

## Dissolved inorganic carbon isotopic compositions in the Upstream Ganga river in the Himalayas

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**Dissolved inorganic carbon (DIC) is a major component of river waters and is derived from atmospheric CO<sub>2</sub>, from reactions for silicate and carbonate rock weathering and biological activities such as photosynthesis and respiration. To distinguish the sources of HCO<sub>3</sub><sup>-</sup> in river waters, it is essential to estimate the amount of CO<sub>2</sub> consumed from the atmosphere during rock weathering and to understand the biogeochemical cycling of carbon. One of the more reliable methods adopted to understand the different sources of DIC in rivers, is the measurements of carbon isotopes in DIC, since the fractionation factors between the different carbonate species in dissolved river water and gaseous CO<sub>2</sub> are well established. The present study is aimed at understanding the source of DIC in the Alakananda and Bhagirathi rivers in the Himalayas by measurements of <sup>δ</sup><sup>13</sup>C<sub>DIC</sub> in water samples. From the measurements made on these rivers in India through the present study, we find that the river waters have highly depleted <sup>δ</sup><sup>13</sup>C<sub>DIC</sub>, which indicates the importance of carbonate rock weathering and bacterial respiration as the major processes for dissolved inorganic carbon.**

**Keywords:** Dissolved inorganic carbon, Ganga, Himalayas.

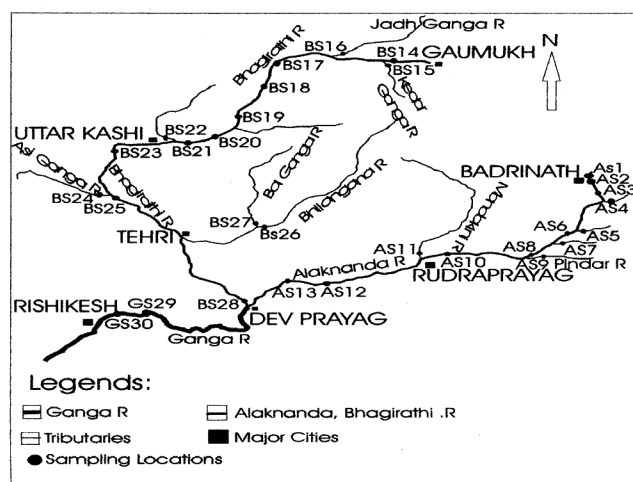
THE study area (Figure 1) covers Ganga river from near its origin in the Himalayan mountains until Rishikesh. The source of the Ganga, the Gangotri glacier in the Kumaun Himalayas, is at an elevation of about 7000 m. The main stream of the Ganga is formed at Devprayag after the confluence of Bhagirathi and Alakananda; both the rivers originate in the Higher Himalayas and flow initially over medium to high grade metamorphic rocks. The Alakananda and its tributaries flow over limestones, dolomites, marbles, quartzites, phyllites and micaceous greywackes, before its confluence with the Bhagirathi river. The Bhagirathi and its tributaries predominantly drain over greywackes, shales, slates, carbonates, quartzites, granites, gneisses, schist and calcilicates<sup>1</sup>.

Water samples from 30 locations as shown in Figure 1, were collected from Alakananda and Bhagirathi rivers and their major tributaries in May 2004. Samples for <sup>δ</sup><sup>13</sup>C<sub>DIC</sub> analysis were collected in 100 ml air tight glass bottles. The samples were not filtered, since the risk of changing the

concentration of dissolved CO<sub>2</sub> during filtration is high. Because the samples were collected during the pre-monsoon period, the suspended sediment concentrations were extremely low or negligible and hence removal of suspended sediments through filtration was not necessary. Samples for analysis of major cations and anions were collected in laboratory pre-cleaned polypropylene bottles and filtered through 0.45 μm cellulose nitrate membrane filter papers.

The <sup>δ</sup><sup>13</sup>C<sub>DIC</sub> was determined on a FINNIGAN MAT Delta S Mass Spectrometer at the Geological Institute of the Ruhr University in Bochum (RUB), Germany, following the methods of preparation of samples as described by Buhl *et al.*<sup>2</sup>. The overall analytical precision with reference to NBS standard was 0.2‰ (1σ). The <sup>δ</sup><sup>13</sup>C<sub>DIC</sub> results are expressed in permil (‰), with reference to a standard as,  $\delta^{13}C_{DIC} = (R_{Sample}/R_{Standard}) * 1000 [‰]$ , where  $R_{Sample}$  and  $R_{Standard}$  are the ratios of <sup>13</sup>C/<sup>12</sup>C in the sample and standard respectively<sup>3</sup>. Ca and Mg in water samples were determined by ion chromatograph (Metrohm) at IIT Roorkee and HCO<sub>3</sub><sup>-</sup> was analysed by determining end-point by successive titrations (Gran Plot) with diluted HCl. Other major cations (Na, K) and anions (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) in the water samples were also analysed, but are not reported here. Cation–anion mass–charge balance indicates the accuracy of sample analysis to be within ± 5%.

Results of the analyses are presented in Table 1. Because the samples were collected during pre-monsoon, the results discussed pertain to this particular weather condition only. HCO<sub>3</sub><sup>-</sup> concentration in the rivers varies from 110 to 1320 μmoles l<sup>-1</sup>. This large variation is caused by the flow of rivers in the silicate terrains in the upstream region characterized by granites and gneisses (low HCO<sub>3</sub><sup>-</sup>) and in carbonate terrains (high HCO<sub>3</sub><sup>-</sup>) and a mixing of the two (intermediate HCO<sub>3</sub><sup>-</sup> concentrations). The <sup>δ</sup><sup>13</sup>C<sub>DIC</sub> values in the present study vary from –5.22 to –16.84‰. These values are comparable to Rhine river<sup>2</sup>, Ottawa river<sup>4</sup> and St. Lawrence river<sup>5</sup>. The variation in the two rivers, Alakananda



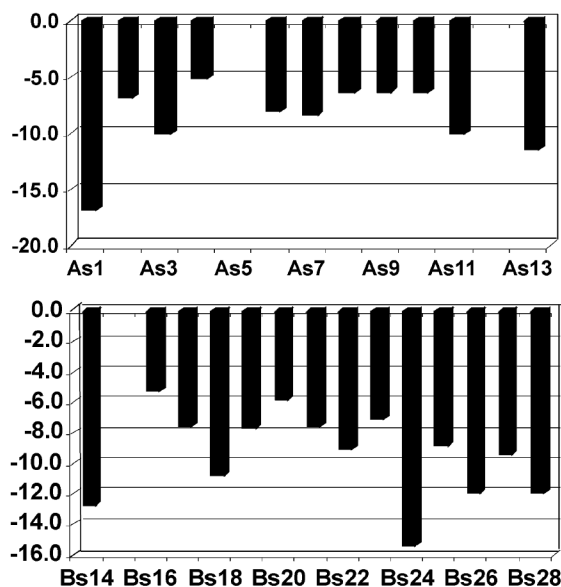
**Figure 1.** Location of study area and sampling locations (not to scale).

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**Table 1.**  $\delta^{13}\text{C}_{\text{DIC}}$  composition in river water samples

Sample no	Location	Stream	Ca ( $\mu\text{mol/l}$ )	Mg ( $\mu\text{mol/l}$ )	$\text{HCO}_3^-$ ( $\mu\text{mol/l}$ )	$\delta^{13}\text{C}_{\text{DIC}}$
AS1	Mana	Saraswati	179	1	114	$-16.84 \pm 0.03$
AS2	Mana	Alakananda	126	16	116	$-6.72 \pm 0.01$
AS3	Pandukeshwar	Alakananda	204	5	118	$-10.05 \pm 0.02$
AS4	Vishnuprayag	Dhauliganga	603	242	670	$-5.12 \pm 0.01$
AS5	Birahi	Birahiganga	761	525	1320	
AS6	Chamoli	Alakananda	454	163	560	$-8.02 \pm 0.02$
AS7	Nandprayag	Nandakini	591	245	980	$-8.26 \pm 0.01$
AS8	Karnaprayag	Alakananda	424	104	550	$-6.25 \pm 0.02$
AS9	Karnaprayag	Pinder	537	190	754	$-6.23 \pm 0.02$
AS10	Ratura	Alakananda	423	141	470	$-6.37 \pm 0.02$
AS11	Rudraprayag	Mandakini	321	67	580	$-10.04 \pm 0.01$
AS12	Srinagar	Alakananda	455	132	406	–
AS13	Kirtinagar	Alakananda	140	1	110	$-11.37 \pm 0.03$
BS14	Gangotri	Bhagirathi	465	136	560	$-12.71 \pm 0.02$
BS15	Gangotri	Kedarganga	239	75	58	–
BS16	Bhaironghati	Jadhganga	394	312	174	$-5.22 \pm 0.02$
BS17	Harsil	Bhagirathi	–	–	–	$-7.48 \pm 0.05$
BS18	Dabrani	Bhagirathi	248	133	116	$-10.78 \pm 0.02$
BS19	Malla	Bhagirathi	348	162	230	$-7.69 \pm 0.01$
BS20	Maneri	Bhagirathi	335	156	248	$-5.85 \pm 0.02$
BS21	Uttarkashi	Bhagirathi	315	140	245	$-7.54 \pm 0.01$
BS22	Gangori	Asiganga	342	59	465	$-9.01 \pm 0.01$
BS23	Dunda	Bhagirathi	307	135	235	$-7.02 \pm 0.02$
BS24	Dunda	Dhanerigad	555	245	875	$-15.32 \pm 0.01$
BS25	Dharasu	Bhagirathi	330	137	280	$-8.76 \pm 0.02$
BS26	Ghansyali	Bhilangana	232	51	256	$-11.86 \pm 0.03$
BS27	Ghansyali	Bhagirathi	411	172	638	$-9.38 \pm 0.01$
BS28	Devprayag	Bhagirathi	306	118	285	$-11.92 \pm 0.03$
GS29	Shivpuri	Ganga	439	168	580	$-7.34 \pm 0.01$
GS30	Laxmanjhulla	Ganga	453	175	468	$-7.76 \pm 0.02$

– Indicates data not available.



**Figure 2.** Variations in  $\delta^{13}\text{C}_{\text{DIC}}$  in Alakananda–Bhagirathi rivers and their tributaries.

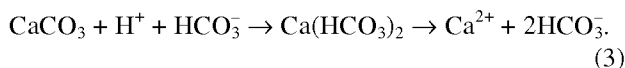
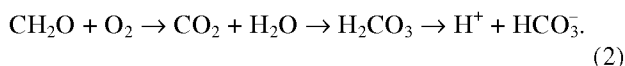
( $-8.26$  to  $-16.84\text{‰}$ ) and Bhagirathi ( $-5.22$  to  $-12.71\text{‰}$ ) and the various tributaries are significant (Figure 2).

Rivers linking the terrestrial system and the ocean, transport about  $2.5\text{--}5.0 \times 10^{13}$  moles of carbon annually to the oceans, in both particulate and dissolved forms<sup>6</sup>. Hence they play a crucial role in the global biogeochemical cycling of carbon. The dissolved inorganic carbon in river water has sources from soil  $\text{CO}_2$ , dissolution of carbonate minerals and atmospheric  $\text{CO}_2$  in exchange with air–water interface. Dissolved carbon isotopic studies can reveal which of these processes are dominant in water chemistry. The riverine dissolved inorganic carbon (DIC) can decrease due to consumption by water plants, by photosynthesis or seepage into the groundwater systems. Any increase in DIC results in consumption by algal matter and degassing.

Carbon isotopic composition has widely been used as an effective tool for distinguishing carbon originating from a variety of sources. The characteristic values for the most common carbon reservoirs are<sup>4</sup> (Figure 3) about  $-7$  to  $-8\text{‰}$  for atmospheric  $\text{CO}_2$  and  $-24$  to  $-34\text{‰}$  for plant organic matter ( $-28\text{‰}$  on average). Because soil  $\text{CO}_2$  is derived mostly from decomposed organic matter, it has the same  $\delta^{13}\text{C}_{\text{DIC}}$  values as the plant organic matter. The dissolution of soil  $\text{CO}_2$  into water results in the fractionation of about  $+7\text{‰}$ , giving  $\delta^{13}\text{C}_{\text{DIC}}$  values of about  $-17$  to  $-21\text{‰}$ . In contrast, dissolution of atmospheric  $\text{CO}_2$  yields DIC with  $\delta^{13}\text{C}$  of about  $-1\text{‰}$ . The  $\delta^{13}\text{C}_{\text{DIC}}$  in the bedrock aquifers would therefore

vary from about  $-17$  to  $-21\text{‰}$  for soil  $\text{CO}_2$  involved in silicate weathering to about  $-10$  to  $+2\text{‰}$ , if carbonate weathering is involved. Hence the highly depleted  $\delta^{13}\text{C}_{\text{DIC}}$  values obtained for the present study indicate that the biologically enhanced carbonate dissolution plays a major role in DIC concentrations in these rivers.

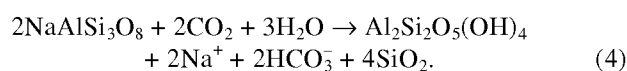
DIC concentrations in rivers from carbonate dissolution are accomplished by the following chemical reactions,



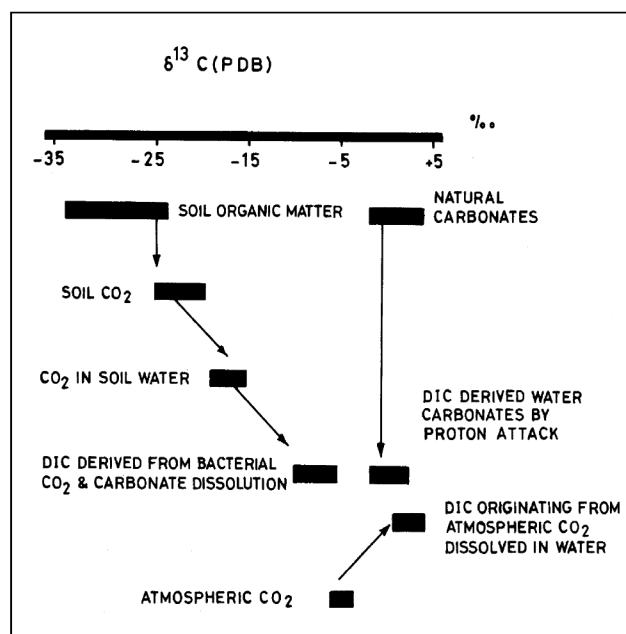
Reaction (1) is significant only in highly acidic conditions<sup>7</sup> and where acidity is not sufficiently neutralized due to lack of carbonate rock types. This results in  $\delta^{13}\text{C}$  values of  $-5$  to  $2\text{‰}$  and without any more fractionation. However, reactions that are carried out by biological activities in the soil root zone (reaction 2), results in  $\delta^{13}\text{C}$  values<sup>8</sup> between  $-21$  and  $-17\text{‰}$ . The bicarbonate thus produced, percolates to ground-water and reacts with carbonate rocks to produce bicarbonate (reaction 3) with  $\delta^{13}\text{C}$  values<sup>9</sup> of about  $-10$  to  $-14\text{‰}$ . Although we have not been able to analyse any groundwater samples in the present study, at least ten of our analysed samples from the rivers show values within the range  $-9.38$  to  $-16.84\text{‰}$ , pointing to the DIC derived from bacterial  $\text{CO}_2$  and carbonate dissolution in an open system. The remaining comparatively positive samples ( $-5.12$  to

$-8.76\text{‰}$ ) are due to the reactions in a slightly more closed system, where influence of groundwater on river water composition could be significant. Salomons and Mook<sup>9</sup> observed that dissolution of calcite in soils and groundwaters results in  $\delta^{13}\text{C}_{\text{DIC}}$  values of  $\approx 16\text{‰}$ , if the soil  $\text{CO}_2$  originates from decay of C3 plants, and  $\approx 13\text{‰}$ , if it results from decomposition of C4 plants. The Himalayan region is characterized more by C4 plants, and hence slightly positive  $\delta^{13}\text{C}_{\text{DIC}}$  can be expected in these waters derived from decay of the C4 plants.

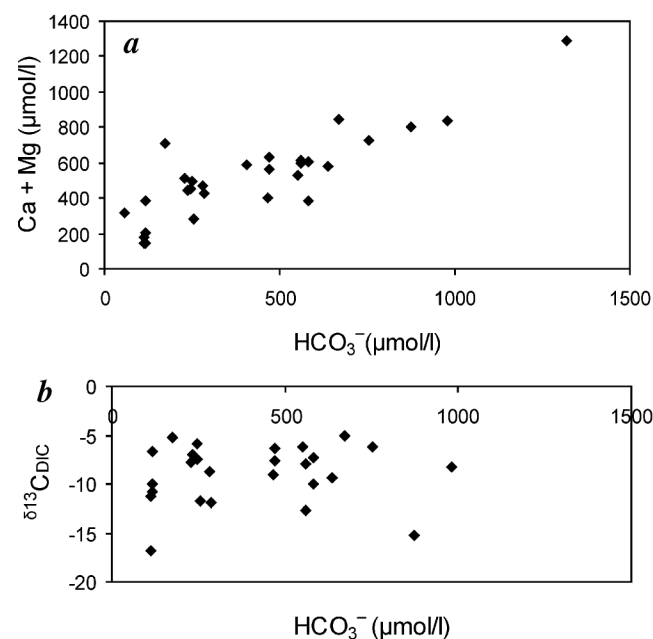
$\text{CO}_2$  from atmosphere and soils is also consumed by silicate weathering of primary minerals, such as albite to secondary clay minerals such as kaolinite by the reaction<sup>10</sup>:



The  $\delta^{13}\text{C}_{\text{DIC}}$  composition derived from silicate weathering aided by atmospheric  $\text{CO}_2$  is  $-17$  to  $-21\text{‰}$ , with no further fractionation. Since our sample measurements gave  $\delta^{13}\text{C}_{\text{DIC}}$  values of  $-5$  to  $-16\text{‰}$ , we infer that silicate weathering is not the dominant source for DIC in Alakananda and Bhagirathi river basins. This is further corroborated by the relationship between  $\text{Ca} + \text{Mg}$  and  $\text{HCO}_3^-$ , and  $\text{HCO}_3^-$  and  $\delta^{13}\text{C}_{\text{DIC}}$  (Figure 4). The dominance of carbonate rock weathering in the upland Himalayan rivers has been reported earlier. Blum *et al.*<sup>10</sup> reported 82% of  $\text{HCO}_3^-$  as derived from weathering of carbonate minerals in the Raikhot watershed in the Higher Himalayan crystalline series. Similarly, Harris *et al.*<sup>11</sup> suggest that carbonates are



**Figure 3.** Isotopic composition of DIC derived from various sources<sup>4</sup>.



**Figure 4.** Relationship between  $\text{Ca} + \text{Mg}$  and  $\text{HCO}_3^-$  (a) and  $\text{HCO}_3^-$  and  $\delta^{13}\text{C}_{\text{DIC}}$  (b).

the predominant lithology undergoing dissolution within the Lesser Himalayas.

The dissolution of CO<sub>2</sub> in water and redistribution of aqueous carbonate is accompanied by different isotope fractionation factors, which are temperature-dependent<sup>12</sup>. Rainwater is an important contributor of DIC, which depends on the partial pressure of CO<sub>2</sub> and temperature of the ambient air. The partial pressure of CO<sub>2</sub> decreases with rising altitude. Generally, rainwater shows DIC concentrations of 10<sup>-2</sup> to 5 × 10<sup>-2</sup>, implying that despite lower pCO<sub>2</sub>, comparable DIC concentrations in rain may be attained in high altitude basins. Assuming a <sup>δ</sup>13C of -7.6‰, for atmospheric CO<sub>2</sub> and a 1.2‰ depletion in <sup>δ</sup>13C due to conversion of CO<sub>2(gas)</sub> to CO<sub>2(aq)</sub>, the isotopic composition of DIC in unaltered rainwater<sup>12</sup> would be about -8.8‰. In the present study, water recharge to the river was not due to rainfall, since the samples were collected before the monsoon season and hence contribution of DIC from rainwater can be neglected. Among the other possible sources of DIC, contribution from silicate weathering is also insignificant. However, the Himalayan terrain supports thick vegetation with C3 and C4 plants. C3 and C4 plants contribute enormously to depleted DIC even in silicate terrains. This is evident in some of the presently studied locations (e.g. AS11, BS14 and BS18), where biogenic CO<sub>2</sub> from deep forests seems to contribute to the depleted <sup>δ</sup>13C<sub>DIC</sub>. Carbon isotopic measurements on organic carbon in sediment cores from the Bengal Fan showed a dramatic 10‰ increase beginning 7 Ma ago, reflecting the changes of mixing ratio of terrigenous carbon derived from C3 and C4 plants. The rapid increase in <sup>δ</sup>13C<sub>DIC</sub> of Bengal Fan at 7 Ma (late Miocene) resulted due to the extensive C4 plants in the Siwalik Himalayan Foreland<sup>13</sup>. In general, however, carbonate dissolution is the main contributor for DIC in the present study and the highly depleted <sup>δ</sup>13C observed indicates, the major role of carbonate rock weathering and microbial respiration as the main contributor for DIC in the upland rivers of the Ganga. The present study clearly signifies the major role of carbonate rock dissolution and bacterial respiration as the major inputs of DIC in the head waters of the Ganga river.

<sup>δ</sup>13C<sub>DIC</sub> values also trace the seasonal changes in flow characteristics or the dominant activities (dams) carried out in rivers<sup>4,14</sup>. Based on a diffusion model, Telmer and Veizer<sup>4</sup> estimated CO<sub>2</sub> evasion to the atmosphere from the Ottawa river and its tributaries to be 1.3 × 10<sup>10</sup> mol C/a or 30% of DIC flux. Major rivers such as the Amazon, Yangtze and Rhine show CO<sub>2</sub> concentrations up to 10–15 times greater than the atmospheric equilibrium values, indicating that rivers are not only major pathways for transport of CO<sub>2</sub> from continents to oceans, but also actively degas CO<sub>2</sub> into the atmosphere with the evasion rate approximated at around 10<sup>13</sup> g/a. With such a large flux, the consequences for global carbon budget could be significant. The Ganga river is characterized by dominance of carbonate rock weathering. Hence it would be interesting to calculate the equilibrium and evasion, if any, of CO<sub>2</sub> from the basin. However, we are severely constrained

by lack of seasonal carbon isotopic compositions as well as discharge data of Ganga river.

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ACKNOWLEDGEMENTS. The study was supported by funds from the Department of Science and Technology, Government of India Project (No. SR/54/ES-18/2002) and INSA–DFG Fellowship 2004–05 to G.J.C. Dieter Buhl, Ulrike Schulte and Beate Ghynen of RUB, Germany and R. K. Saini, R. Purushottaman and Sri Krishan Yadav of IIT, Roorkee are acknowledged for help in laboratory and field sampling respectively.

Received 27 October 2004; revised accepted 13 April 2005