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First assessment of water and carbon cycles in two tropical coastal rivers of south-west India: an isotopic approach[†]

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RATIONALE: The contribution of tropical coastal rivers to the global carbon budget remains unmeasured, despite their high water dynamics, i.e. higher run-off with their basin characteristic of warm temperature. Two rivers draining the western part of the Western Ghats, the Swarna (length 80 km) and Nethravati (147 km) Rivers, were studied for water and carbon cycles.

METHODS: The stable isotope ratios of oxygen ($\delta^{18}\text{O}$ values), hydrogen ($\delta^2\text{H}$ values) and carbon ($\delta^{13}\text{C}$ values) were used to understand the water circulation, the weathering processes and the carbon biogeochemical cycle. The river water samples were collected during the dry post-monsoonal season (November 2011).

RESULTS: The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of river water suggested that the monsoonal vapour source and its high recycling have a dominant role because of the orographical and tropical conditions. The absence of calcareous rocks has led to dissolved inorganic carbon (DIC) mainly originating from atmospheric/soil CO_2 , via rock-weathering processes, and the low soil organic matter combined with high run-off intensity has led to low riverine dissolved organic carbon (DOC) contents. The $\delta^{13}\text{C}$ values increase from upstream to downstream and decrease with increasing pCO_2 . There is a positive relationship between the $\delta^{13}\text{C}_{\text{DIC}}$ values and the DOC concentrations in these two rivers that is contrary to that in most of the studied rivers of the world.

CONCLUSIONS: The higher evapotranspiration supported by tropical conditions suggests that there are higher vapour recycling process in the Swarna and Nethravati basins as studied from the water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. The basin characteristics of higher rainfall/run-off accompanied by warm temperature suggest that the $\delta^{13}\text{C}$ value of riverine DIC is mainly controlled by the weathering of source rocks (silicates) with variation along the river course by CO_2 degassing from the river water to the atmosphere and is less dominated by the oxidation of DOC. Copyright © 2013 John Wiley & Sons, Ltd.

Fluvial systems play a distinct role in monitoring the global carbon budget in the biosphere, because they not only act as the carbon carriers from the terrestrial source to the marine environment, but also stimulate various *in situ* processes that could significantly affect the carbon content. The carbon concentration, including its form, could be altered by natural processes such as gas exchange with the atmosphere (particularly the degassing of CO_2), storage as river-bottom sediments (by microbial degradation of organic matter) and

higher plankton production mainly by anthropogenic activities leading to higher nutrient input from sources such as agricultural land, domestic sewage and industry. In freshwater river systems, dissolved organic carbon (DOC), mainly originating from plant decomposition, is a very dynamic and reactive fraction of the whole carbon cycle on Earth. In contrast, the dissolved inorganic carbon (DIC) is derived from atmospheric CO_2 through weathering of silicate and carbonate rock, and soil organic matter consumption. To determine the sources of inorganic carbon in river water, it is essential to estimate the amount of CO_2 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 measurement of carbon isotopes in DIC, because the fractionation factors between the different carbonate species in dissolved river water and gaseous CO_2 are well established.^[1–3] The stable isotope ratios of oxygen ($\delta^{18}\text{O}$ values) and hydrogen ($\delta^2\text{H}$ values) in river water are well established for determining the sources of these waters in the river basins. This would also determine the signatures of carbon in the river water accurately.

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The main objective of this work was to assess the water and carbon cycle, particularly the use of the carbon isotope ratio, for the first time, to understand the hydrological and biogeochemical functioning of the western coastal tropical rivers originating in the Western Ghats, south India. The Swarna and Nethravati river basins that support very high run-off intensity displaying typical features of a tropical environment were studied for their water characteristics with the stable isotope ratios of oxygen ($\delta^{18}\text{O}$ values), hydrogen ($\delta^2\text{H}$ values) and carbon ($\delta^{13}\text{C}$ values). These short river courses receive high rainfall inputs and have high drainage intensity on old granitic-gneiss rock. The anthropogenic pressure is high in these narrow coastal river basins with high population density and intense agricultural practice. The first part of the paper discusses water circulation, river and ground-water exchange and water vapour recycling using the stable isotope ratios, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. In the second part, the carbon cycle and its relation with land-use changes and weathering are discussed. The stable isotope ratios of carbon ($\delta^{13}\text{C}$ values) and oxygen ($\delta^{18}\text{O}$ values) in DIC and particulate organic carbon (POC) along with the concentrations of bicarbonate (HCO_3^-) and DOC were measured to identify the sources of inorganic and organic carbon and determine the roles of different controlling factors (chemical weathering of non-calcareous rocks, organic matter oxidation, phytoplankton production and CO_2 degassing) on the riverine DIC $\delta^{13}\text{C}$ values. This study adds to the knowledge on the contribution of silicate-dominated terrains of tropical coastal rivers to the total carbon budget. An attempt is also made to distinguish the processes that could modify the carbon concentration as well as its form, which would otherwise contrast the source delineation of carbon in these river waters.

EXPERIMENTAL

General characteristics of study area

The Swarna and Nethravati Rivers originate in the Western Ghats at an altitude of 1100 m and 1900 m above mean sea level (asl), respectively, and flow west into the Arabian Sea near Hangarkatte (Udupi) and Mangalore, respectively, with specific basin characteristics, as shown in Table 1. These river basins represent the dominance of the typical characteristics of the Western Ghats. The densely vegetated Western Ghats (1600 km) host a narrow tropical coastal zone 40 to 75 km in width towards the west and form an abrupt edge of the

Deccan Plateau towards the north-east. The Ghats escarpment (1300 to 1800 m) serves as an orographic barrier blocking the bulk of the south-west monsoon rainfall along the Sahyadri Range. The second-highest amount of annual rainfall (7460 mm) has been recorded at Agumbe, Karnataka (645 m asl), a hot spot famous for its rainforest and biodiversity. The rainfall decreases abruptly to 4500 and 4000 mm as it reaches the western coastal regions of Udupi and Mangalore, respectively. There is a strong seasonality of rainfall in this region caused by the dual monsoon system. During the period from February to May preceding the summer monsoon, the region experiences dry conditions and hot temperatures, with a mean temperature of over 30 °C. Between March and May, the potential evaporation gradually increases and can reach 240 mm/month.^[4] The presence of highly undulating terrain and high rainfall has caused the formation of several short rivers with high run-off.

Unlike the northern part of the Western Ghats, such as the Deccan Traps, there is no volcanic rock in the Karnataka state except for the unique case of the small St Mary's Islands, with their famous polygonal columnar basalt formation. The geological formations of the study area consist of an Archean complex made up of Dharwar schist and granitic gneisses. The Ghats mainly comprise schist, whereas the gneiss, granites and charnockite rocks cover the lower undulated landscapes with sandy alluvium along the coast. The morpho-climatic settings explain the distribution of vegetation and soils. For soils, the schematic toposequence includes Plinthosols^[5] in the coastal area, and Acrisols and Lixisols associated with a few Ferralsols on the humid slopes of the Western Ghats. Human activities, particularly agricultural practices, strongly depend on these pedoclimatic conditions. In summary, the coastal area appears as a mosaic of highly diverse and contrasting landscape units, and thus covers the main vegetation types and major soil-crop-climate complexes of southern India.^[6]

On the slopes of the Western Ghats, the tropical rainforests of the mountain undergo strong seasonal climate change, with possible long dry and cold periods in winter. These severe conditions provide a relatively small diversity for the big trees, but this is compensated for by high-nutrient soils.^[7] The hilly tracts of the Western Ghats in Karnataka are famous for their areca nuts, pistachios, coffee and several centuries-old spice orchards. The cultivators apply tree leaves intensely as mulch, and leaf mould and dung as manure, materials that are obtained directly or indirectly from the forest surrounding the orchards.^[8] Other crops include rubber plantations, paddy (rice) cultivation in the valley, different legumes, and coconuts along the coast. The land-use and land-cover changes have led to a loss of biodiversity, which lowers the resilience of the ecosystems to environmental stresses and reduces their ability to remove carbon from the atmosphere. More directly, it often leads to the release of carbon from terrestrial ecosystems into the atmosphere.

Sample collection and analysis

Surface water samples were collected during the post-monsoonal season (November 2011) at six different stations along the two tropical river courses, the Swarna River flowing through Udupi and the Nethravati River flowing through Dakshin Kannada, Karnataka, south-western India.

Table 1. Distinct characteristics of two river basins

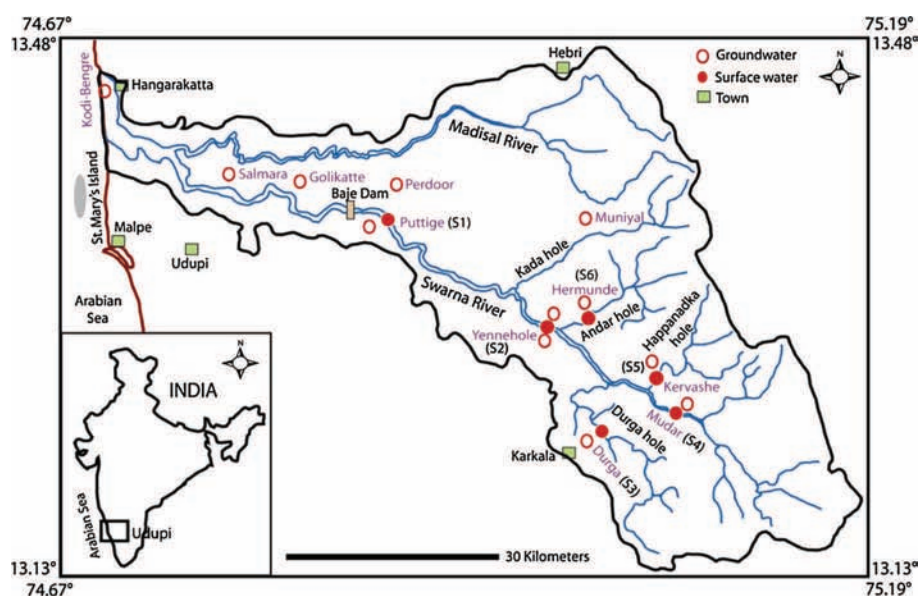
	Swarna basin	Nethravati basin
River length (km)	80	147
Basin surface (km ²)	603	3657
Mean discharge (m ³ /s)	54	373
Mean air temperature (°C)	30	30
Annual rainfall (mm)	4500	4000
Land use for agriculture (%)	75	60
Population density (h/km ²)	894	518

The physicochemical parameters of water samples were measured on-site at each sampling station for temperature ($^{\circ}\text{C}$), pH, conductivity ($\mu\text{S cm}^{-1}$) and dissolved O (mg/L) using the Hach multi-parameter apparatus attached to the pH, conductivity and LDO (luminescent dissolved oxygen) probes, respectively, available at the Manipal Institute of Technology (Manipal, India). River-water samples were collected to measure the stable isotope ratios of oxygen ($\delta^{18}\text{O}$ values), hydrogen ($\delta^2\text{H}$ values) and carbon ($\delta^{13}\text{C}$ values), and carbon concentrations in both organic (DOC) and inorganic (HCO_3) form. Additional samples of groundwater were collected adjacent to river-water samples for the measurement of water isotope ratios ($\delta^{18}\text{O}$ and $\delta^2\text{H}$ values)

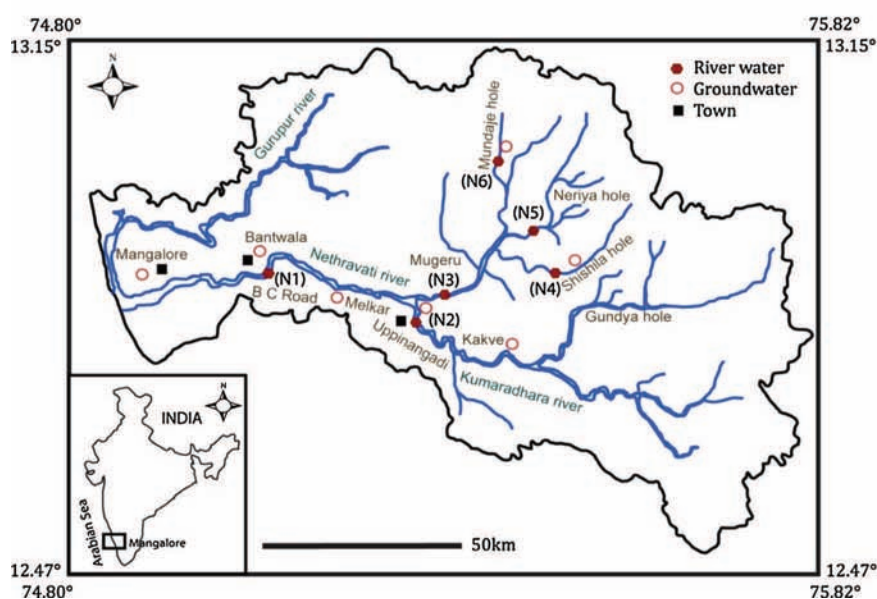
to understand the seasonal buffering effect on the river water. The river-water and ground-water stations of both the Swarna and the Nethravati river basins are shown in Figs. 1(a) and 1(b). The Swarna River water samples are labelled as S1–S6 and the Nethravati River water samples are labelled as N1–N6 (Figs. 1(a) and 1(b)).

Stable isotopes for water

Samples of river water (from the centre of the stream) and the adjacent ground water were collected in 10 mL tight-capped glass vials for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements and were kept at a stable temperature until analysis. In the laboratory, 0.3 mL



(a)



(b)

Figure 1. Base maps showing (a) the sampling stations on the Swarna–Madisal river basin, stations S1–S6 and (b) the sampling stations on the Nethravati–Gurupur river basin, stations N1–N6.

aliquots of the water were taken in capped 3.7 mL Exetainer vials (Labco Ltd, High Wycombe, UK). To measure the $\delta^{18}\text{O}$ values of the water samples, the samples and the internal standards were flushed offline with a gas mixture of 5% CO_2 in He. The Exetainer vials were then left to equilibrate at 40 °C for about 8 h. The analytical precision of the measurements was ± 0.25 per mil (‰). To measure the $\delta^2\text{H}$ values of the samples, Hokko beads were added to the Exetainer vials containing the water samples and the internal standards before the vials were flushed offline with a gas mixture of 5% H_2 in He. The Exetainer vials were left to equilibrate at 40 °C for about 8 h. The analytical precision of the measurements was ± 2.5 ‰.

The spectrometer was calibrated by using four working standards that are traceable to the primary reference standards V-SMOW2 (Vienna-Standard Mean Ocean Water) and V-SLAP2 (Vienna-Standard Light Antarctic Precipitation) distributed by the International Atomic Energy Agency (IAEA, Vienna, Austria). The results are expressed in per mil on the V-SMOW/SLAP scale, for oxygen:

$$\delta^{18}\text{O}_{\text{V-SMOW2}}(\text{‰}) = \left(\left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \right) - 1 \right) \times 1000$$

and for hydrogen:

$$\delta^2\text{H}_{\text{V-SMOW2}}(\text{‰}) = \left(\left(\frac{(^2\text{H}/^1\text{H})_{\text{sample}}}{(^2\text{H}/^1\text{H})_{\text{standard}}} \right) - 1 \right) \times 1000$$

For the calculation of the deuterium excess, the equation for the Global Meteoric Water Line defined by Craig,^[9] which was later redefined as given in the following equation by Dansgaard^[10] for the meteoric water lines, was used:

$$\text{d-excess} = \delta^2\text{H} - (8 \times \delta^{18}\text{O})$$

Carbon stable isotopes

To study the carbon isotope ratios, water samples were collected at the same station as for the water isotope ratios: S1–S6 for the Swarna River (Fig. 1(a)) and N1–N6 for the Nethravati River (Fig. 1(b)). At each station, 1 L of river water was filtered in the field through a 0.7 μm ashed GF/F glass fibre filter (Millipore, Billerica, MA, USA). For the DOC, 125 mL of this water was collected in polyethylene bottles (Nalgene) and acidified with concentrated HCl. For the DIC, 125 mL of the water was collected in similar bottles and treated with mercuric chloride to avoid any bacterial activity. All the bottles were carefully sealed, taking care to ensure that no trapped air remained in contact with the sample, and stored at 4 °C. The filters were placed in small plastic bags (zip lock) to determine the amounts of POC.

To extract the DIC, a 0.3 mL aliquot of the sample was acidified inside the 3.7 mL Exetainer vials with concentrated phosphoric acid, and kept at 70 °C for 8 h. The evolved CO_2 was then purified and analysed. The resulting analytical precision of the measurements was ± 0.2 ‰. The results are reported as δ values with reference to the Vienna Pee Dee Belemnite (VPDB).^[11]

$$\delta^{13}\text{C}_{\text{VPDB}}(\text{‰}) = \left(\left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \right) - 1 \right) \times 1000$$

For the POC, the filters were dried and weighed, and a part of the filter was placed in a tin cup for C elemental analysis. The carbon isotopic composition ($\delta^{13}\text{C}$ value) was measured using an isotope ratio mass spectrometer coupled to an elemental analyser.

All the isotopic analyses of the samples were carried out in the Shiva Isotopic Platform in Toulouse (France) on an Isoprime 100 continuous flow isotope ratio mass spectrometer coupled with a Geo-Multiflow for the water–gas equilibration, and a microcube elemental analyser (all from Elementar, Hanau, Germany). The C and N elemental analyses results were used to calculate the C/N ratios.

Other chemical analysis

The Specific UV Absorbance (SUVA) was measured at 245 μm on a UV Light XT5 absorption spectrophotometer (Secoman, Ales, France). The concentrations of DIC in water samples were measured using a Titrino 716 DMS Autotitrator (Metrohm, Villebon-sur-Yvette, France). DOC and the Total Organic Carbon (TOC) was determined with a Shimadzu TOC 5000 A (Shimadzu, Noisiel, France). The major anions (sulfate, chloride, nitrate and phosphate) were analysed using ion chromatography (Dionex DX-120, eluted with KOH on a column KOH AS11-HC; Dionex, Villebon-sur-Yvette, France).

RESULTS

Isotopic approach of water cycle

The stable isotope ratios of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$ values) are given in Fig. 2 and Table 2. The overall mean $\delta^{18}\text{O}$ values were -2.91 ± 0.44 ‰ (n=6) for the Swarna River and -3.61 ± 0.49 ‰ (n=6) for the Nethravati River. The lower value for the Nethravati River water could be explained by the continental effect because of the larger basin. There is no altitude effect on the tropical saturated air moisture.

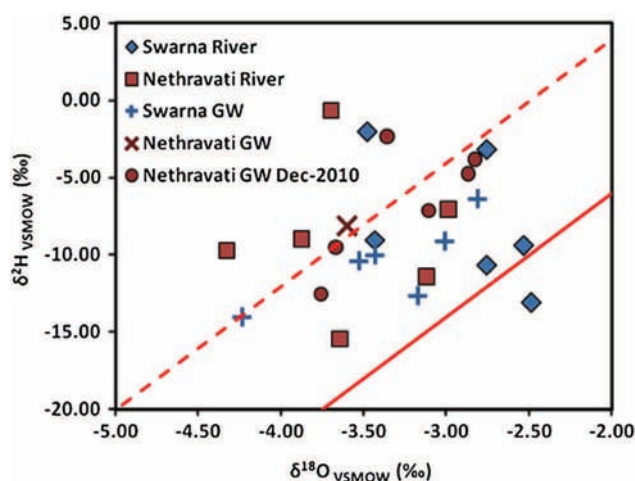


Figure 2. $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ relationship of the Swarna River and Nethravati River for the six sample stations, compared with the nearby groundwater (GW). The Global Meteoric Water Line is represented by a thick line (slope of 8, d-excess of 10) and winter monsoon water line by a dashed line (same slope, d-excess of 20).

Table 2. Physicochemical and water isotope characteristics at 12 sampling locations, S1–S6 for the Swarna River and N1–N6 for the Nethravati River

Sampling date	Sampling station	Sample No.	T (°C)	pH	Conductivity (µS/cm)	DO (mg/L)	Altitude (m asl)	δ ¹⁸ O values (‰ SMOW)	δ ² H values (‰ SMOW)	d-excess
Swarna River										
26/11	Puttige	S1	27.1	7.22	38.2	7.57	11	−2.53	−9.41	10.85
26/11	Yennehole	S2	26.7	6.62	30.7	7.62	25	−2.49	−13.07	6.83
26/11	Durga	S3	26.5	6.94	30.0	7.83	59	−2.76	−10.69	11.35
26/11	Mudar	S4	26.0	6.67	30.4	7.69	52	−3.43	−9.05	18.40
26/11	Kervashe	S5	26.2	6.78	28.0	7.59	51	−3.48	−2.05	25.80
26/11	Hermunde	S6	26.3	6.45	29.2	7.68	41	−2.76	−3.21	18.83
		mean	26.5	6.78	31.1	7.66	40	−2.91	−7.91	15.34
		<i>sd</i>	<i>0.4</i>	<i>0.3</i>	<i>3.6</i>	<i>0.09</i>	<i>18</i>	<i>0.44</i>	<i>4.34</i>	<i>6.9</i>
Nethravati River										
29/11	Bantwal	N1	27.8	7.39	45.8	7.77	9	−3.70	−0.64	28.96
29/11	Uppinangadi	N2	27.4	7.48	42.9	7.90	29	−2.99	−7.06	16.88
29/11	Mugeru	N3	27.9	7.33	43.7	8.01	36	−3.88	−8.99	22.03
29/11	Shishila hole	N4	28.9	7.45	38.1	8.25	105	−3.64	−15.44	13.72
29/11	Neriya hole	N5	28.1	7.26	39.2	7.87	90	−3.12	−11.38	13.60
29/11	Mundaje	N6	27.3	7.55	50.0	7.94	101	−4.33	−9.72	24.92
		mean	27.9	7.41	43.3	7.96	62	−3.61	−8.87	20.02
		<i>sd</i>	<i>0.6</i>	<i>0.11</i>	<i>4.4</i>	<i>0.16</i>	<i>42</i>	<i>0.49</i>	<i>4.92</i>	<i>6.30</i>

The local ground water also shows similar isotopic values of $\delta^{18}\text{O} = -2.97 \pm 0.67$ ‰ ($n=11$) for the Swarna basin and $\delta^{18}\text{O} = -3.6$ ‰ ($n=1$) for the Nethravati basin, except along the narrow coastal stretch of these basins from Mangalore (Nethravati basin) to Kodi–Bengre (Swarna basin) where the value was close to -2.0 ‰. Although only one sample was collected for the ground water of the Nethravati basin, the ground-water values earlier reported for the same season by Lambs *et al.*^[12] represent similar behaviour, as observed in Fig. 2. The spatial and seasonal variability of the isotopic composition of the ground water suggest a fractured soil water pool because of the hard rock terrains and the complexity of the hill and valley patchwork. In addition, the amount effect, which is known to amplify the heavy isotope depletion on these small basin scales, is less predominant.^[13]

The calculated d-excess ranged between 10 and 25, showing poor or no evaporation process in both the Swarna and the Nethravati basins. These higher d-excess values suggest the effect of the continental wind pattern over the region during the north-east winter monsoon or a similar wind pattern, and a higher vapour recycling process. The latter effect is mainly due to the high evapotranspiration of the tropical vegetation and the permanent fog condition, resulting in relative air humidity ranging between 65 and 95%.

Isotopic approach of the carbon biogeochemical cycle

The DOC, POC and DIC concentrations and their isotopic compositions measured at different locations along the main channel of the two rivers and their tributaries are given in Table 3. The carbon isotope composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$ values) ranged from -9.0 ± 1.0 ‰ for the Swarna basin to -8.1 ± 0.8 ‰ for the Nethravati basin. This indicates atmospheric/soil CO_2 as the principal source of riverine DIC that is leached from the weathering of non-calcareous rocks.

The DOC concentrations for both river basins were very low and represent similar average values of 0.72 ± 0.09 mg/L (Swarna River) and 0.62 ± 0.11 mg/L (Nethravati River) for the sampling season. This could be due to minimal contribution from the forested region and the possible ground-water source to the riverine DOC for the sampling period.

The spatial variation in $\delta^{13}\text{C}_{\text{DIC}}$ values in the two river basins from the riverine source to the mouth is shown in Fig. 3. The $\delta^{13}\text{C}_{\text{DIC}}$ value becomes less negative when the water flows down from the mountain sources. The $\delta^{13}\text{C}_{\text{DIC}}$ values measured for river water in the upper part of the basin were consistent with input from soil CO_2 produced by the organic matter oxidation of C_3 vegetation, prevalent in the Western Ghats. Further downstream, the general enrichment in the ^{13}C of DIC could have been caused by degassing of the isotopically light aqueous CO_2 into the atmosphere, as already shown by Amiotte-Suchet *et al.*,^[14] Brunet *et al.*^[15,16] and Doctor *et al.*^[17] The isotopic effect of degassing is pH dependent. Under open system conditions that are favourable for rapid exchange of CO_2 , kinetic isotope fractionation can result in greater isotope enrichment than is expected for the equilibrium condition. Thus, while degassing is the process primarily responsible for the large losses of CO_2 from the river, it is unlikely that it can account for the progressive downstream increase in $\delta^{13}\text{C}_{\text{DIC}}$ values unless it is accompanied by rapid pH increases towards the cross-over point at $\text{pH}=6.4$, where DIC is predominantly HCO_3^- leading to significant isotopic enrichment.^[18] It is therefore more realistic to propose, like Brunet *et al.*^[16] and Barth *et al.*,^[19] that at least some of the progressive downstream increase in $\delta^{13}\text{C}_{\text{DIC}}$ results from photosynthesis that preferentially consumes ^{12}C , particularly for the Nethravati River, where the pH values vary between 7.26 and 7.55, and for the downstream station (S1) of the Swarna River, where the pH is 7.22. Similar behaviour was observed in another tropical river catchment in Cameroon and this

Table 3. Carbon concentrations and carbon isotope ratios at 12 sampling locations, S1–S6 for the Swarna River and N1–N6 for the Nethravati River

Sample No.	HCO ₃ ⁻ (mg/L)	log pCO ₂	δ ¹³ C _{DIC} values (‰ PDB)	δ ¹⁸ O _{DIC} values (‰ SMOW)	DOC (mg/L)	SUVA (L/m/mg)	δ ¹³ C _{POC} values (‰ PDB)	POC (mg/L)	C/N
Swarna River									
S1	29.9	-2.68	-9.09	-5.81	0.80	5.66	-26.95	5.69	2.45
S2	21.4	-2.23	-7.34	-5.05	0.68	6.81	-26.37	2.60	2.40
S3	22.6	-2.52	-8.60	-1.02	0.80	6.40	-26.36	3.53	2.24
S4	18.9	-2.33	-10.23	-4.23	0.72	5.91	-26.42	3.73	2.94
S5	24.4	-2.33	-9.41	-5.35	0.55	10.73	-26.30	2.90	2.62
S6	22.6	-2.03	-9.51	-3.41	0.75	7.22	-26.82	5.30	2.66
mean	23.28	-2.41	-9.03	-4.14	0.72	7.12	-26.54	3.96	2.55
<i>sd</i>	3.71	0.23	0.99	1.75	0.09	1.86	0.28	1.26	0.24
Nethravati River									
N1	39.7	-2.73	-6.93	-4.95	0.51	9.91	-27.58	4.37	2.69
N2	31.7	-2.91	-7.72	-5.29	0.66	7.04	-26.14	2.89	1.73
N3	40.9	-2.65	-8.95	-5.23	0.55	9.40	-26.80	0.63	3.64
N4	26.2	-2.97	-7.71	-5.62	0.82	5.50	-26.61	4.92	3.51
N5	34.2	-2.66	-8.91	-4.84	0.56	9.74	-26.91	4.65	2.52
N6	42.1	-2.86	-8.28	-5.54	0.63	9.75	-26.25	4.71	(11,39)
mean	35.79	-2.79	-8.08	-5.24	0.62	8.56	-26.71	3.69	2.82
<i>sd</i>	6.18	0.13	0.78	0.31	0.11	1.84	0.52	1.67	0.78

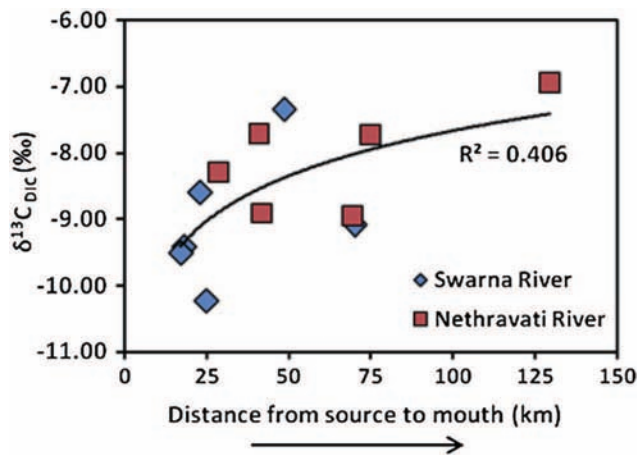


Figure 3. Spatial variability of δ¹³C DIC values along the two river courses, from the source (0 km) to the mouth (80 km for Swarna River and 147 km for Nethravati River).

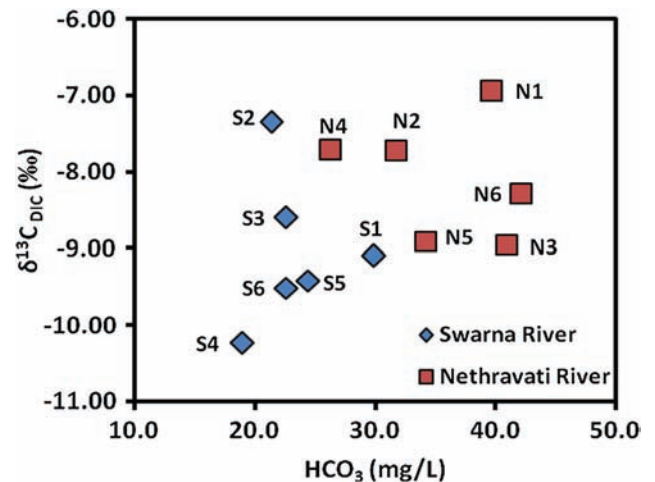


Figure 4. δ¹³C_{DIC} values versus bicarbonate ion concentrations for the two rivers.

was attributed to the selective utilisation of carbon by phytoplankton.^[15] Furthermore, the presence of a few patches of charnockite rocks in the downstream region of the Nethravati River could contribute to the relatively lower negative carbon isotope ratio value than that in the Swarna River.

The bicarbonate concentration is compared with the δ¹³C_{DIC} values for the two rivers in Fig. 4. These two rivers cluster differently, with each of them having a higher bicarbonate concentration for the downstream sample, S1 and N1. The Nethravati River water shows relatively higher HCO₃⁻ concentration and δ¹³C_{DIC} than the Swarna River water. The depleted ¹³C isotope in the Swarna River could be due to the intense silicate rock weathering and the extensive agricultural activities in the river basin from the foothills of the Western Ghats towards the coast.

The variation in DOC concentration with δ¹³C_{DIC} values is shown in Fig. 5. The δ¹³C_{DIC} value shows an increasing trend in DOC concentration for both rivers, contrary to what is generally observed for most rivers in the world,^[16,20,21] where the δ¹³C_{DIC} value decreases with increasing DOC concentration because of DOC oxidation releasing DIC with more negative δ¹³C values. However, the latter trend is observed when the average δ¹³C versus DOC for the Swarna and Nethravati Rivers are plotted. The average carbon isotopic compositions of POC (δ¹³C_{POC} values) for the two rivers were similar, with a mean value of -26.54 ± 0.28 ‰ for the Swarna River and -26.71 ± 0.52 ‰ for the Nethravati River. The average SUVA values measured for the Swarna and Nethravati Rivers were 7.12 ± 1.86 and 8.56 ± 1.84 L/m/mg of C, respectively. This relationship between high DOC concentrations and low SUVA values explains the lower δ¹³C values of DIC for the Swarna

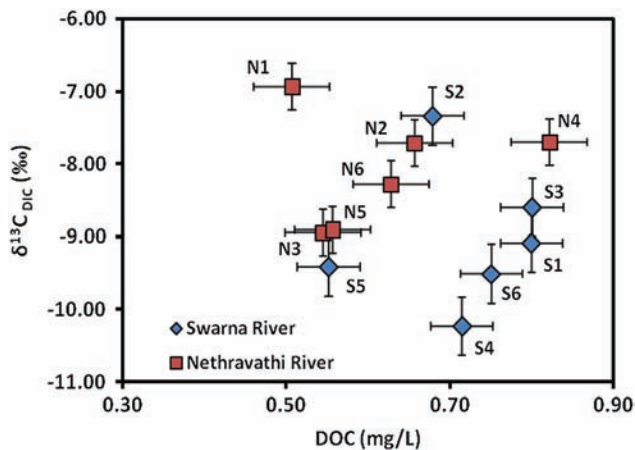


Figure 5. Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ values and DOC concentration for the two tropical rivers.

River because of higher oxidation of DOC, which releases SIC with more negative $\delta^{13}\text{C}$ values (Table 3). The average C/N ratios in the river water during the sampling period were 2.55 ± 0.24 and 2.82 ± 0.78 for the Swarna and Nethravathi Rivers, respectively.

The calculation of CO_2 partial pressure (pCO_2) in surface water also presents interesting results for the two rivers. Figure 6 shows the pCO_2 versus $\delta^{13}\text{C}_{\text{DIC}}$ values, with classical isotopic depletion when the pCO_2 increases.

DISCUSSION

Water cycle

Previous isotopic studies on the water cycle carried out in India^[22] and in the Mangalore area^[12] found that the Western Ghats coast displays very specific characteristics: a small river basin, high rainfall and run-off, a dual monsoon system, less depletion in heavy isotopes ($\delta^{18}\text{O} = -3.0$ ‰), no evaporation and, in contrast, high excess values of deuterium. Even at the same latitude in south India on the eastern coast, the ground-water display is more depleted in heavy isotopes ($\delta^{18}\text{O} = -6.0$ ‰). This reduction of around 3 ‰ from the west coast to the east coast can be explained by a progressive rainout of inflowing moisture from the Arabian Sea during

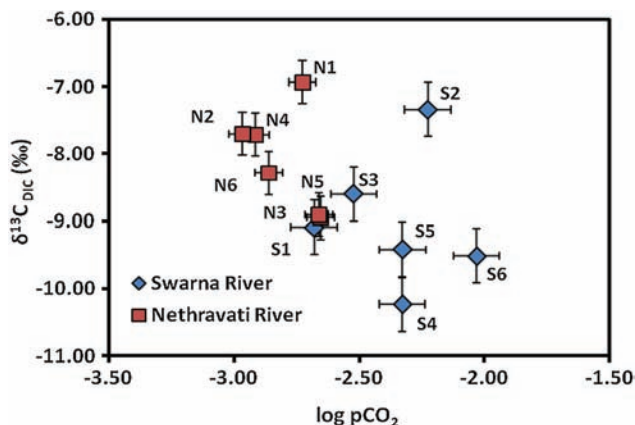


Figure 6. Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ values and the CO_2 partial pressure (pCO_2) for the two rivers.

the summer monsoon period with south-westerly winds.^[23,24] The high deuterium excess found here cannot be explained only by the winter monsoon, which is relatively dry. The marine origin of the south-west monsoon samples is clear from its d-excess value of around 10. The continental contribution to the north-east monsoon samples is evident from the higher d-excess of around 14.^[13] The pre-monsoon showers in the region show greater fluctuations in d-excess, probably because of the varying amounts of secondary effects occurring beneath the cloud base. These effects are being controlled by meteorological conditions. High water vapour recycling on the foothills of the Western Ghats, as in the tropical mist forest,^[25] could be due to the observed mist and foggy conditions, as well as to the high evapotranspiration rate.^[4] Rainfall sampling in the basin could explain the seasonal effects, as well as the influence of the coast-line and the Ghats uplift, on the d-excess values.

Carbon cycle

The carbon isotopic composition of DIC and POC, the oxygen isotopes of DIC and the carbon concentrations in the form of HCO_3^- and DOC were studied to understand the carbon cycle in these two tropical river basins. The $\delta^{13}\text{C}_{\text{DIC}}$ values depict the atmospheric CO_2 signals; however, the direct contribution to carbon in river water is known to be negligibly small.^[26] The mean isotopic values in these basins suggest that the atmospheric CO_2 utilised by plant photosynthesis (mainly C_3 in this case study) is released to the soil after organic matter oxidation and used as carbonic acid for rock-weathering processes. In the geological context of non-calcareous rocks, the hydrolysis of silicate minerals releases DIC into the river water with a more negative $\delta^{13}\text{C}$ value than on carbonate rocks. Consequently, in these two river basins, the riverine DIC mainly originated from atmospheric/soil CO_2 via soil respiration and weathering of silicate minerals. The intense weathering of source rocks was well supported by the basin characteristics of higher run-off coupled with warm temperature, suggesting the dominant atmospheric carbon input into the river water. The average $\delta^{13}\text{C}_{\text{DIC}}$ values for the Nethravathi samples were less negative than those for the Swarna samples. The main reason for this relatively heavier isotope composition could be the observed patches of carbon fluid-bearing charnockite rocks in the Nethravathi basin and the possible contribution from weathering of some carbonates towards the carbon isotopic composition of DIC compared with the more silicate-dominated Swarna basin.^[27] In addition, the average $\delta^{13}\text{C}_{\text{DIC}}$ values of Nethravathi River water samples were in good agreement with those from a study performed on the charnockite rocks of southern India.^[28]

The increase in $\delta^{13}\text{C}_{\text{DIC}}$ values from the upstream section to the downstream section of the river suggests that the soil was the CO_2 source because of organic matter oxidation of C_3 vegetation (rice, beans, potatoes, coconut, banana, areca nut, rubber trees) prevalent in the middle and downstream areas of these river basins. The two samples from Puttige (downstream of the Swarna River) and Mugeru (midstream of the Nethravathi River) show displacement from this observed trend with a slight reduction in the $\delta^{13}\text{C}_{\text{DIC}}$ values. This could be attributed to the removal of carbon from the river water by the higher phytoplankton growth during the low-flow season. This proposed rapid phytoplankton growth could well occur

in these locations because of the presence of a dam in the Swarna River, located 3 km downstream of Puttige, and a bund in Mugeru at the sampling points that obstruct continuous river water flow at these locations. This observation is supported by the relatively higher pH in these stations. Thus, the carbon isotopic composition remains more negative, with higher *in situ* plankton production for the sampling period.

The DOC concentration and POC carbon isotopic composition are very low in these two rivers compared with other rivers around the world.^[29] The reason for the low DOC in our study area could be the rapid oxidation of organic matter in the dominant red/lateritic soil coupled with warm temperature and higher humidity, resulting in low soil organic carbon. In addition, studies carried out on the soils of Karnataka, particularly in the Mangalore region, show lower soil organic carbon: 26.2 to 38.0 mg kg⁻¹ of Water-Soluble Carbon in the 0–15 cm soil depth.^[30] The ground water is known to have a low DOC and this could contribute to the lower DOC in the river water. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values measured for river and ground water suggested the mixing of river water and ground water in these basins during the sampling period, thus pointing towards the ground water as the source of the river DOC during the low-flow season.

The carbon isotopic compositions of POC measured in these basins show the dominance of soil carbon transport towards the river-suspended material. This is supported by the fact that the river isotope values ($\delta^{13}\text{C}_{\text{POC}}$) have the isotopic composition of C₃ plants (–26 ‰),^[31] that are prevalent in these basins. The carbon-enriched soil undergoing erosion in the terrestrial region reaches the fluvial system and is further transported by the river to the sea and then to the ocean, with a higher percentage in the inorganic carbon form attributed to the microbial degradation of the organic matter at various stages of its transport from the source to the ocean. In the ocean, it gets sequestered as sediments, and hence the movement of carbon in different compartments takes place, forming a cycle. The isotopic compositions of POC in downstream samples from both rivers were relatively more negative than the upstream samples. The more negative downstream carbon composition could be explained by the role of *in situ* phytoplankton production that can supply the POC.

Although lower concentrations were measured for organic carbon in both rivers, the DOC and POC in the Swarna River were relatively higher than those in the Nethravati River, in contrast with the inorganic carbon. These higher DOC concentrations were accompanied by lower SUVA values, indicating that more labile DOC (with less aromaticity) was exported within the Swarna basin during the dry season. The C/N values in POC also show that the organic carbon is 'fresher' and is probably more autochthonous than in the Nethravati River: the C/N values are closer to autochthonous production (C/N: 2–6) than to allochthonous origin (C/N: 8–20). These observations could be explained by the fact that the land use in the Swarna watershed is more agricultural than in the Nethravati basin. Agricultural lands generally export significant amounts of nutrients to rivers, and participate in enhancing autochthonous productivity. Autochthonous organic carbon production is more labile and less aromatic.^[32] Consequently, the average $\delta^{13}\text{C}_{\text{DIC}}$ value was more negative in the Swarna River than in the Nethravati River because of more efficient oxidation of DOC and POC, although both these values were very low.

Nevertheless, the $\delta^{13}\text{C}_{\text{DIC}}$ values increase from upstream to downstream and vary with the CO₂ degassing from the river water column to the atmosphere and – depending on the pH values – to phytoplankton production, which preferentially uses ¹²C. Here, for both rivers, the DOC concentrations decrease along the river length when the pCO₂ increases, contrary to other rivers around the world.^[16] This effect was certainly linked with the very low DOC values, and the potential oxidation of DOC, which was more labile as observed from the SUVA values. This observation also supports the higher trace metal concentrations reported for the Swarna basin during the low-flow period,^[33] as the labile DOC could hold them in dissolved mode for a longer time, and hence support biogeochemical cycling of trace elements in this river water. However, the mean values of both rivers present a positive correlation between pCO₂ and DOC, with the Nethravati River showing low pCO₂ and low DOC, while the Swarna River has higher pCO₂ values and DOC concentrations. Thus, the carbon cycle in these two tropical river basins depends on both terrestrial and *in situ* river plants, in addition to intense weathering of source rocks in the basin, for the carbon transfer from the atmosphere to the hydrological compartments. The time-series data on the carbon concentration and its isotopic composition will help to provide better understanding of the biogeochemical cycle of carbon in these tropical rivers.

CONCLUSIONS

This study strengthens the use of stable isotope ratios to understand the water circulation and carbon transport within different compartments of the biosphere as a whole. The study on the stable isotope ratios of oxygen ($\delta^{18}\text{O}$ values) and hydrogen ($\delta^2\text{H}$ values) reveals the sources of water in different hydrological compartments within two tropical river basins and is attributed to the continental wind pattern dictating the north-east winter monsoon and higher vapour recycling process occurring in these basins. The carbon isotopic composition ($\delta^{13}\text{C}$ value) of both organic and inorganic river carbon clearly reveals the distinct dominance of carbon from autochthonous and allochthonous origins in understanding the biogeochemical cycling of carbon in the Swarna and Nethravati Rivers during the low water-flow season. With the presence of lower organic carbon concentrations, the river carbon is mainly controlled by the atmospheric/soil CO₂ via source rock weathering in these basins. This conclusion is also supported by the relative difference in average carbon isotopic compositions in these two rivers, with the Nethravati water reflecting the average $\delta^{13}\text{C}_{\text{DIC}}$ values of carbon fluid bearing charnockite composition.

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