma Flux)^*_{cat}$	$(CER)^*_{cat}$	
				10^{12} ℓ	10^3 km^2	10^4 tons yr^{-1}		tons km^{-2} yr^{-1}	mm kyr^{-1}
Himalaya									
	Yamuna	Oct-98	Batamandi	10.8	9.8	66	64	65±14	
	Ganga	May 03	Rishikesh	23.9	21.7	58	57	26±6	
	Ghaghra	Nov-94	Kotilaghat	63.4	57.6	331	328	57±12	
	Gandak	Jun-93	Narayanghat	49.4	31.8	169	163	51±12	
	Total				**121**	**624**	**612**		**20±3**
Plain									
	Gomti	Oct-06	Ghazipur	7.4	30.5	66	61	20±4	
	Yamuna		Plain		124	267	247	20±4	
	Ghaghra		Plain	31	70.4	135	136	19±18	
	Gandak		Plain	2.8	14.5	34	40	28±41	
	Total				**239**	**502**	**484**		**8±2**
Peninsular									
	Yamuna	Oct-06	Allahabad		232	291	171	7±6	
	Son	Oct-06	Koilawar	31.8	71.3	113	107	15±3	
	Chambal$^{\&}$	Sep-82	Dholpur	30	129	161	143	11±3	
	Betwa$^{\&}$	Nov-83	Hamirpur	10	46	88	81	18±4	
	Total				**303**	**404**	**278**		**3.7±1.8**
Ganga									
	Ganga	**Oct-06**	**Rajmahal**	**380**	**935**	**1607**	**1554**	17±4	**6.6±1.5**

*: for data sources see Table-4.7

&: These rivers are not considered in **Total** estimates

Two approaches have been used for calculating $(\mathrm{CER})_{\mathrm{cat}}$. One is based on rivers flowing through a single sub-basin, e.g. Gomti (Plain), Ganga at Rishikesh (Himalaya) and Chambal (peninsular). The second approach is based on flux by difference and uses data from rivers flowing through multiple sub-basins, e.g. the Ghaghra and the Gandak (Himalaya and plain) and the Yamuna (Himalaya, penisular and plain). In this case knowledge of elemental fluxes along the course of the river, at or near the exits of individual sub-basins is required. In this case the $(\mathrm{CER})_{\mathrm{cat}}$ from a particular sub-basin is calculated using the relation:

$$((CER)_{\mathrm{cat}})_i = \frac{\sum(F_t - F_j)}{A_i} \qquad \text{.........................} \quad (4.1)$$

where, F is the elemental/cation flux (tons yr^{-1}), A is the drainage area (km^2); i and j are the two sub-basins contributing to the total flux F_t. For majority of rivers, the chemistry of Oct 2006 samples (Tables-4.1& 4.2) have been used for calculating F_t, whereas F_j is based on available data in literature. For example, in the case of Ghaghra F_t is the measured flux at Revilganj and F_j is the Himalayan flux calculated from the data of Galy and France-Lanord (1999) for the sample at Kotilaghat, collected in November 1994. The calculated elemental fluxes and $(\mathrm{CER})_{\mathrm{cat}}$ are given in Tables 4.7-4.9.

(i) Ganga plain

The Gomti river which has its entire drainage in the plain, provides one estimate for elemental fluxes and $(\mathrm{CER})_{\mathrm{cat}}$ from the Ganga plain. More estimates of $(\mathrm{CER})_{\mathrm{cat}}$ in the plain can be derived from the Ghaghra and the Gandak data at Revilganj and Hazipur respectively, as at these locations both these rivers have part of their drainage in the plain. The elemental fluxes and $(\mathrm{CER})_{\mathrm{cat}}$ at these sampling sites are composites of contributions from the Himalayan and the Ganga plain sub-basins. From these composite fluxes, $(\mathrm{CER})_{\mathrm{cat}}$ in the Ganga plain, is derived by subtracting the Himalayan contribution based on eqn. (4.1).

The estimates (Figs.-4.11, 12; Table-4.8) show that $(\mathrm{CER})_{\mathrm{cat}}$ for the Gomti, Ghaghra and the Gandak plains are roughly similar ~21 tons km^{-2} yr^{-1}, the fluxes of individual elements, however, vary typically by factors of 2-4 and do not seem to show any discernible trend with run off. The major difference in the erosion rate (tons $km^{-2}yr^{-1}$) is for Na with highest for the Gomti plain (7.6 tons km^{-2} yr^{-1}) and the lowest for the Gandak plain (0.2 tons km^{-2} yr^{-1}). In the Gandak, the Na flux measured at Hazipur nearly matches that reported at Narayanghat (Galy and France-Lanord, 1999) close to the exit of the river in the Himalayan sub-basin. This leads to infer that Na supply to the Gandak from the plain sub-basin is quite low, possibly due to limited occurrence of saline/alkaline soils in this sub-basin coupled with limited silicate erosion.

(ii) Peninsular Sub-basin

The Chambal, Betwa and the Son data provide elemental fluxes and $(CER)_{cat}$ for the peninsular sub-basin of the Ganga. The Chambal and Betwa represent the western peninsular region, dominated by the Deccan traps and Vindhyan whereas the Son from the eastern peninsula drains mainly Vindhyan and the Archean crust. In addition, the Yamuna data also have been used to determine fluxes and erosion rates of its peninsular basin after making appropriate corrections for contributions from its Himalayan and Ganga plain sub-basins. The contribution from the Himalayan sub-basin is calculated from the data of Dalai et al. (2002) at Batamandi sampled during October 1999 (Table- 4.2). The contribution from the Ganga plain to the Yamuna fluxes is estimated by scaling the Gomti fluxes based on drainage area. The $(CER)_{cat}$ for these peninsular basins are roughly similar, 12-19 tons km^{-2} yr^{-1} (Table-4.8). The elemental fluxes among these basins vary by a factor of ~2 (Table-4.7, Figs-4.11, 12). The Chambal (Dholpur) and Betwa (Hamirpur) data used in these calculations are from Sarin et al. (1989).

(iii) Himalayan Sub-basin

The elemental fluxes and $(CER)_{cat}$ for the Himalayan sub-basin of the Ganga is based on data of the Ganga at Rishikesh, Yamuna at Batamandi, Ghaghra at Kotilaghat and the Gandak at Narayanghat. The Ghaghra and the Gandak data are from Galy and France-Lanord (1999).

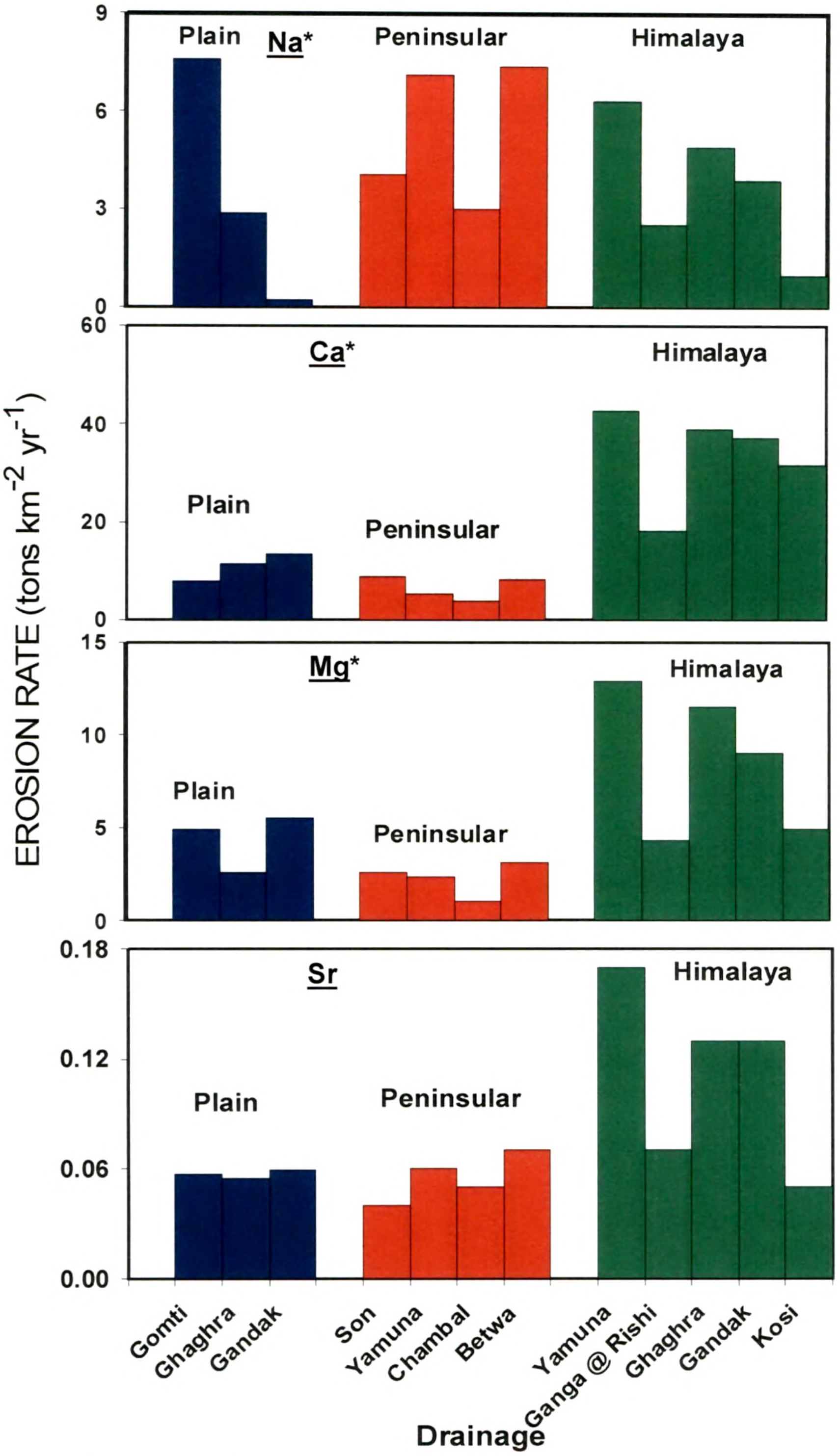


Fig-4.11: Erosion rates of Na*, Ca*, Mg*, and Sr in the various sub-basins of the Ganga. The Ca, Mg and Sr erosion rates are higher in the Himalaya compared to that in the plain and peninsular drainages; whereas Na* erosion rate is similar in all the sub-basins (except for the Gandak).

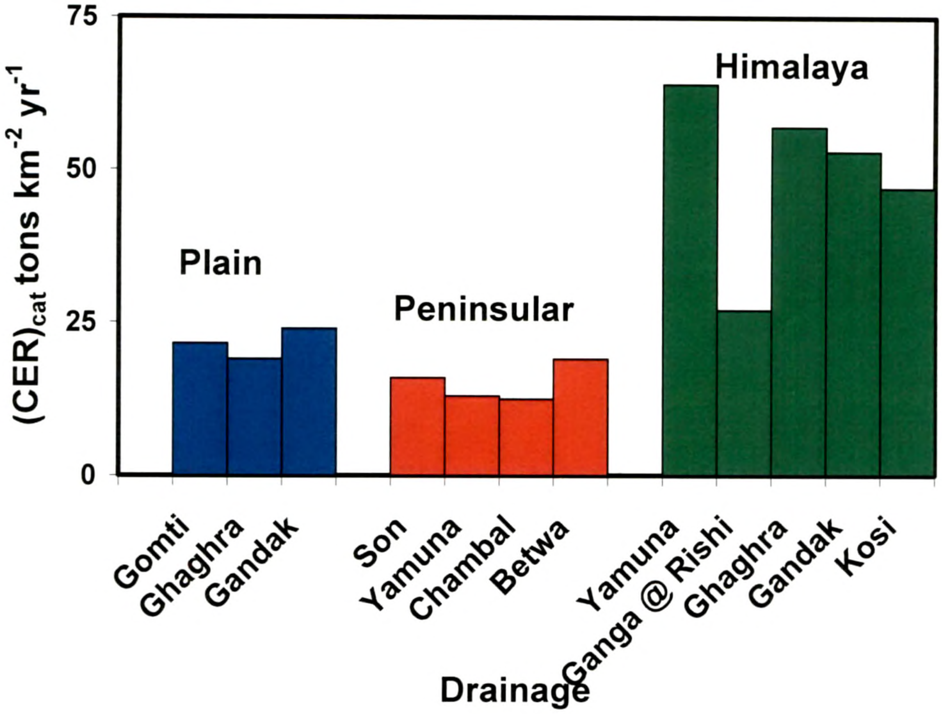


Fig 4.12: Chemical Erosion rates of cations, $(CER)_{cat}$, in the various sub-basins of the Ganga. $(CER)_{cat}$ in the Himalaya is 2-3 times higher than those in the peninsular and plain drainages. The higher runoff and relief of the Himalayan drainage are the major contributors to this difference.

Among the three sub-basins of the Ganga $(\mathrm{CER})_{\mathrm{cat}}$ is the highest for the Himalayan drainage, ranging from 27 to 67 tons km^{-2} yr^{-1}, with the Yamuna basin having the highest erosion and the Ganga at Rishikesh, the lowest (Fig-4.12). Kosi data has not been included in this range as it is a composite of erosion in the Himalayan and plain sub-basins.

It is seen from Tables-4.8 and 4.9 that the erosion rates of elements from the plain and peninsular sub-basins are generally lower than that from the Himalaya. The area weighted $(\mathrm{CER})_{\mathrm{cat}}$ in the peninsular region is ~13 ± 4 tons km^{-2} yr^{-1}, within errors similar to that for the Ganga plain, ~21 ± 6 tons km^{-2} yr^{-1}. It is also seen that the $(\mathrm{CER})_{\mathrm{cat}}$, particularly $(\mathrm{CER})^{*}_{\mathrm{cat}}$ [$(\mathrm{CER})*_{\mathrm{cat}}$ is $(\mathrm{CER})_{\mathrm{cat}}$ corrected for halite input of Na. Na** = $(Na_{riv} - Cl_{riv})$] of the Chambal, Betwa and the Yamuna peninsular basins bracket the erosion rate for the Son basin, despite the fact that the peninsular drainages of the Yamuna and its tributaries have significant exposures of more easily weatherable Deccan basalts and alkaline/saline soils compared to granite/gneisses and shales/slates of the Son drainage. The similarity in their $(\mathrm{CER})_{\mathrm{cat}}$ therefore has to be assigned to other causes, such as cumulative effect of higher rain fall, runoff and relief in the Son catchment compared to the peninsular drainage of the Yamuna and its tributaries.

It is interesting to note that though the overall $(\mathrm{CER})_{\mathrm{cat}}$ of the peninsular and plain drainages of the Ganga is 2-4 times lower compared to that of its Himalayan zone (Table-4.9), their erosion fluxes (tons yr^{-1}) are comparable. This is because the total drainage area of the peninsular and plain zones of the Ganga basin is ~4 times the area of its Himalayan sub-basin. The higher $(\mathrm{CER})_{\mathrm{cat}}$ in the Himalayan basin is attributable to its high relief and runoff coupled with its higher physical erosion as has been observed for other river basins from this region (Singh and France-Lanord, 2002; Thiede et al., 2004; Singh et al., 2008). In addition, the endoreic nature of the peninsular and plain basins and their semi-arid climate retards chemical erosion in them.

Galy and France-Lanord (1999), based on fluxes of major elements from the headwater basins of the Gandak and the Ghaghra in the Himalaya and that of the Ganga in Bangladesh, estimated that the sum of silicate and carbonate erosion rates in the Ganga plain is ~5 mm kyr^{-1}, 5-12 times lower than that in the Himalayan drainage and 2-3 times lower than that in the Ganga drainage as a whole. They also noted that chemical erosion rates in the Himalaya are dominated by carbonate erosion and hence are dependent on the abundance of carbonates in the basin, for example in the Bheri basin the carbonate erosion rate was more than an order of magnitude higher than its silicate erosion rate. $(\mathrm{CER})^{*}_{\mathrm{cat}}$, estimated in this study (Table-4.8) can be compared with the sum of silicate and carbonate erosion rate estimates of Galy and France-Lanord (1999). The results (Table-4.9) show that the average erosion in the Himalayan sub-basin, ~20±3 mm yr^{-1}, is twice the average in the plain, ~8±2 mm yr^{-1}, similar to the trend reported by Galy and France-Lanord (1999). The lower erosion rate in the plain is attributable to its lower runoff, 0.3 m yr^{-1}, ~3 times less than that in the Himalaya. This interpretation differs from that of Galy and France-Lanord (1999) who have explained the lower erosion in plain in terms of its lower carbonate content. The observation that Ca and Mg concentrations in the Gomti is similar to or more than that in the Himalayan tributaries of the Ganga is an indication that the role of carbonates in contributing to the major ion chemistry of all these rivers is roughly similar. Further, the occurrence of carbonates in the form of kankar, calcretes and detrital carbonates dispersed through out the plain in varying concentrations (Agarwal et al.,1992; Singh et al.,2004; Singh, 1996) suggest that paucity of carbonates available for weathering may not be a controlling factor for the low chemical erosion rate of the region. A more likely cause, therefore, for the low chemical erosion is the low runoff in the plain compared to that in the Himalaya. Further, the lower relief of the plain reduces the intensity of physical erosion, which in turn can retard chemical erosion.

The October 2006 data further show that the sum of the elemental fluxes measured in various tributaries of the Ganga rivers exceeds those measured in the Ganga mainstream at its outflow, Rajamahal (Tables-4.7 and 4.9). This could either be due to interannual variations in water discharge of the rivers or that part of the dissolved material is retained in the plain. If the water discharge of various rivers for the year 2006 is different from the average value (Rao, 1975; http://www.grdc.sr.unh.edu) used for calculation then such imbalances can occur. Similarly, there are evidences for the retention of river solutes in the plain in the form of alkaline/saline soils. Among the major ions measured in rivers, the largest discrepancy is in the budget for Na, a major constituent of saline/alkaline soils. However, as these soils are formed mainly during summer when the rivers are nearly dry their impact during October, when the river stage is high, is expected to be minor.

(iv) Uncertainties in the estimates of fluxes and erosion rates

The fluxes of major elements and their erosion rates from the sub-basins of the Ganga and its tributaries are estimated, as mentioned earlier, by two approaches. The sources of errors in these estimates are those associated with (i) analytical measurements. This is generally ≤ ± 5% (ii) use of October or June or November concentration data as the annual average.

Time series analysis of the Yamuna at Allahabad, Ganga at Rishikesh and the Alaknanda at Srinagar (Tripathy, unpublished data), based on biweekly/monthly sampling during 2004-05 show that the October and November concentrations of different elements on average are ~ 45% higher than the annual discharge weighted value and that of June ~55% higher. Thus, the use of concentration data measured in October or November or June would on average overestimate the annual discharge weighted concentration (and hence flux) by ~50%. This is a scaling factor for deriving annual flux from measurements made during these months (iii) inter annual variations in elemental fluxes from the different sub-basins. This is particularly important for the flux by difference approach (eqn. 4.1) as the elemental fluxes for the different sub-basins were obtained during different years. There is, however no data on yearly variations in elemental fluxes from the locations of interest, hence the uncertainties arising from this source are estimated indirectly. A major contributor to variations in elemental fluxes is inter-annual variations in water discharge.

Table-4.10: Variability in the annual water discharge of the Ganga and Yamuna during different time periods

Period	Discharge (m^3s^{-1})			Reference
	Average	±1σ	%Deviation	
Ganga at Farrakka				
1950-1960	12492	1557	12	UNESCO, 1971
1965-1973	10996	2652	24	UNESCO, 1993
1991-2001	9993	2552	26	http://rbis.sr.unh.edu
Yamuna at Allahabad				
1991-2001	2494	1318	53	http://rbis.sr.unh.edu
Average uncertainty			29	

This data for the Ganga at Farakka for the periods 1950-1960 and 1965-1973 (UNESCO, 1971, 1993) yield ineterannual variations of 12 % and 24 % respectively (Table-4.10). Similarly, for the Yamuna a value ± 53% is calculated based in its discharge data at Allahabad for the period 1990-2001 (http://rbis.sr.unh.edu/explorer/basin.cgi?basin=00000&bounds=75,90,19,34&point=0.00,0.00&type=eh_discharge_pristine&date=&town=1&pot=0&map_switch=1). The variations in elemental fluxes are expected to be less than that in water discharge as elemental concentrations in general are negatively correlated with water discharge. Therefore, based on these data and above considerations an uncertainty of ± 30% has been assigned to the elemental flux data. This uncertainty is propagated suitably for estimating fluxes by difference and cation erosion rates (eqn. 4.1). As will be discussed later, the sum of fluxes from the Ganga tributaries differ from that measured at its out flow on average by ~30%; possibly due to interannual variations in elemental fluxes. As an independent exercise, interannual variations in concentrations of major ions (Na, K, Mg and Ca) were estimated for the Ganga at Rishikesh for which data were available for the month of September for several years, 1982, (Sarin et al., 1989), 1996 (Krishnaswami et al., 1999; Bickle et al., 2003), 1999 (Dalai et al., 2002; Bickle et al., 2003, 2004;Tripathy et al., 2008). These data yield an average uncertainty of ± 27% (Table-4.11).

Table-4.11: Interannual variation in the major ion concentrations of the Ganga river at Rishikesh (for the month of September)

Element	1982	1996	1996	1996	1999	1999	2004	2004	Mean	±1σ	%
Na	145	65	61	103	82	76	84	157	97	36	37
K	40	43	37	40	37	37	58	48	42	7	17
Ca	353	355	316	412	409	397	330	516	386	64	16
Mg	153	122	103	235	146	150	137	285	166	62	37
							Average uncertainty				27

Source: Sarin et al., 1989 ; Krishnaswami et al., 1999 ; Dalai et al., 2002; Bickle et al., 2003 ;Tripathy (unpublished data)

The elemental fluxes and $(CER)_{cat}$ for the Himalayan sub-basins based on data of the Ganga (Rishikesh), Yamuna (Batamandi), Ghaghra (Kotilaghat) and the Gandak (Narayanghat), the Ganga plain from the data of the Gomti and the peninsular basin from the Chambal and Betwa data (Tables-4.7-4.9) all have an uncertainty of ~ ±30%. The errors associated with estimates of fluxes and erosion rates of the Ghaghra and the Gandak plains and the peninsular basin of the Yamuna are derived by suitably propagating the uncertainties associated with fluxes of individual sub-basins and eqn (4.1).

4.4 Silicate Erosion Rates (SER) and associated CO_2 Consumption in the Ganga Basin:

Many earlier studies (Edmond and Huh, 1997; Singh et al., 1998; Gaillardet et al., 1999; Galy and France Lanord, 1999; Krishnaswami et al., 1999; English et al., 2000; Dalai et al., 2002; Jacobson et al., 2002; Oliver et al., 2003; Bickle et al., 2005; Hren et al., 2007) used major ion concentration and Sr isotope composition of rivers to derive silicate weathering contribution to their solute composition. Among the various dissolved component in rivers other than for Si (H_4SiO_4) which is entirely of silicate origin, all other major ions have multiple sources, as listed below.

$$Na_r = Na_a + Na_{sil} + Na_e \quad \text{.........................(4.2)}$$

$$Ca_r = Ca_a + Ca_{sil} + Ca_e + Ca_c \quad \text{........................(4.3)}$$

$$Mg_r = Mg_a + Mg_{sil} + Mg_c \quad \text{.........................(4.4)}$$

where the subscript r, represents river, a – atmospheric, e – evaporite including alkaline/saline soils, sil – silicate, c – carbonate. The relative contribution from different sources for a particular cation may vary from basin to basin. Therefore, to derive silicate weathering contributions to river solutes, contributions from sources other than silicates have to be suitably accounted.

The contribution from different lithologies to the major ion abundance of rivers is generally assessed following either the forward model (Singh et al., 1998; Galy and France-Lanord,1999; Krishnaswami et al.,1999) or the inverse model (Negrel et al.,1993; Gaillardet et al.,1999; Millot et al., 2003; Wu et al., 2005; Moon et al., 2007). The forward model relies on the use of Na corrected for cyclic salts and evaporites, ($Na^{**} = Na_r - Cl_r$) as an index of silicate weathering contribution along with assigned values for Ca/Na and Mg/Na released from silicates to rivers. The Ca/Na and Mg/Na ratios are generally taken to be the ratios in parent rocks, i.e. catchment silicates. The model therefore assumes congruent release of Na, Mg and Ca from silicate of the drainage basin to river water. In the inverse model, the contributions of different sources are derived from the measured concentrations based on budgets for elemental raios (Negrel et al., 1993; Gaillardet et al., 1999; Millot et al., 2003; Moon et al., 2007). In this approach, a priori knowledge of "representative" end member is not critical, as the models are suitably designed to derive the best estimates for elemental ratios and the contribution of various end members to river water chemistry. The reliability of the forward model to derive silicate weathering contribution requires that Na** as calculated is sourced *only* from silicates. In this study, this assumption is very likely to be valid for rivers in the Himalayan basin where silicate, atmospheric deposition and halite dissolution are likely to be the only sources of Na. In contrast in the Ganga plain, particularly in the Yamuna, Gomti and Ganga (downstream Allahabad) basins, the occurrence of saline, alkaline or sodic soils containing various sodium salts can serve as additional sources of dissolved Na. As the magnitude of this Na contribution is difficult to assess, estimate of silicate erosion rates based on Na** may not be quite reliable for these river basins. This constrains the determination of silicate erosion rates in the Ganga plain and peninsular sub-basins and therefore in the Ganga basin as a whole, based on the water chemistry downstream of Allahabad.

In this study, therefore Na** based silicate weathering rates are derived only for the Ganga head waters and its Himalayan tributaries (the Ghaghra, the Gandak and the Kosi). The estimates are based on the water chemistry of samples collected in May 2004 at Bhagirathi (Devprayag), Alaknanda (Devprayag), Ganga (Rishikesh), Ghaghra (Faizabad), Gandak (Barauli) and Kosi (Dumarighat). Further these estimates use values of 0.7±0.3 and 0.3±0.2 respectively for Ca/Na and Mg/Na molar ratios for release from silicates to rivers. (based on their abundances in granites/gneisses; soil profiles and selected streams, Krishnaswami et al., 1999). The calculated silicate derived cations $(\Sigma Cat)_{sil}$ [defined as $(\Sigma Cat)_{sil} = (Na_{sil} + K_r + 0.7Na_{sil} + 0.3Na_{sil})$ moles] is given in Table (4.12). From this, the fraction of silicate contribution to the major ion abundances of river is estimated to vary from 14 to 40% with an average of 28±8%. Highest silicate fraction was in the Kosi (~40%) and lowest in the Gandak (~14%) which is consistent with the observation about low IC in the Kosi and high IC in Gandak sediments. Previous studies (Krishnaswami et al., 1999) have also reported values in the range of ~30% for silicate fraction in the Ganga at Rishikesh during March/April. As sampling was done during low stages of the rivers, the estimated erosion rates are expected to be higher than the annual average. The Na** concentration in the Ganga at Rishikesh during May is 33% higher than the discharge weighted annual concentration (Tripathy unpublished data). This coupled with K and SiO_2 abundances show that SER in the Himalayan tributaries are ~15% more if calculated based on May data than the annual average.

Abundances of major cations in rivers originating from weathering of silicates (Na_{sil}, K_{sil}, Ca_{sil} and Mg_{sil}) and silica along with runoff are the parameters needed to estimate the silicate erosion rates. Silicate erosion rates (SER) have been calculated for the Ganga mainstream and its major Himalayan tributaries based on the relation: $[(SER) = (\Sigma(Cat)_{sil} + SiO_2].Q)$ where Q is the run off and $\Sigma(Cat)_{sil}$ is the sum of silicate derived Na, K, Mg, and Ca as calculated above $\Sigma(Cat)_{sil}$ and SiO_2 are expressed in mg ℓ^{-1}.

In the above calculation only samples which have chloride concentration less than or equal to100 µM are considered for estimation of SER as an additional caution to minimize the impact of evaporites contributing to Na. Assuming an average density 2.7 g.cm^{-3} for silicate rocks, SER vary from ~4 ±0.4 mm kyr^{-1} (~12 ±1.1 tons km^{-2} yr^{-1}) for Kosi to ~7 ±0.5 mm kyr^{-1} (~18 ±1.4 tons km^{-2} yr^{-1}) in the Gandak basin. Among the various sub-basins of the Ganga the Gandak river basin has the highest SER (Table-4.12). This result is consistent with the observation that this basin also has the highest physical erosion rate among the Ganga sub-basins (Chapter-3, Singh et al., 2008) and hence attesting the fact that physical erosion promotes chemical erosion. The CO_2 consumption in the basins of Himalayan tributaries and Ganga headwaters is roughly same, $(4 \pm 1)\times 10^5$ mole km^{-2} yr^{-1}. It is also born out from the results that in the Ganga basin the Ghaghra sub-basin is the major sink for atmospheric CO_2. Results of this study on silicate erosion rates are similar within uncertainties, to the earlier work on Central Himalyan rivers, the Trishuli, Bheri and Narayani etc (Galy and France-Lanord, 1999) varying between 7±3 to 11±2 mm kyr^{-1}.

Table-4.12: Silicate erosion rates (SER) and associated CO_2 consumption in the Ganga headwaters and its Himalayan tributaries.

Sample	River	Location	Area	Discharge	$(TDS)_{sil}$		SER				$(\Sigma cat)_{sil}$		CO_2 drawdown	
							(i) tons km^{-2} yr^{-1}		(ii) mm kyr^{-1}				10^5 (mole km^{-2} yr^{-1})	
			km^2	10^{12} ℓ.y^{-1}	mg $ℓ^{-1}$	±		±		±	μE$ℓ^{-1}$	±		
Headwaters														±
RW03-3	Bhagirathi	Devprayag	7800	8.3	14.5	1.1	15.5	1.1	6	0.4	334	70	3.6	0.7
RW03-4	Alaknanda	Devprayag	11800	14.1	11.4	0.8	13.6	0.9	5	0.3	253	51	3.0	0.6
RW03-2	Ganga	Rishikesh	19600	22.4	12.5	0.8	14.3	1.0	5	0.4	272	55	3.1	0.6
Tributaries														
BR-354	Ghaghra	Faizabad	127950	*63.4*	33.5	2.9	16.6	1.4	6	0.5	986	190	4.9	0.9
BR-334	Gandak	Barauli	46300	*49.4*	17.2	1.3	18.3	1.4	7	0.5	380	87	4.1	0.9
BR-327	Kosi	Dumarighat	74500	48.2	26.1	2.3	16.9	1.5	6	0.6	724	155	4.7	1.0
BR06-501	Kosi	Dumarighat	74500	48.2	18.7	1.7	12.1	1.1	4	0.4	544	114	3.5	0.7

Average silicate density ~2.7 g cm^{-3} ; $(TDS)_{sil}$ is the sum of cations derived from silicate and SiO_2.

4.5 Impact of Chemical erosion in the plain and peninsular sub-basins on estimates of silicate erosion rates in the Ganga basin and elemental fluxes

One of the important findings of this study is that the peninsular and plain sub-basins contribute significantly to the fluxes of major ions transported by the Ganga to the Bay of Bengal. Among the major ions the contribution of Na, sourced mainly from alkaline/saline soils, is the dominant. It is also observed that Na in the plain and peninsular rivers is in considerable excess over Cl. The ultimate source of this Na in excess of chloride, in the absence of anthropogenic input, is silicate weathering. In spite of this, the use of Na** (= Na_r-Cl_r) as a proxy to determine silicate erosion rates is in doubt, as its relation to contemporary silicate weathering of these river basins is unclear. The use of Na** to estimate silicate weathering rates is based on the assumption that its abundance in rivers is due entirely to present day silicate weathering of their basins. This requirement may be violated if part of Na in the Ganga and its tributaries is a result of leaching saline/alkaline soils formed in the past and/or from excessive use of groundwater (Goldsmith and Hildyard, 1984). In such cases the silicate erosion rates derived from Na** can be overestimates of the present day value. The aerial coverage of saline/alkaline soils in the plains and peninsular sub-basins of the Ganga are reported to be steadily increasing with time (Goldsmith and Hildyard, 1984) suggesting that the formation of these soils is an ongoing process. The uncertainty in the use of Na** precludes the calculation of silicate erosion rates of the Ganga downstream of Kanpur and its tributaries such as the Gomti and the Yamuna in the Ganga plain. This 'Na source problem' can be more widespread and can compromise estimation of silicate erosion rates of river basins from semi-arid regions and with poor drainage. The Bhima river and it tributaries draining the Deccan Traps of India fall in this category. Similarly, Singh et al., (2006) have demonstrated that in the Brahmaputra, a significant source of Na (and Sr) is saline deposits and lakes from cold and arid regions of Tibet. The peninsular and plain sub-basins supply most of Na and 40 to 80 % of Ca, Mg and Sr (in that order) to the Ganga at its outflow at Rajmahal. The Ca<Mg<Sr trend may be due to preferential removal of dissolved Ca from rivers by calcite precipitation.

4.6 Impact of saline/alkaline salts in Sr geochemistry of the Ganga in plain and erosion rates of Sr in the Ganga sub-basins.

Sr concentration in the Ganga mainstream vary widely, from 467 nM in Kosi (October 2006) to 5889 nM in the Yamuna (May 2004). The Yamuna value is one of the highest Sr concentrations measured in the Ganga system. The concentration of Sr in the Ganga mainstream varies linearly with Na with a very strong positive correlation with Na (Fig-4.13). This trend can be explained in terms of two end member mixing, the Himalayan (Ganga at Rishikesh) and the Yamuna (Allahabad). The correlation also highlights the role of the Yamuna in regulating the concentration of both Na and Sr in the Ganga main stream, most likely through recycling Na and Sr as a part of saline/alkaline soils and raises additional concerns on the potential application of Sr as a proxy of silicate weathering in the Ganga basin downstream of Allahabad.

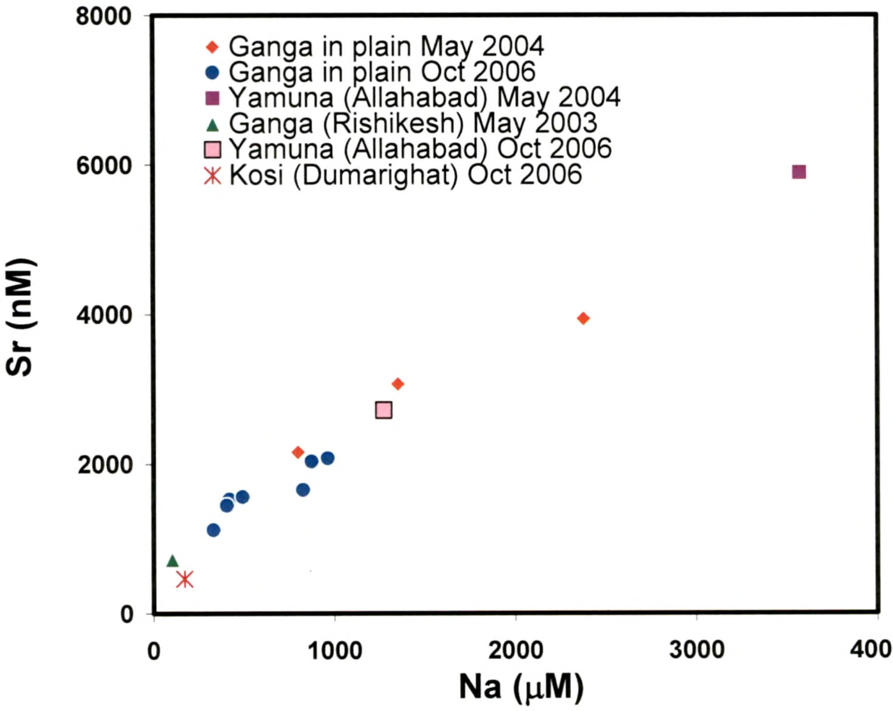


Fig-4.13: Variation of Sr with Na in the Ganga mainstream. Strong positive correlation between Na and Sr is a result of mixing between the Yamuna (higher concentration) with the Himalayan tributaries (lower concentration). The strong correlation brings out the role of recycling of both Na and Sr.

The erosion rate of Sr in the plain and peninsular drainage varies within narrow range of 0.04 to 0.07 tons km^{-2} yr^{-1} (Table-4.8).The Sr erosion rates in the plain sub-basins of the Gandak and the Ghaghra are similar to that of the Gomti and yield an average value of 0.06 tons km^{-2} yr^{-1}. For the Himalayan drainage, Sr erosion rate follows the trend of chemical erosion rates with the highest in the Yamuna basin and the lowest in the Kosi (Tables-4.7, 4.8). The low chemical and Sr erosion rates in the Kosi are attributable to lower carbonate exposures in its Himalayan sub-basin. This interpretation is also consistent with the $^{87}Sr/^{86}Sr$ data which shows that among the Ganga (Rishikesh), Ghaghra, Gandak and the Kosi, the most radiogenic Sr is in Kosi waters, $^{87}Sr/^{86}Sr$: 0.74806 (May 2004), 0.75732 (October 2006). This can be explained in terms of limited supply of unradiogenic carbonate Sr to the rivers and therefore lesser dilution of radiogenic silicate Sr. Another factor that can contribute to the lower erosion in the Kosi drainage is its lower runoff compared to other Himalayan drainages (Singh et al., 2008), this explanation , however is not consistent with Sr isotope data.

Sr flux of the Ganga (Table-4.13) at its outflow, Rajmahal based on the October 2006 sample is ~3.7×10^4 tons yr^{-1} with $^{87}Sr/^{86}Sr$ ~0.72707. This compares with reported annual flux of 4.1×10^4 tons yr^{-1} Sr with $^{87}Sr/^{86}Sr$ of 0.7239 (Krishnaswami et al.,1992). This yields ^{87}Sr flux of 0.27×10^4 tons yr^{-1} from the Ganga. The Yamuna contributes about 60% of the total Sr and ^{87}Sr to the Ganga at its outflow followed by the Ghaghra which contribute ~30% of Sr. In the Yamuna, more than 90% of Sr is derived from the peninsular and plain drainages. These sub-basins of the Yamuna is also the major supplier of ^{87}Sr to the Ganga despite the fact that an important component of the lithology in the peninsular drainage is Deccan Traps, which is quite unradiogenic in Sr (Peng et al.,1998). The collective flux of Sr from all the tributaries is 4.7×10^4 tons yr^{-1}, ~25% more compared to that measured in the Ganga at its outflow, 3.7×10^4 tons yr^{-1} (Table-4.7). The flux weighted $^{87}Sr/^{86}Sr$ of the Ganga tributaries is 0.7235 for October 2006, marginally lower than the measured value of 0.7271 at its outflow at Rajmahal. Inter-annual variations in water discharge of the tributaries could be a potential cause for this difference.

Table-4.13: Sr concentration and flux for the Ganga and its tributaries^{+}

River	**Location**	**Discharge** $10^{12}\ \ell\ \mathrm{yr}^{-1}$	**Sr (Conc.)** nM	**Sr Flux** 10^{4} ton yr^{-1}
Gomti	Gazipur	7.4	2717	0.18
Son	Koilwar	31.8	944	0.26
Yamuna	Allahabad	93	2717	2.21
Ganga	Rishikesh	23.9	731	0.15
Ghaghra	Revilganj	94.4	1373	1.14
Gandak	Hazipur	52.2	1064	0.49
Kosi	Dhumarighat	62	467	0.25
Ganga	Rajmahal	380	1122	3.73

$^{+}$ Based on Oct 2006 samples, except Ganga at Rishikesh which was sampled in May 2003.

For example, if the Yamuna water flux was low by ~25% in 2006 compared to the average value of 93 km^3 yr^{-1} (Rao, 1975) the agreement between the measured flux at Rajmahal and the sum of the fluxes from the tributaries would be better.

4.7 Behaviour of Ca and Sr in the Ganga river system: Clues from Ca/Sr and ^{87}Sr/^{86}Sr of waters.

One of the important issues in quantifying the budget of Sr in river waters in terms of its contribution from different sources pertains to the knowledge of the behaviour of dissolved Ca. If Ca behaves conservatively, the apportionment of Sr concentration between silicates and carbonates would be valid, however, if it is non-conservative then the apportionment based on the forward model (Krishnaswami and Singh, 1998; Galy and France-Lanord, 1999; Krishnaswami et al., 1999) would under estimate the carbonate component of Ca and hence that of Sr. The impact of loss of Ca is also not considered in the inverse model.

In this study, efforts have been made to assess the behaviour of Ca in the Ganga system rivers based on their ^{87}Sr/^{86}Sr and Ca/Sr. The approach is based on the assumption that only two sources silicate and carbonate weathering contribute to dissolved Ca and Sr. This assumption is expected to be satisfied better in rivers draining the Himalayan sub-basin of the Ganga. This is because the Ganga in plain receives dissolved Sr and Ca from its other sub-basins such as the plain and peninsular regions (Rai et al., 2008; Rengarajan et al., 2008) which compounds the Ca and Sr budgets. The "Ca Behaviour" problem has been addressed in some of the earlier work (Jacobson et al., 2002; Bickle et al., 2003, 2005; Tipper et al., 2008) which show that a significant part of dissolved Ca in the Ganga system rivers are removed via calcite precipitation.The ^{87}Sr/^{86}Sr and Ca/Sr of the Ganga headwaters and its tributaries in the Himalaya are plotted in the Fig-4.14. The water samples have a wide range of ^{87}Sr/^{86}Sr values, from ~0.7266 to ~0.7896 with Ca/Sr molar ratios generally <1x10^{3}. Also shown in the plot are the values for the two end members, the Pre Cambrian (Pc-C) carbonates and Himalayan silicates. The ^{87}Sr/^{86}Sr and Ca/Sr of Pc-C carbonates are from Singh et al. (1998) whereas for silicates, it is based either on bank sediments analysed in this study (Chapter-3) or on the compilation of available data on ^{87}Sr/^{86}Sr of silicate and carbonate rocks in various river basins in the Ganga drainage of the Himalaya (Table-4.14; Galy, 1999; Bickle et al., 2001; Harris et al., 1998; Oliver et al., 2003; Quade et al.,2003). The data in Table-4.14 though show significant variation in ^{87}Sr/^{86}Sr among the river basins, their range and average overlaps with those measured in this study for silicates in the bank sediments (Fig-4.14).

Table-4.14: ^{87}Sr/^{86}Sr of silicates and carbonates of various basins in the Ganga drainage

Basin	Silicates	±σ	(n)	Carbonates	±σ	(n)	Reference
Bhagirathi	**0.783**	**0.005**	3	**0.711**	**0.004**	4	This work, Singh et al., 2008
Alaknanda	**0.758**	**0.004**	3	**0.717**	**0.009**	6	This work, Singh et al., 2008 Bickle et al., 2001, 2005
Ghaghra	**0.773**	**0.012**	7	**0.726**	**0.007**	6	Galy, 1999; This work Singh et al., 2008
Gandak	**0.744**	**0.013**	18	**0.725**	**0.016**	10	Galy, 1999; This work Singh et al., 2008
Kosi	**0.816**	**0.025**	4	**0.715**	**0.000**	5	Oliver et al., 2003; This work Singh et al., 2008
Mean	**0.775**	**0.027**		**0.720**	**0.007**		

It is seen from Fig-4.14 that most of the samples from the Bhagirathi and the Kosi fall within the mixing envelope of silicate-carbonate suggesting that in these waters, the ^{87}Sr/^{86}Sr and Ca/Sr are consistent with two end member mixing and therefore both Ca and Sr can be considered as behaving conservatively.

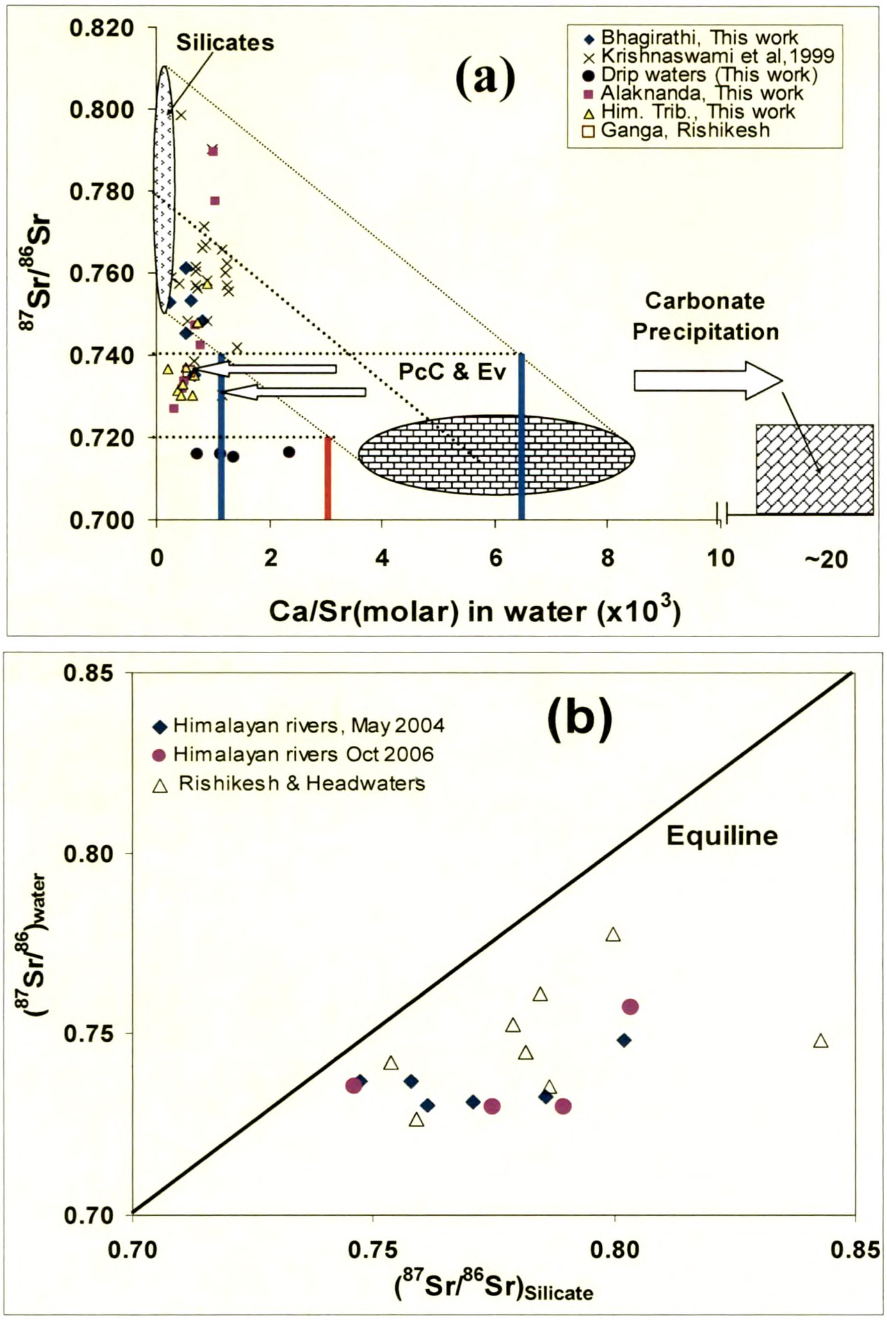


Fig-4.14:(a) Plot of $^{87}Sr/^{86}Sr$ vs Ca/Sr in river waters of the Ganga system from the Himalayan sub-basin. The values for the two end members are also shown. The arrows show the direction of movement of Ca/Sr in water following precipitation of $CaCO_3$. Precipitation decreases the Ca/Sr ratio in water without affecting the $^{87}Sr/^{86}Sr$.
(b) $^{87}Sr/^{86}Sr$ of the Ganga water and silicate component of bank sediments. The data show that $^{87}Sr/^{86}Sr$ of waters are much lower than those in silicate due to mixing with unradiogenic Sr from carbonate. The deviation from 1:1 line has been used to derive the silicate: carbonate supply ratio for Sr and from that the Ca budget.

This is consistent with the reported observations that these rivers are under saturated in calcite (this work; Quade et al., 1997, 2003; Jacobson et al., 2002; Tipper et al, 2006) In contrast, many samples particularly from the Alaknanda, Ghaghra and the Gandak fall even below the lower bound of the mixing envelope. This observation suggests that the Ca/Sr in these water samples is less than that would be expected for their $^{87}Sr/^{86}Sr$. The trend in Fig-4.14 is similar to those reported by Krishnaswami and Singh, (1998) for the head waters of the Ganga and Dalai et al., (2003) for the Yamuna in the Himalaya. These authors attributed the trend to the supply of Sr to water from an additional source with low $^{87}Sr/^{86}Sr$ and Ca/Sr, potential candidates being evaporites/phosphates. Alternatively, removal of Ca from river water by precipitation of calcite can also serve as a mechanism to decrease Ca/Sr in water. This is because the precipitation of calcite preferentially removes Ca over Sr from water as the partition coefficient of Sr to calcite is <<1 (Banner 1995; Rimstidt et al., 1998). The low partition coefficient would yield carbonate precipitates with Ca/Sr higher than that in water.

To check on this, Ca, Mg, Sr and $^{87}Sr/^{86}Sr$ were measured in seepage/ dripping water and precipitated carbonates from regions adjacent to these waters. These data are presented in Table-4.15 and also plotted in Fig-4.14. As expected, the precipitated carbonates have $^{87}Sr/^{86}Sr$ similar to the source waters, with Ca/Sr ~2-20 times the water (Table-4.15) supporting the preferential removal Ca.

Thus the precipitation of $CaCO_3$ would decreases Ca/Sr in water relative to its original value. The impact of this decrease on $^{87}Sr/^{86}Sr$ and Ca/Sr plot would be to cause a shift in the data points away from the mixing line towards lower Ca/Sr (shown by arrows in Fig-4.14). The precipitation process does not change the $^{87}Sr/^{86}Sr$, as isotopic fractionation of Sr during the process is insignificant (Faure, 1986). Considering that for a two end member mixing Ca/Sr of water should fall within the mixing envelope if both Ca and Sr behave conservatively, an explanation for the data falling below the envelope is that Ca is lost from the dissolved phase via calcite precipitation. The extent of departure from the mixing line provides a means to estimate the magnitude of Ca loss. This is calculated based on the following relations.

$$f_p = \left(\frac{Ca_w}{Ca_0}\right) = \left(\frac{\left(\frac{Ca}{Sr}\right)_0}{\left(\frac{Ca}{Sr}\right)_w}\right)^{\left(\frac{1}{(K_d-1)}\right)} \qquad \text{..................} \qquad (4.5)$$

where $\left(\frac{Ca}{Sr}\right)_0$ is the ratio prior to precipitation of calcite and $\left(\frac{Ca}{Sr}\right)_w$ is the measured value. $\left(\frac{Ca}{Sr}\right)_0$ is the (Ca/Sr) ratio expected for a given $^{87}Sr/^{86}Sr$ and is calculated from the $\left(\frac{^{87}Sr}{^{86}Sr}\right)$ - $\left(\frac{Ca}{Sr}\right)$ mixing line. For example, in samples with $^{87}Sr/^{86}Sr$ of 0.720, a $(Ca/Sr)_0$ of at least 3 is expected. Similarly for $^{87}Sr/^{86}Sr$ of 0.740, the $(Ca/Sr)_0$ is expected to be in the range of 1.3 to 6.5 (Fig-4.14). K_d is the relative distribution coefficient for Sr to Ca in calcite. f_p is the fraction of Ca left in river water after precipitation (Albarede, 1995).

Calculation of f_p has been carried out for the headwaters of the Ganga and its Himalayan tributaries (the Ghaghra, Gangdak and the Kosi). The latter group of rivers has part of their basin in the plain, where drainage is retarded. Samples from this study and from Krishnaswami et al. 1992 are plotted in Fig-4.14a. Several samples of this study and two samples from the study of Krishnaswami et al. (1992) from the Alaknanda fall out side the mixing envelope. The Ca loss calculated for samples which plot outside the mixing envelope in Fig-4.14a are listed in Table-4.15. Results of this study show that ~60-80% (Table-4.16) of initial calcium can be lost by precipitation as calcite in the Ghaghra and Gandak rivers during both summer (May 2004) and post monsoon (Oct 2006) samples. The observation that one of the Bhagirathi samples (RW03-8) also falls out side the mixing envelope is intriguing. Earlier studies (Bickle et al., 2005, Jacobson et al., 2002; Tipper et al., 2008) have also reported a high degree of Ca loss, ~70% for the Himalayan streams .This result highlights the role of calcite precipitation in determining the abundance of dissolved Ca in the Ganga and its tributaries.

Table-4.15: Chemical and isotopic composition of precipitated carbonates, evaporites and corresponding waters

Sample ID	Ca (%)	Sr $\mu g\ g^{-1}$	Ca/Sr (molar)x10^3	$^{87}Sr/^{86}Sr$	Sample ID	River Water	Sr nM	Ca μM	Ca/Sr (molar)x10^3	$^{87}Sr/^{86}Sr$
RS03-6[+]	39.3	219	3.9	0.75608	**RW03-7**	Gang Nani (spring)	2295	1516	0.7	0.75615
RS03-39	35.3	127	6.1	0.72190	**RW03-20**	Seepage water (Lokhandi)	1598	1323	0.8	0.72204
-	-	-	-	-	**RW03-21**	Seepage water (Lokhandi)	913	692	0.8	0.72615
RS03-34B[+]	28.6	34.6	18.1	0.71173	**RW03-17**	Dipping water (Sahashra Dhara)	16461	3687	0.2	0.71093
RS03-38	39.6	47.9	18.1	0.70976	**RW03-18**	Sulphur water (Sahashra Dhara)	84715	13773	0.2	0.70977
-	-	-	-	-	**RW03-19**	Stream water (Kempty Fall)	28607	4304	0.2	0.70950
RS03-35(evap)	22.3	131	3.7	0.71656						
RS03-36(evap)	22.6	148	3.4	0.71494						
RS03-6(L)		239		0.75609						
RS03-34B(L)		37.9		0.71134						

[+]Leached samples

Table-4.16: Ca loss due to calcite precipitation in Ganga system rivers.

River	Sample	Location	(Ca/Sr) μM/nM		^{87}Sr/^{86}Sr	Ca loss$^+$
			$(Ca/Sr)_m$	$(Ca/Sr)_0$		(%)
Bhagirathi	RW03-5	Gangotri (Bhagirathi)	0.52		0.76101	nd
	RW03-8	Uttarkashi (Bhagirathi)	0.53	0.66	0.74512	21
	RW03-10	Ghanshyali (Bhilangana)	0.81		0.74828	nd
	RW03-9	Syansu Gad (Trib. Bhagirathi)	0.24		0.75268	nd
	RW03-3	Devpryayag (Bhagirathi)	0.61		0.75330	nd
	RW03-6	Glacer melt (Higher Himalaya)	0.67		0.73504	nd
Alaknanda	RW03-4	Devpryayag (Alaknanda)	0.49	1.74	0.73368	74
	RW03-11	Rudrapryayag (Alaknanda)	0.47		0.73158	nd
	RW03-12	Rudrapryayag (Mandakini)	0.69		0.74709	nd
	RW03-13	Birahi (Birhi tributary)	1.03		0.78955	nd
	RW03-14	Birahi (Birahi Ganga)	1.05		0.77738	nd
	RW03-15	Birahi (Alaknanda)	0.32	2.39	0.72662	88
	RW03-16	Pindar Valley (Pindar)	0.78	0.91	0.74231	15
Ganga	RW03-2	Rishikesh (Ganga)	0.57	1.54	0.73572	65
Ghaghra	BR06-901	Revilganj (Ghaghra)	0.63	2.07	0.73001	72
	BR-342	Revilganj (Ghaghra)	0.39	1.96	0.73125	82
	BR-354	Faizabad (Ghaghra)	0.47	1.81	0.73282	76
	BR-363	Gorakhpur (Rapti)	0.44	2.07	0.73009	81
Gandak	BR06-705	Hazipur (Gandak)	0.67	1.58	0.73526	60
	BR-334	Barauli (Gandak)	0.51	1.41	0.73707	66
	BR-311	Hazipur (Gandak)	0.19	1.44	0.73675	68
Kosi	BR06-501	Dumarighat (Kosi)	0.90		0.75732	nd
	BR-327	Dumarighat (Kosi)	0.73		0.74806	nd

$^+$ Based on lower bound of end members; nd- no detectable loss

If such a loss of Ca indeed is prevalent then it would (i) underestimate Ca (and hence Sr) contribution to river waters from carbonates. This underestimation may be a cause for invoking the need for additional source of Sr to rivers (Krishnaswami and Singh, 1998; Dalai et al., 2003) and (ii) it would redistribute Ca from one sub-basin to another; for example Ca dissolved from the Himalaya sub-basin can precipitate in the plain.

An alternate approach to assess the Ca loss is by comparing the ^{87}Sr/^{86}Sr of river water with that of the silicate phase of bank sediments. This comparison is shown in Fig-4.14b. It is seen from the figure that Sr isotope ratios in water are significantly lower than those in silicates. The lower ^{87}Sr/^{86}Sr in water can be explained in terms of two end member mixing of Sr, that derived from radiogenic silicates and unradiogenic carbonates. Therefore, the deviation from the equiline is a measure of carbonate:silicate mixing proportion for Sr. From this and knowledge of (Ca/Sr) in silicate and carbonate end members the expected Ca abundance in water can be derived. This is compared with the measured Ca concentration to obtain Ca loss. The calculation is made for the Ganga at Rishikesh as given below, using end member values listed in Table-4.17. This approach assumes congruent release of both Sr and Ca from the end members and that release of Sr to water from silicates do not involve any change in its isotopic ratio. The $^{87}Sr/^{86}Sr$ of silicate end member (Table-4.17) is based on the bank sediment measured in this study. The uncertainties are based on replicate analysis and spatial and temporal variations.

Table-4.17 Calculation of silicate component for Rishikesh Sample

End member value	($^{87}Sr/^{86}Sr$)	±	(Ca/Sr)	±
Silicate	**0.7865**	0.0056	220	120
Carbonate	**0.720**	0.007	5500	2000
Mixture				
River Water	**0.7357**	0.007	574	

Silicate component of Sr in Ganga at Rishikesh (f_{sil}) is given as:

$$f_{sil} = \frac{(R_{water} - R_{carb})}{(R_{sil} - R_{carb})} \qquad \dots\dots\dots\dots\dots\dots\dots(4.6)$$

where R_i is the $^{87}Sr/^{86}Sr$ ratio in end members (carbonate and silicates) and mixture (river water). Calculation shows that the silicate component of Sr in the Rishikesh is about 24±13%. This coupled with (Ca/Sr) in silicate and carbonate end member yield a Ca loss ~90%. Extending the calculations to head waters of the Ganga and its Himalayan tributaries show that Sr_{sil} in them vary between 14 to 63% with an average of ~35±17 similar to the earlier reported estimates (Krishnaswami et al., 1999). All these estimates have significant uncertainties arising from wide range of Sr isotope composition and (Ca/Sr) ratio in the end members. For example, in the Rishikesh sample calculated Ca loss could be in the range of ~80% to 95% considering $\pm 1\sigma$ uncertainties.

One of the major impacts of calcium removal from water via calcite precipitation is on the Sr budget. In the forward model, (Krishnaswami et al., 1999) Sr contribution from the carbonate is calculated as

$$Sr_c = \left(\frac{Sr}{Ca}\right)_c . Ca_c \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.7)$$

$$Ca_c = \left(Ca_r - Ca_{sil}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.8)$$

where Ca and Sr are the calcium and strontium concentrations and the sucscripts, c, r and sil refer to carbonates, river and silicates. $\left(\frac{Sr}{Ca}\right)_C$ is the $\left(\frac{Sr}{Ca}\right)$ abundance ratio in Pc-C carbonates, Ca_r is the dissolved Ca concentration measured in rivers. If calcium is removed from dissolved phase then Ca_r would be less than that expected from weathering input. As a result, carbonate contribution of both Ca and Sr to rivers would be under estimated. The estimates of Ca_{sil} would not be affected as it is based on Na_{sil} and $\left(\frac{Ca}{Na}\right)_{sil}$ (Krishnaswami et al., 1999). Thus if there is 75% removal of Ca as calcite, it would result in underestimation of Sr_c by a factor of four. These arguments indicate that attempts to balance Sr budget in the Ganga system rivers should include the effect of calcite precipitation.

4.8 Biweekly variation in major ions, Sr concentration and $^{87}Sr/^{86}Sr$ of the Ganga

Erosion of river basins, particularly in tropical regions, are highly dependent on monsoon rains and exhibit significant variations as their discharge varies over orders of magnitude during an annual cycle. Therefore time series study of chemical erosion at a given site over an annual cycle will provide a more realistic estimate of chemical erosion in the basin than that based on a single sample collected during the year. Further, such a study will also yield a better understanding of the relation between chemical erosion and runoff in the basin as other parameters such as lithology and relief all remain nearly the same.

There have been a few studies on monthly/seasonal variation in major ion chemistry of the Ganga head waters and some of its tributaries in the Himalaya (Dalai et al., 2002; Bickle et al., 2003; Tipper et al., 2006; Chakrapani et al., 2008). These studies brought out the variability in the relative erosion rates of silicates and carbonates, with carbonate being weathered more intensely during monsoon. This result was explained in terms of faster dissolution kinetics of carbonate minerals (Tipper et al., 2006) variable relative input due to rainfall and glacial melt from different lithological units (Bickle et al., 2003), shorter interaction time for weathering during monsoon coupled with slower dissolution kinetics of silicates relative to carbonates (Rai and Singh, 2007) and enhanced chemical erosion due to higher physical erosion (Krishnaswami et al., 1999).

In this work, time series analysis of major ions and Sr isotopes have been made in the Ganga mainstream in the plain and its largest tributary the Yamuna. The Ganga at Allahabad after its confluence with the Yamuna shows large variation, over two orders of magnitude, in its discharge (185 to 20881 m^3s^{-1}). To characterize the impact of such a large variation in discharge on major ion abundances and chemical erosion, Ganga waters were sampled at Chhatnag (near Allahabad after the confluence with Yamuna). In addition, the Yamuna waters (near Yamuna bridge, Allahabad) were also sampled. Variations in the major ion composition of the Ganga and the Yamuna (Fig-4.15) show significant correlation for Na, Mg and Sr. The Na data however has more scatter. Ca abundance in the Yamuna and the Ganga do not show large variation.

4.8.1 General observations:

The following general observations have been made from these measurements. The abundances of all major elements and Sr decrease with increase in discharge in both the Yamuna and the Ganga (Fig-4.16). The chemistry of the Ganga at Chhatanag (near Allahabad) seems to be governed largely by mixing with the Yamuna (Fig-4.15). The Na data in the Ganga show a significant scatter in its concentration at low discharge. During this period much of Na in the Ganga is due to supply from the Yamuna mainly from saline/alkaline soils (section-4.2.2).

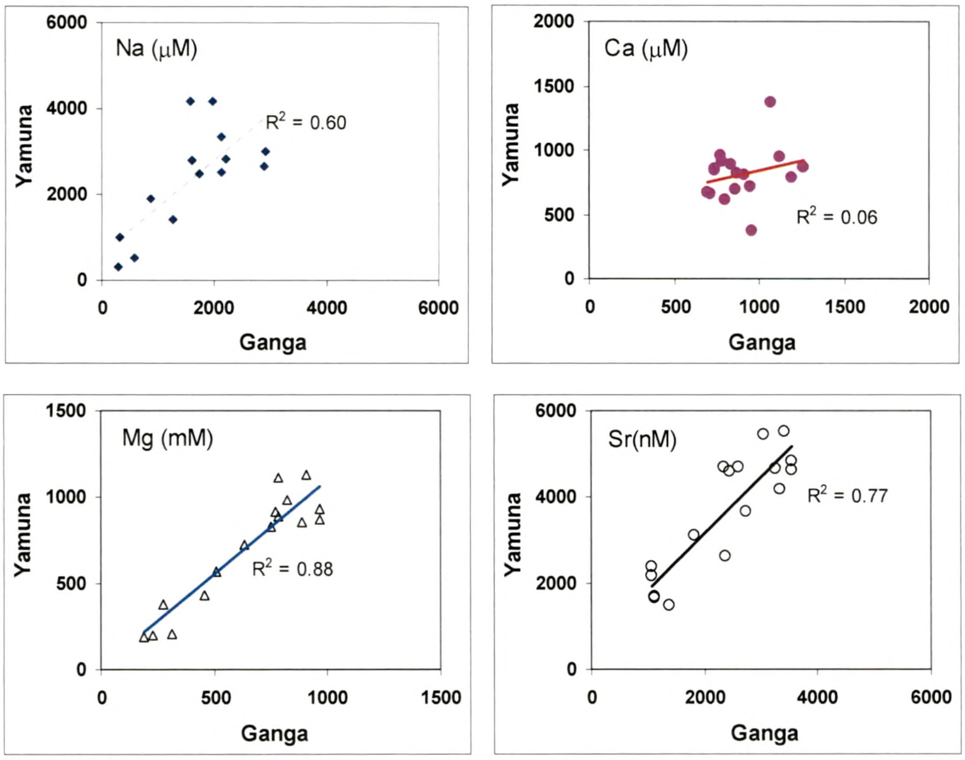


Fig-4.15: Co-variation in Na, Ca, Mg and Sr abundances in the Yamuna and the Ganga after its confluence with the Yamuna.

Variation in this supply can contribute the scatter in Na concentration at low discharge (Fig-4.16). Overall Na varies by a factor of ~10 from ~250 to 2858 μM and in general decreases with discharge. Ca concentrations also show a decreasing trend with discharge however its range is less pronounced (a factor of ~ 2) relative to Mg and Na. This is an indication that other factors such as calcite saturation or dissolution kinetics of carbonates (relative to silicates, the source for Na) may be controlling its abundance in these waters. These range in elemental concentration are much less than the range in discharge which is a factor of ~30. The results show that Na, Mg, Ca and Sr erosion rates from the basin range by a factor of ~5 for Na, ~6 for Mg, ~22 for Ca and 13 for Sr, if the anomalously high concentration sample of July15, 2005 is excluded. The erosion fluxes of various major ions and Sr are listed in Table-4.18 and plotted in Fig-4.17 for the date of sampling. The data show that flux estimated from single sampling can differ from the annual discharge weighted average by a factors of ~2-3 for Na*, Mg* and Sr and by a factor of ~5 for Ca* (* corrected for rain input).

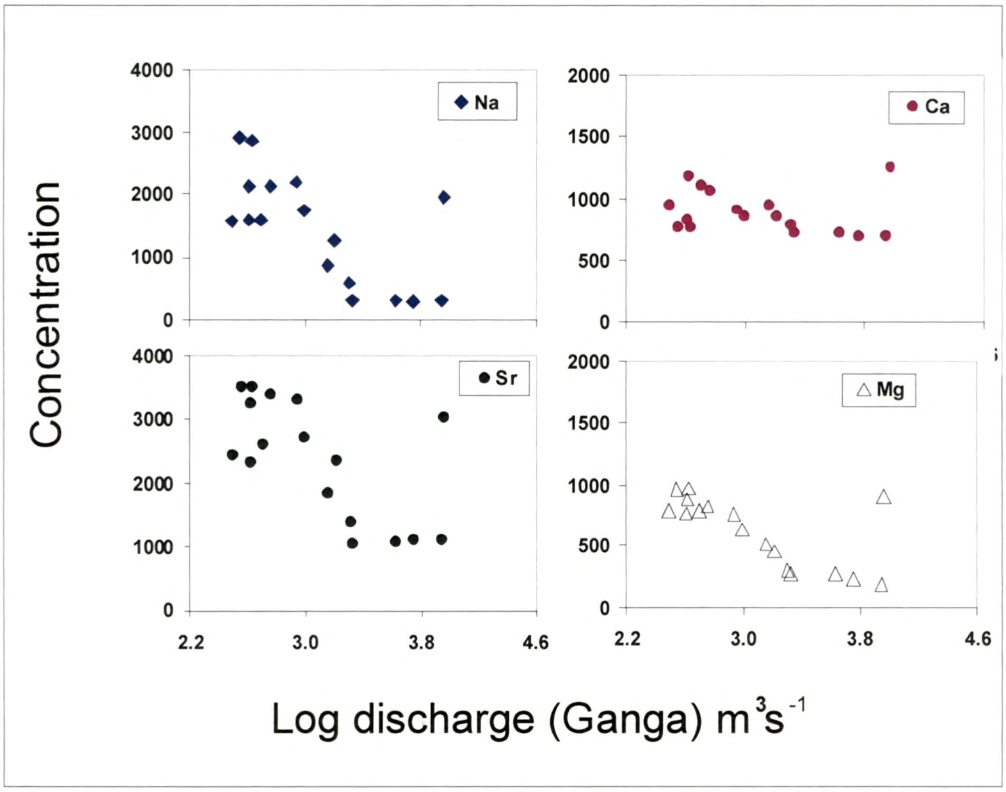


Fig-4.16: Variation in concentration of elements with discharge in the Ganga river at Chhatanag after the confluence with the Yamuna. Sharp peak in the elemental concentration is seen on the 15th July sample. Na, Ca and Mg concentrations are in μM and Sr in nM.

The annual erosion fluxes for Na*, Mg*, Ca* and Sr (Table-4.18) show that chemical erosion of different elements are season dependent with high values during monsoon. Annual fluxes for Ca* and Mg* flux calculated from September sample are similar to that of the average annual fluxes. This indicates that September sample can represent the yearly fluxes for Ca* and Mg*. However, chemical erosion flux of Na* in September shows variation lower by a factor of ~2. This most likely is due to inter annual variations. A unique feature of the results is the pronounced high in the abundances of Na, Mg, Ca and Sr (Fig-4.17) the Ganga samples collected on the July 15th during the peak discharge of the rivers.

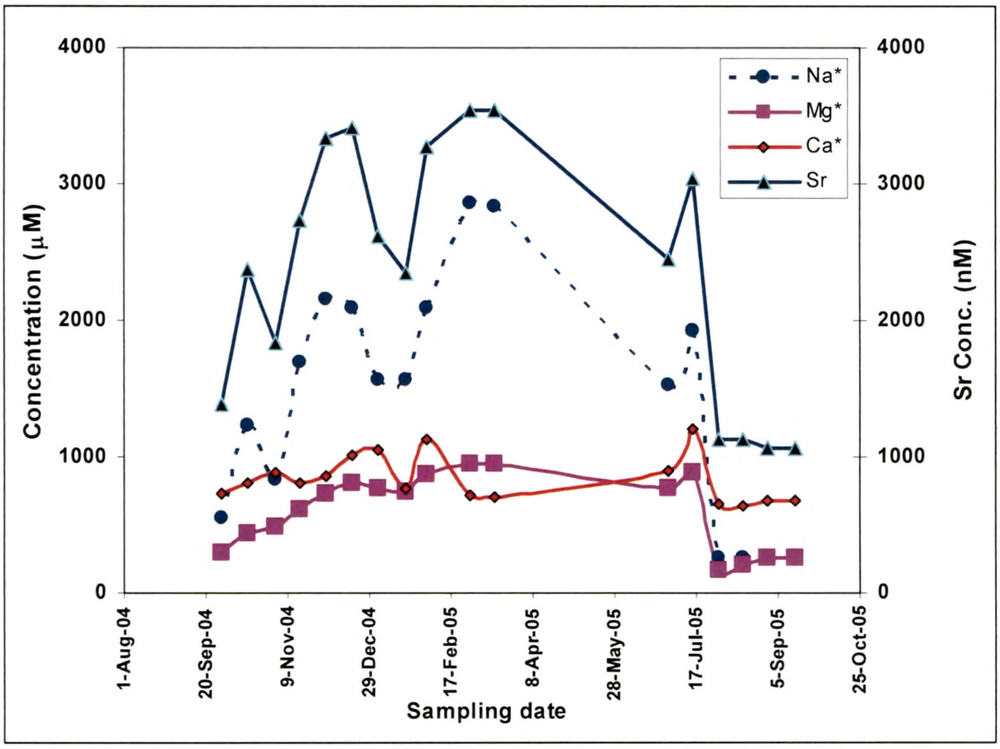


Fig-4.17: Temporal variation of dissolved elements (corrected for atmospheric input) in the Ganga river at Allahabad (After its confluence with Yamuna). The scales of Na, Mg and Ca is on the left and for Sr on the right.

One possible explanation for such a result is the solution of salts from saline/alkaline soils from the river basin during floods associated with early periods of monsoon. The higher abundances of Cl and SO_4 in the July 15th sample relative to the rest of the monsoon periods though is consistent with such a hypothesis, the role of such soils in contributing to increase in Ca needs to be assessed. Interestingly, Rai and Singh (2007) reported a sharp peak (15th June 2000) in the abundances of major ions in time series sampling over a period of one year of the Brahmaputra at Guwahati. This result was explained in terms of a flash flood in the Brahmaputra due to a natural dam burst in the Yigong River of Tibet.

Table-4.18: Chemical erosion fluxes of elements in Ganga at Allahabad (after the confluence with the Yamuna) expressed in tons d^{-1}.

Date	Sample	Discharge m^{3}s^{-1}	Na* µM	Flux	Mg* µM	Flux	Ca* µM	Flux	Sr nM	Flux
30-Sep-04	RWG-1	2035	545	2204	292	1247	735	5183	1390	21
16-Oct-04	RWG-2	1624	1226	3956	438	1493	808	4544	2374	29
2-Nov-04	RWG-3	1441	828	2371	494	1493	885	4418	1832	20
16-Nov-04	RWG-4	978	1695	3295	613	1259	803	2721	2732	20
2-Dec-04	RWG-5	872	2158	3741	734	1344	855	2582	3333	22
18-Dec-04	RWG-6	575	2088	2387	803	971	1010	2013	3409	15
3-Jan-05	RWG-7	502	1562	1559	765	806	1057	1838	2621	10
20-Jan-05	RWG-8	411	1562	1275	750	647	774	1101	2351	7
2-Feb-05	RWG-9	417	2084	1725	871	762	1132	1633	3270	10
1-Mar-05	RWG-10	353	2858	2007	945	701	717	878	3536	9
16-Mar-05	RWG-11	426	2831	2398	950	851	711	1050	3544	11
30-Jun-05	RWG-12	310	1521	938	763	497	892	959	2455	6
15-Jul-05	**RWG-13**	**9167**	**1921**	**34988**	**889**	**17103**	**1201**	**38145**	3042	**211**
31-Jul-05	RWG-14	8781	257	4478	170	3128	649	19747	1127	75
15-Aug-05	RWG-15	5613	251	2800	210	2475	637	12380	1128	48
30-Aug-05	RWG-16	4261	263	2228	255	2283	677	9990	1070	35
16-Sep-05	RWG-17	2097	264	1100	255	1124	677	4918	1063	17
	Max$^+$	*8781*	*2858*	*4478*	*950*	*3128*	*1132*	*19747*	3544	75
	Min$^+$	*310*	*251*	*938*	*170*	*497*	*637*	*878*	1063	6
	Average$^+$	***1919***	***1375***	***2404***	***582***	***1318***	***814***	***4747***	**2327**	**22**

$^+$ *excludes the July 15 sample*

Annual fluxes 10^4 tons yr^{-1}	Na*	Mg*	Ca*	Sr
Average	88	48	173	0.8
September$^+$	40-80	41-46	179-189	0.6-0.8
March$^+$	73-88	26-31	32-38	0.3-0.4

$^=$ two values represent the two measurements during the months.

In the Ganga, ^{87}Sr/^{86}Sr during the annual cycle varies from 0.71696 to 0.73001, significantly higher than the variation in the Yamuna (0.71522 to 0.71233).

The lower range in $^{87}Sr/^{86}Sr$ in the Yamuna is expected as it receives inputs predominantly from the Deccan and Vindhyan lithologies, both of which have less radiogenic $^{87}Sr/^{86}Sr$ and within a narrow range (chapter-3, Table-3.6). In contrast, the $^{87}Sr/^{86}Sr$ of the Ganga at Chhatnag (after confluence with Yamuna) will be governed by mixing of Sr brought from the Himalaya and the peninsular drainages. The $^{87}Sr/^{86}Sr$ values of the Yamuna waters seem to show a marginal decreasing trend during monsoon (Fig-4.18) probably due to enhanced contribution from the Vindhyan carbonates.

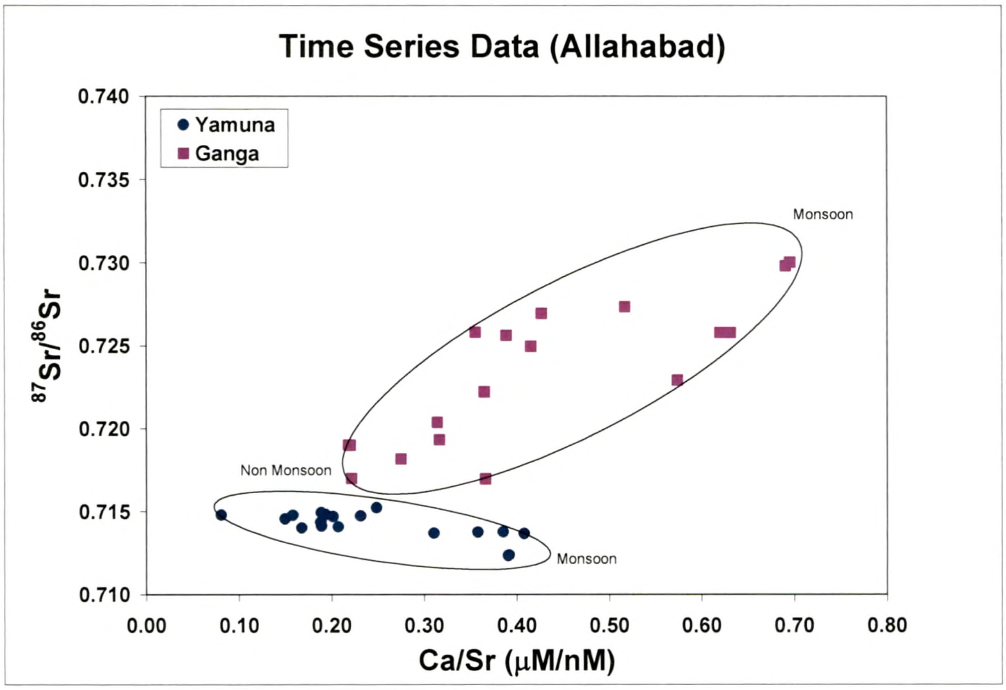


Fig-4.18: Time series (Sep.2004- Sep.2005) variation of Ca/Sr and $^{87}Sr/^{86}Sr$ in the Yamuna and Ganga River (at Allahabad after confluence). Variations in Ca/Sr and $^{87}Sr/^{86}Sr$ in the Ganga exhibit trend opposite to that of Yamuna. The trend in the Ganga can be explained in terms of mixing of two distinct sources, from the Himalaya and the Peninsular India

Considering that the Ganga sample at Chhatnag receives both Himalaya and peninsular Sr, the higher $^{87}Sr/^{86}Sr$ during monsoon is probably a result of enhanced Sr contribution from the Himalayan drainage. Sampling of the Ganga before its confluence with the Yamuna is needed to confirm this hypothesis.

4.9 Summary

Elemental and Chemical erosion rates in the plain and peninsular sub-basins of the Ganga drainage have been determined from the major ion chemistry and Sr isotope systematics of the Ganga and its tributaries. These rates in general are 2-4 times lower than those in the Himalayan sub-basin of the Ganga, mainly due to the lower run off in the peninsular and plain sub-basins and the endoreic nature of their drainages. The fluxes of various major cations and Sr from the plain and peninsular sub-basins, however, are comparable to those from the Himalayan sub-basin as their aerial coverage is a few times that of the Himalayan sub-basin. Among the major ions, Na is unique with high concentration in some of the Ganga tributaries draining the plain and peninsular sub-basins, contributing to its high flux and erosion rate from these regions. This property of Na is due to its release from various sodium salts formed in the endoreic river basins during wetting-drying cycles. Such inputs of sodium to rivers in the Ganga plain and peninsular basins restrict its application as a proxy of silicate weathering in their basins and that of the Ganga downstream of Kanpur. The results also bring out the importance of rivers draining the Ganga plain and peninsular basin as a major source of Na, Mg, Ca and Sr to the Ganga. Budget calculations show that the plain and peninsular regions together account for most of Na and 40% to 80 % of the annual flux of Mg, Ca and Sr of the Ganga at its outflow (Rajmahal). This input, therefore needs to be accounted for while estimating the chemical weathering rates of the Ganga basin in the Himalaya, based on major ion chemistry of the Ganga downstream of Kanpur.

$^{87}Sr/^{86}Sr$ and Ca/Sr of the Ganga head waters and its Himalayan tributaries in plain were used to estimate the precipitation of $CaCO_3$ from river waters. This study is based on a two end member mixing model, carbonate and silicate rocks supplying Ca, Sr and Sr isotopes to the river. Results show that about two thirds of the Ca is removed by precipitation from the Ghaghra and the Gandak, the tributaries of the Ganga. Such precipitation of carbonates in the

Ganga plain can be an important mechanism for the formation of 'Kankar' carbonates. The Bhagirathi and the Kosi do not seem to be affected by such precipitation loss of Ca. Time series (biweekly) water sampling of the Yamuna and the Ganga river show that chemical erosion of different elements are season dependent and vary over the year attributable to differences in weathering kinetics of different lithologies in the basin.