

Associate Editor Comments – Author Responses

L18-22 make only one sentence, no need to repeat twice “keeling plote & miller Tans..” in the abstract

These two sentences were combined to avoid the repetition of ‘Keeling plot and Millter-Tans plot’. P.1, L. 19-21.

L21: “the similar ^{13}C of DIC source”: what DIC sources and where, all rivers? Rephrase

The sentence was deleted during the revision.

L22-23 not clear what you mean by “pH and DIC speciation on measured ^{13}C -DIC”; the sentence about ^{13}C DIC in the abstract can be more focused on main result

This sentence was deleted to maintain the focus on main results of the study, i.e, stable isotopes of DIC and its spatial variability. P. 1, L.16-25

L24-25 it seems strange that ^{13}C DIC trends are not mentioned here: depleted when heterotrophic respiration and enriched in autotrophic sites?

Spatial variability of $\delta^{13}\text{C}_{\text{DIC}}$ was given now. Relatively enriched $\delta^{13}\text{C}_{\text{DIC}}$ values were found in rivers of the southeast region in which autotrophic production is dominant. Whereas depleted $\delta^{13}\text{C}_{\text{DIC}}$ values were observed in the other monsoonal rivers where heterotrophic respiration is predominant. P.1, L 16-25.

L38-40 you basically repeat what was said before in the abstract without giving more detailed interesting information such as : where is autotrophy favoured (and why), where is heterotrophy favoured and why? Abstract could be improved to provide more precise information, avoiding too general statements, and repetitions

Repeated sentences were deleted and detailed information on the spatial variability of $\delta^{13}\text{C}_{\text{DIC}}$ was given. Too general statements were deleted to maintain the focus of our main results.

L58 and L68 Raymond et al 2013 is not the appropriate reference for DIC export fluxes to coastal regions

Raymond et al. (2008) at L 58 was deleted and Richey et al. (2002) was added. P. 2, L. 53

Raymond et al. (2013) at L 68 was replaced with Joesoef et al. (2017). P. 3, L. 63

L105 it is not clear here if “equilibrium” is the right word, rather than “isotopic equilibration”. If “Isotopic equilibration with the atmosphere” refers to the changes in ^{13}C -DIC due to selective $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ fluxes at the water-air interface, then the process is very significant when water pCO_2 is high such as in small streams. (Deirmendjan and Abril 2018 JoH, and refs therein from J. Barth group). Please update the statements here L105-110.

The statements given at L 105-110 were modified. **“Though, rivers are generally in disequilibrium with atmospheric CO₂ (Raymond et al., 2013) and emit CO₂ to atmosphere due to oversaturation (Oquist et al., 2009; Campeau et al., 2017), the isotopic equilibration between the DIC and CO₂ in the atmosphere significantly influences the $\delta^{13}\text{C}_{\text{DIC}}$ in rivers (Abongwa and Atekwana, 2014; Deirmendjian and Abril, 2018) due to selective fluxes of ¹²CO₂ and ¹³CO₂ at the water-air interface. Hence, the influence of biogeochemical processes within the rivers must be considered while interpreting the $\delta^{13}\text{C}_{\text{DIC}}$ results for identification of DIC sources”**. P. 4-5, L. 100-106

L154 remove “rather than headwaters” no need

“rather than headwaters” was removed. P. 6, L.150-151

L225 and L382 under-saturation, not “unsaturation”

Sorry for the mistake. ‘unsaturation’ at L 225 and L382 were corrected to “under-saturation” P. 9, L. 219 and P. 15, L. 377

L300 exchange of CO₂ with the atmosphere, and not “exchange with atmospheric CO₂”

It was changed to “exchange of CO₂ with the atmosphere” P. 12, L. 294

L323 “Bouillon” not “bouvillion”

Sorry for the mistake: It was corrected to “Bouillon” P. 13, L. 317

L354 “interpreted “as” not “to”

The sentence was changed to “.....interpreted ‘as’ the influence of in-stream processes” P. 14, L. 348

L372 “DIC ... is largely contributed by” please rephrase

The sentence was rephrased as “These results indicated that chemical weathering of carbonate and silicate minerals by soil CO₂ (-10 to -9‰) is the major source of DIC in the Indian rivers.” P. 15, L. 366-367

L394 “the remaining into the Arabian Sea” please rephrase

The sentence was rephrased as “Nearly three fourth of this amount (7.8 Tg) reaches to the Bay of Bengal while the Arabian Sea receives only one fourth (2.5 Tg)”. P. 16, L. 387-388

L397 not sure “far less” here is correct English

“far less” was changed to “lower” P. 16, L. 391

What does shaded area mean in table 1?

It was explained in the caption of the table now. “Rivers located in the northern region (north of 16°N) of India were shown by the shaded (grey) area. Of these shaded rivers, Mahisagar to Narmada (west flowing rivers) and Godavari to Haldia (east flowing rivers) represent the rivers of the northwestern (NW) and northeastern (NE) regions of India respectively. P. 30, L. 965-968

Fig 1 is of poor graphical quality, please improve

Quality of the figure was improved. Names of all the rivers sampled are clearly visible now. The quality of labels for different types of soils was improved.

Fig2 I could not understand why degassing at pH <6.4 and at pH > 6.4 have different effect on $\delta^{13}\text{C-DIC}$. Degassing will make $\delta^{13}\text{C-DIC}$ converge to about zero per mil
Weathering by “carbonic acid derived from dissolution of atmospheric CO_2 ” is something strange, and likely not significant in soils where most of the CO_2 comes from soil respiration. Where do these statements come from? Please revise this figure and improve the legend

Figure 2 was modified and the legend was improved. Weathering of carbonate and silicate rocks by carbonic acid formed by the dissolution of atmospheric CO_2 was deleted as it is minor in soils. Biogeochemical processes influencing the $\delta^{13}\text{C-DIC}$ were also modified.

Export fluxes of dissolved inorganic carbon to the Northern Indian Ocean from the Indian monsoonal rivers

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Abstract. Rivers are an important source of dissolved inorganic carbon (DIC) to the adjacent coastal waters. In order to examine the spatial variability in the distribution and major sources of DIC in the Indian monsoonal rivers and to quantify their export flux to the north Indian Ocean, 27 major and medium rivers were sampled during the discharge period. Significant spatial variability of DIC concentrations (3.4 – 73.6 mg l⁻¹) was observed and it is attributed to spatial variations in the precipitation pattern, size of rivers, pollution, and lithology of the catchments. The stable isotopic composition of bulk-DIC ($\delta^{13}\text{C}_{\text{DIC}}$) also showed strong spatial variability (-13.0 to -1.4‰) in the Indian monsoonal rivers with relatively depleted $\delta^{13}\text{C}_{\text{DIC}}$ values were observed in rivers of the northwestern region of India (-11.1±2.3‰) while enriched values were found in rivers of the southeastern region of India (-3.5±2.3‰). This indicates that predominant contribution of DIC is from chemical weathering of carbonate and silicate minerals by soil CO₂. As the in stream processes significantly alter the $\delta^{13}\text{C}_{\text{DIC}}$ in rivers, results of the least square linear regression models of two different graphical mixing models techniques, Keeling plot and Miller-Tans plots, were used to approximate the $\delta^{13}\text{C}$ of DIC source. Approximated $\delta^{13}\text{C}$ values (-2.0 to -3.0‰) indicated that chemical weathering of carbonate and silicate minerals by soil CO₂ is the major source of DIC in the Indian monsoonal rivers. Spatial variability in the deviation of $\delta^{13}\text{C}_{\text{DIC}}$ from the approximated $\delta^{13}\text{C}$ of source indicated that may probably due to dominant autotrophic production predominantly controls the $\delta^{13}\text{C}_{\text{DIC}}$ in rivers of the southeast region whereas, heterotrophic decomposition of organic matter largely influences in the other Indian

30 ~~monsoonal rivers. Least square linear regression models of both Keeling and Miller Tans~~
31 ~~plots approximated the similar $\delta^{13}\text{C}$ of DIC source (-2.0 and -3.0‰ respectively). Further,~~
32 ~~the $\delta^{13}\text{C}$ of CO_2 was approximated in order to filter the influence of pH and DIC speciation~~
33 ~~on the measured $\delta^{13}\text{C}_{\text{DIC}}$. Our results indicated that DIC in the Indian rivers is contributed by~~
34 ~~chemical weathering of carbonate minerals, but largely influenced by autotrophic production~~
35 ~~in rivers from the southeast region and heterotrophic decomposition of organic matter in the~~
36 ~~other Indian monsoonal rivers.~~ It is estimated that the Indian monsoonal rivers annually
37 export ~10.3 Tg of DIC to the northern Indian Ocean, of which the major fraction (75%)
38 enters into the Bay of Bengal and the remaining reaches to the Arabian Sea. This is
39 consistent with the freshwater flux which is three times higher to the Bay of Bengal (~378
40 $\text{km}^3 \text{ yr}^{-1}$) than to the Arabian Sea (122 $\text{km}^3 \text{ yr}^{-1}$). Despite discharge from the Indian
41 monsoonal rivers account for only 1.3% of the global freshwater discharge, they
42 disproportionately export 2.5% of the total DIC export by the world major rivers. Despite
43 rivers from the SW region of India export an order of magnitude lower DIC (0.3 Tg yr^{-1}) than
44 the rivers from other regions of India, the highest yield of DIC was found in the former and it
45 is attributed to intense precipitation (~3000 mm), favorable natural vegetation of tropical
46 moist deciduous and tropical wet evergreen and semi evergreen forests, -tropical wet climate,
47 high soil organic carbon and the dominance of red loamy soils in catchments of the rivers
48 from SW region. ~~Our study demonstrates that significant spatial variability of the~~
49 ~~hydrological, lithological and environmental conditions in the catchments and in stream~~
50 ~~processes (autotrophic production and heterotrophic decomposition of organic matter)~~
51 ~~strongly controls the DIC in the Indian monsoonal rivers.~~

52 *Keywords:* dissolved inorganic carbon, export flux, Indian rivers, Bay of Bengal, Arabian
53 Sea, North Indian Ocean

54 **1. Introduction**

55 Dissolved inorganic carbon (DIC) is one of the major constituent of carbon species in
56 rivers. DIC in rivers mainly originates from the geogenic (weathering of carbonate and
57 silicate rocks) and biogenic (decomposition of organic matter in soils) sources (Meybeck,
58 1987; Mook and Tan, 1991; Gaillardet et al., 1999, Dessert et al., 2001; Viers et al., 2007;
59 Raymond et al., 2008; Tamooh et al., 2013). The former consumes atmospheric carbon
60 dioxide (CO₂) while the latter releases CO₂ fixed by the terrestrial plants. In addition to these
61 major sources in the catchment, DIC is also contributed by various physical and biological
62 processes within the rivers. For instance, heterotrophic decomposition of organic matter,
63 photo-oxidation of dissolved organic carbon (DOC), autotrophic respiration and dissolution
64 of atmospheric CO₂ contribute DIC to rivers. On the other hand, autotrophic production by
65 aquatic plants (photosynthesis) and evasion of CO₂ to atmosphere with draw DIC from rivers.
66 All these processes in the catchments and within the rivers are strongly coupled to
67 atmospheric CO₂ because they act as either sink or source of atmospheric CO₂ (e.g. Berner et
68 al., 1983; Mook and Tan, 1991; Gaillardet et al., 1999; ~~Raymond et al., 2008~~[Richey et al.,
69 2002](#)). The DIC in rivers and its export to the coastal oceans is thus intimately linked to the
70 global carbon cycle (Campeau et al., 2017)

71 Riverine export fluxes of DIC to coastal regions of the world oceans have been
72 estimated on the global (Gaillardet et al., 1999; ~~Raymond et al., 2013~~) and regional scales
73 (Richey et al., 2002; Wallin et al., 2013; Crawford et al., 2014; Campeau et al., 2014; Kocio
74 et al., 2015) to understand the component of DIC in the global carbon budget. Annual export
75 flux of DIC from the world major river systems to the global ocean has been estimated as
76 ~327 - 385 Tg (1Tg=10¹²g) (Ludwig et al., 1998; Meybeck and Vorosmarty, 1999). However,
77 many of the regional studies on DIC export fluxes were limited only to the major river
78 systems (e.g. Gaillardet et al., 1999; ~~Raymond et al., 2013~~[Joesoef et al., 2017](#)), for example,
79 the Mississippi (Raymond and Cole, 2003; Raymond et al., 2008; Cai et al., 2008),

80 Changjiang and Pearl (Cai et al., 2008) and Congo (Wang et al., 2013) rivers etc. Regional
81 studies on the riverine export fluxes of DIC are very important for the global carbon cycle
82 and budget as the export fluxes are largely dependent on the hydrological, lithological and
83 environmental conditions, which are highly variable on the regional scales. However, DIC
84 measurements are still lacking in several medium rivers from different regions of the world in
85 general and Asia in particular.

86 Studies on the sources and export fluxes of DIC from the Indian rivers are very
87 limited. Though DIC measurements were conducted in some Indian estuaries, for example,
88 Mandovi and Zuari (Sarma et al., 2001), Godavari (Sarma et al., 2011), Cochin (Gupta et al.,
89 2009; Bhavya et al., 2018), Hooghly (Mukhopadhyay et al., 2002; Samanta et al., 2015),
90 Mahanadi (Pattanaik et al., 2017) and Chilka (Gupta et al., 2008; Muduli et al., 2013), they
91 were confined only to the internal cycling of DIC and exchange of CO₂ at the air-water
92 interface, but not focused on the sources and export fluxes of DIC. The major sources of DIC
93 in the Indian rivers remain unclear, except only a couple of rivers, Krishna (Das et al., 2005;
94 Laskar et al., 2014) and Ganges (Samanta et al., 2015). Further, the quantity of annual DIC
95 export by the Indian rivers to the coastal regions is unknown. Here, we made an attempt to
96 understand the major sources of DIC in the Indian monsoonal rivers (Fig. 1) using $\delta^{13}\text{C}_{\text{DIC}}$ as
97 a potential tracer, and to estimate the riverine export flux of DIC to the north Indian Ocean
98 from the Indian subcontinent.

99 The stable isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) is widely used to identify the major
100 sources of DIC in the aquatic systems (e.g. Singh et al., 2005; Tamooch et al., 2013; Samanta
101 et al., 2015; Zou, 2016). The isotopic composition of DIC originated by dissolution of
102 atmospheric CO₂ is about 0‰ (Coplen et al., 2002) whereas it is about -27 to -26‰ if the
103 DIC is derived from oxidation of organic matter produced by C₃ plants (O’Leary, 1988). The
104 $\delta^{13}\text{C}$ of DIC generated by carbonic acid (formed by soil CO₂ dissolution) weathering of

105 silicates is about -21 to -17‰ (Solomon and Cerling, 1987) while it is in the range of -10 to -
106 9‰ for carbonate rocks because half of the carbon comes from carbonate rocks (0‰, Land,
107 1980) during weathering. The weathering of silicate and carbonate minerals yield $\delta^{13}\text{C}_{\text{DIC}}$ in
108 the range of -8 to -7‰ and -4 to -3‰, respectively, if the carbonic acid formed by the
109 dissolution of atmospheric CO_2 . Though the $\delta^{13}\text{C}$ of DIC derived from different sources is
110 well separable (Deines et al., 1974), the isotopic fractionation by in-stream physical and
111 biological processes alters the $\delta^{13}\text{C}$ of DIC source (Fig. 2). For example, photosynthesis and
112 ~~equilibration with atmospheric CO_2 degassing~~ enriches (O'Leary, 1988; Finlay, 2004; Parker
113 et al., 2005, 2010; [Polsenaere and Abril, 2012](#); [Venkiteswaran et al., 2014](#)) while the
114 heterotrophic decomposition of organic matter and photo-oxidation of dissolved organic
115 carbon depletes the $\delta^{13}\text{C}$ of DIC (Opsahl and Zepp, 2001; Finlay, 2003; Waldron et al., 2007;
116 Vahatalo and Wetzel, 2008) (Fig. 2). ~~Of these processes, equilibrium with atmospheric CO_2~~
117 ~~is of less significance because~~ Though, rivers are generally in disequilibrium with atmospheric
118 CO_2 (Raymond et al., 2013) and emit CO_2 to atmosphere due to oversaturation (Oquist et al.,
119 2009; Campeau et al., 2017), the isotopic equilibration between the DIC and CO_2 in the
120 atmosphere significantly influences the $\delta^{13}\text{C}_{\text{DIC}}$ in rivers (Abongwa and Atekwana, 2014;
121 Deirmendjian and Abril, 2018) due to selective fluxes of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ at the water-air
122 interface. Nevertheless Hence, the influence of ~~internal biogeochemical~~ processes within the
123 rivers must be considered while interpreting the $\delta^{13}\text{C}_{\text{DIC}}$ results for identification of DIC
124 sources. The main objectives of this study are to (i) identify the major sources of DIC in the
125 Indian monsoonal rivers, (ii) estimate the export flux and yield of DIC to the north Indian
126 Ocean and (iii) examine the major processes in the catchments and within the rivers
127 controlling DIC in the Indian monsoonal rivers.

128 2. Study region, sampling and methods

129 2.1 Study Area

130 The Indian peninsula bifurcates the north Indian Ocean into the Bay of Bengal and the
131 Arabian Sea. Although these two basins occupy the same latitudinal belt, their
132 oceanographic processes were reported to be remarkably different due to higher freshwater
133 flux into the Bay of Bengal ($1.63 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$) than to the Arabian Sea ($0.3 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$;
134 Subramanian, 1993; Gauns et al., 2005). The large freshwater influx leads to the formation
135 of a strong vertical salinity stratification in the Bay of Bengal (Varkey et al., 1996) that
136 prevents vertical mixing of nutrient rich sub-surface water with the surface (Prasanna Kumar
137 et al., 2004). As a result, the Bay of Bengal is considered to be relatively less productive
138 (Prasannakumar et al., 2002) than the adjacent Arabian Sea, which is one of the highly
139 productive zones in the world (Madhupratap et al., 1996; Smith, 2001; Barber et al., 2001)
140 due to injection of nutrients into the surface through the seasonal upwelling and convective
141 mixing (Shetye et al., 1994; Madhupratap et al., 1996; Muraleedharan and Prasannakumar,
142 1996).

143 Discharge from the Indian monsoonal rivers is largely fed by the monsoon induced
144 precipitation over the Indian subcontinent, which receives >80% of its annual rainfall during
145 the southwest (SW) monsoon period (June-September) (Soman and Kumar, 1990). Though
146 some amount of rainfall occurs during the northeast (NE) monsoon (December-March), it
147 does not generate discharge as it will be stored within the dam reservoirs for domestic,
148 industrial and irrigation purposes. Discharge from the Indian monsoonal rivers mainly occurs
149 during the SW monsoon season (Vijith et al., 2009; Sridevi et al., 2015) hence, these rivers
150 are called as monsoonal rivers. Since the major portion of the annual freshwater discharge
151 occurs only during the SW monsoon, the entire estuary is filled with freshwater (Vijith et al.,
152 2009; Sridevi et al., 2015) during this period. As discharge is small during the rest of the
153 year, the discharge during the SW monsoon (wet period) is considered to be equivalent to the
154 annual discharge of the monsoonal rivers. Based on rainfall intensity, forest cover, vegetation

155 and soil type in the catchment, rivers sampled in the present study were categorized into 4
156 groups, namely the northwest (NW), southwest (SW), southeast (SE) and northeast (NE)
157 rivers of India (Fig. 1). The SW region of India is characterized by the intense rainfall during
158 SW monsoon (~3000 mm) following the NE (1000-2500 mm), SE (300-500 mm) and NW
159 (200-500 mm) regions of India (Soman and Kumar, 1990). The SW rivers drain red loamy
160 soils while the NW rivers drain black soils. Except the major rivers Godavari and Krishna,
161 all the rivers reaching Bay of Bengal (NE and SE rivers) drain red loamy and alluvial soils in
162 their upper and lower catchments respectively. The Godavari and Krishna rivers drain black
163 soils in their upper catchment whereas red loamy and alluvial soils in their middle and lower
164 catchments respectively (Geological Survey of India; www.gsi.gov.in). Based on discharge,
165 the monsoonal rivers in this study were divided into two types, namely, the major ($>150 \text{ m}^3 \text{ s}^{-1}$)
166 and medium ($<150 \text{ m}^3 \text{ s}^{-1}$) rivers.

167 2.2 Sample collection

168 Water samples were collected from the freshwater regions of the estuaries ~~rather than~~
169 ~~from head waters~~ to obtain reliable export fluxes of DIC to the coastal ocean. Samples were
170 collected at 2 to 3 locations to minimize the spatial variability within the freshwater zone of
171 the estuary. Further, to minimize the inter-annual variability in DIC concentrations, sampling
172 was conducted in two different years and the mean was used for export flux estimations.
173 Further, samples were collected in mid-stream of the river using a local mechanized boat to
174 avoid the contamination from river banks.

175 *In-situ* measurements and sample collection were conducted in 27 rivers of the Indian
176 subcontinent (Fig. 1) during the SW monsoon season of the years, 2011 and 2014. Surface
177 water samples at each location were collected for phytoplankton biomass (Chl-*a*), DIC and
178 dissolved oxygen (DO). Samples for DIC were collected in air-tight crimp-top glass bottles
179 and added poison (mercuric chloride) to arrest the biological activity. DO analysis was

180 carried out at a temporary shore laboratory set up for sample processing after the completion
181 of sampling on each day. Water samples were filtered through GF/F (nominal pore size of
182 0.7 μ m) under moderate vacuum and stored in liquid nitrogen for Chl-*a* analysis.

183

184

185 **2.3. Methods**

186 Temperature and salinity at the sampling locations were measured using a
187 conductivity-temperature-density (CTD) profiling system (Sea Bird Electronics, SBE 19 plus,
188 United States of America). Concentration of DO was determined by a Winkler's method
189 (Carritt and Carpenter, 1966) using an auto titrator (Metrohm, Switzerland) with
190 potentiometric end point detection. The analytical precision of the method was $\pm 0.07\%$
191 (RSD). Dissolved oxygen saturation is computed following formulations given by Garcia and
192 Gordon (1992). DIC concentrations in water samples were measured at our Institute
193 laboratory using Coulometer (UIC Inc., USA) connected to an automatic sub-sampling
194 system. Based on the repeated analysis of samples and standards, the precision of the method
195 was $\pm 0.02 \text{ mg l}^{-1}$. The certified reference materials (CRM) supplied by Dr. A.G. Dickson,
196 Scripps Institute of Oceanography, USA and internal standards were used to test the accuracy
197 of our DIC measurements and it was found to be within ± 0.2 to 0.3% . Potentiometric Gran
198 titration method (Metrohm, Switzerland) was used for determination of pH and total
199 alkalinity and followed the standard operating procedures given by Department of Energy
200 (DOE) (1998).

201 The stable carbon isotopic composition of DIC in the water was measured on Gas
202 Bench coupled with isotope ratio mass spectrometer (EA-IRMS-Delta V,
203 Finnigan, Germany). 50 ml air-tight bottles with rubber septa were filled with 0.5 ml of high
204 purity ortho-phosphoric acid and purged with high purity helium. About 1 ml of water sample

205 is injected to the bottle and incubated at constant temperature of 50°C for 12 hours. The CO₂
206 extracted into the head space is injected to the IRMS through gas bench. The results are
207 expressed relative to conventional standards, that is, pee dee belemnite (PDB) limestone for
208 carbon (Coplen, 1996) as δ values, defined as:

$$209 \quad \delta R = [(X_{\text{sample}} - X_{\text{standard}}) / X_{\text{standard}}] \times 10^3 \text{ ‰}$$

210
211 where R refers to ¹³C and X stands for ¹³C/¹²C. The high-purity tank of CO₂ was used as
212 working standard for carbon. These gases were calibrated with IAEA standards. Standard
213 deviation on 20 aliquots of the same sample was lower than 0.05‰ for δ¹³C. Chlorophyll-*a*
214 (Chl-*a*) on the filter was extracted into di-methyl formamide (DMF) and measured the extract
215 fluorometrically using a spectrofluorophotometer (Varian Eclipse, Varian Electronics., UK)
216 following Suzuki and Ishimaru (1990). Annual mean discharge data of the rivers was taken
217 from Meybeck and Ragu (1995, 1996), Central Water Commission, New Delhi (2006, 2012)
218 and Kumar et al. (2005). Catchment area of the rivers was obtained from Water Resources
219 Information System of India (WRIS, www.india-wris.nrsc.gov.in). Soil organic carbon data
220 was taken from Kishwan et al. (2009) and Sreenivas et al. (2016), and the rainfall data was
221 obtained from Soman and Kumar (1990). Dissolved organic carbon (DOC) data for the
222 Indian rivers was taken from Krishna et al. (2015)

223 Total export flux of DIC from each river was estimated by multiplying the mean
224 concentrations of DIC at near zero salinity (river end member) with the annual discharge.
225 Spatial variability of DIC concentrations within the river was minimized to a large extent by
226 collecting samples from 2 to 3 locations in each river while the inter-annual variability by
227 collecting samples during discharge periods of two years. However, variability in DIC
228 concentrations within the discharge period results in some uncertainties in our estimations of
229 DIC export fluxes. Time series measurements in the Godavari estuary (our unpublished
230 results) revealed that the variability in DIC concentrations within the discharge period is up to

231 10%. Therefore, the error associated with our DIC flux estimates may be about 10%. DIC
232 flux normalized by catchment area (yield) was calculated by dividing the total DIC export
233 flux of the river by its catchment area.

234 **3. Results**

235 *3.1. Hydrographic characteristics*

236 Surface water temperatures were higher in rivers from the NE and SE regions (mean
237 $30.9 \pm 1.2^\circ\text{C}$) than the rivers from SW and NW regions ($27.3 \pm 1.5^\circ\text{C}$) of India. Dissolved
238 oxygen saturation varied from as low as 63% to as high as 105%, with a mean saturation of
239 $90 \pm 11\%$. The rivers from SW region of India recorded more under-saturation of DO ($82 \pm 7\%$)
240 than the rivers located in the NE ($89 \pm 15\%$), NW ($93 \pm 3\%$) and SE ($96 \pm 11\%$) regions of India.
241 Chlorophyll-*a* (Chl-*a*) concentrations varied broadly from 0.8 to 7.5 mg m^{-3} , with relatively
242 higher mean concentrations in rivers of the SE region ($4.7 \pm 2.5 \text{ mg m}^{-3}$) followed by the SW
243 ($2.8 \pm 0.7 \text{ mg m}^{-3}$) regions of India. On the other hand, relatively low Chl-*a* was observed in
244 the medium ($2.6 \pm 1.3 \text{ mg m}^{-3}$) than the major estuaries ($3.2 \pm 2.1 \text{ mg m}^{-3}$).

245 *3.2 DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$*

246 DIC concentrations in the Indian monsoonal rivers widely varied from 3.4
247 (Bharathapuzha) to 73.6 mg l^{-1} (Vellar), with a significant spatial variability (Fig. 3a; Table
248 1). Highest mean DIC concentration was observed in rivers of the SE region ($37.4 \pm 6.3 \text{ mg l}^{-1}$)
249 while the lowest was found in the SW region ($5.2 \pm 2.1 \text{ mg l}^{-1}$) of India. Intermediate values
250 were found in rivers of the NW ($28.4 \pm 8.9 \text{ mg l}^{-1}$) and NE ($17.1 \pm 6.2 \text{ mg l}^{-1}$) regions of India.
251 DIC concentrations were found to be similar in the major ($22.7 \pm 13.6 \text{ mg l}^{-1}$) and medium
252 ($21.1 \pm 13.2 \text{ mg l}^{-1}$) rivers (homoscedastic Student's t-test; $p=0.76$). Mean DIC concentration
253 found in this study ($21.4 \pm 16.3 \text{ mg l}^{-1}$) is similar to those observed earlier in the major river
254 systems of India (Brahmaputra; Singh et al., 2005) and elsewhere in the world, for example,
255 British rivers (Jarvie et al., 2017) and Swedish rivers (Campeau et al., 2017). However, DIC

256 concentrations in the present study are higher than the global mean DIC (10.3 mg l^{-1} ,
257 Meybeck and Vorosmarty, 1999) (Table 1), but lower than those reported in the rivers
258 draining into the Gulf of Trieste (N Adriatic; $37\text{-}66 \text{ mg l}^{-1}$, Tamse et al., 2014).

259 The $\delta^{13}\text{C}_{\text{DIC}}$ varied from -13.0 to -1.4‰ , with a significant spatial variability (Fig. 3d;
260 Table 1) in the rivers sampled. Relatively depleted $\delta^{13}\text{C}_{\text{DIC}}$ values were observed in rivers of
261 the NW region ($-11.1\pm 2.3\text{‰}$) while enriched $\delta^{13}\text{C}_{\text{DIC}}$ was found in rivers of the SE region ($-$
262 $3.5\pm 2.3\text{‰}$) of India (Fig. 3d). The $\delta^{13}\text{C}_{\text{DIC}}$ values found in this study are well within the range
263 of values reported earlier in rivers of India (Das et al., 2005) and elsewhere in the world, for
264 example, Swedish streams (-27.6 to -0.6‰ ; Campeau et al., 2017) and rivers from Italy and
265 Slovenia (-12.8 to -7.7‰ , Tamse et al., 2014).

266 3.3. Export fluxes and yield of DIC

267 Annual export flux of DIC to the coastal ocean from the individual rivers varied
268 broadly from 0.01 Tg (Chalakuadi) to as high as 2.33 Tg (Krishna) (Fig. 3b; Table 1). Among
269 the rivers sampled, rivers of the NE region of India export higher DIC (6.52 Tg yr^{-1}) while
270 the lowest was found from rivers of the SW region (0.24 Tg yr^{-1}) (Table 1). The Indian
271 monsoonal rivers together export about 10.32 Tg yr^{-1} of DIC to the northern Indian Ocean, of
272 which 7.81 Tg (75%) enters into the Bay of Bengal and the remaining into the Arabian Sea
273 (2.51 Tg). The yield of DIC ranged from 2.8 (Bharathapuzha) to $20.7 \text{ g m}^{-2} \text{ yr}^{-1}$ (Baitarani)
274 (3c; Table 1), excluding the exceptionally high yield of $119 \text{ g m}^{-2} \text{ yr}^{-1}$ from Haldia river. The
275 mean yield was found to be more or less similar in rivers from all the four regions of India,
276 i.e, NW ($8.4 \text{ g m}^{-2} \text{ yr}^{-1}$), SW ($8.8 \text{ g m}^{-2} \text{ yr}^{-1}$), SE ($6.6 \text{ g m}^{-2} \text{ yr}^{-1}$) and NE ($7.7 \text{ g m}^{-2} \text{ yr}^{-1}$)
277 regions. Despite the export flux of DIC is lowest from rivers of the SW region (0.24 Tg yr^{-1}),
278 interestingly, the yield from rivers of this region is on par with (even slightly higher than) the
279 other Indian monsoonal rivers (Table 1; Fig. 3b&c). Yields of DIC found in this study are
280 similar to those found earlier in rivers elsewhere in the world (Huang et al., 2012).

281 4. Discussion

282 4.1 Distribution of DIC in the Indian monsoonal rivers

283 Distribution of DIC in the Indian monsoonal rivers showed large spatial variability,
284 with the lowest values in rivers from the SW region of India (Fig. 3a). DIC concentrations in
285 rivers are known to be influenced by the intensity of precipitation over the catchment, basin
286 lithology (Giesler et al., 2013; Lofgren et al., 2014), length of the fluvial network (Hotchkiss
287 et al., 2015) and in-stream physical and biological processes (Mook and Tan, 1991; Raymond
288 et al., 2008). The spatial distribution of rainfall over the Indian subcontinent
289 (www.imd.gov.in) shows that the SW region receives the highest annual rainfall (~3000 mm)
290 than the rest of India (Soman and Kumar, 1990).

291 The intense precipitation over the SW region is expected to cause higher weathering
292 rates and thus higher DIC in rivers (e.g., Gupta et al., 2011), but lower DIC concentrations
293 were found in rivers of this region. It could be due to the influence of dilution because the
294 dense precipitation over the small catchment area (Table 1) might have diluted DIC
295 concentrations in rivers of this region. In order to understand the influence of the density of
296 rainfall on DIC in rivers, we normalized the volume of discharge from the river with its
297 catchment area. The catchment area normalized volume of discharge was found to be much
298 higher in rivers from the SW region ($1.71 \text{ m}^3 \text{ m}^{-2}$) than the rivers from SE ($0.17 \text{ m}^3 \text{ m}^{-2}$), NE
299 ($0.6 \text{ m}^3 \text{ m}^{-2}$) and NW ($0.32 \text{ m}^3 \text{ m}^{-2}$) regions of India. About three times higher catchment
300 area normalized discharge might have diluted DIC concentrations in the rivers of the former
301 region. A strong exponential decrease in DIC concentrations with increasing rainfall over the
302 catchment ($r^2= 0.72$, $p<0.001$; Fig. 4a) also suggests that DIC concentration in the Indian
303 rivers are strongly influenced by density of precipitation over the catchment.

304 Rivers of the SW region are relatively small in size, both in terms of catchment area
305 (total catchment area: $20 \times 10^3 \text{ km}^2$) and the length of the river (mean length: 126 km), than

306 the rivers from other regions (SE, NE and NW) of India (Table 1). Since the contribution of
307 DIC from in-stream processes, such as decomposition of organic matter, has been
308 demonstrated to increase along the course of the fluvial network (Hotchkiss et al., 2015),
309 possibly due to increase in the residence time of water (Catalan et al., 2016), the lowest DIC
310 concentrations found in rivers from the SW region may also, at least partly, be due to their
311 small size. Fairly good positive correlation between DIC concentrations and length of the
312 rivers ($r^2=0.38$, $p<0.01$; Fig. 4b) also support this argument.

313 The major physical and biological processes controlling DIC concentrations in rivers
314 are the exchange of CO₂ with the atmosphere, ie CO₂, autotrophic removal and heterotrophic
315 addition of DIC. Since the Indian monsoonal estuaries have been reported to be a source of
316 CO₂ to the atmosphere during the discharge period due to heterotrophic decomposition of
317 organic matter (Sarma et al., 2001, 2011, 2012; Gupta et al., 2008, 2009; Bhavya et al.,
318 2018), the DIC input from the dissolution of atmospheric CO₂ may be unlikely. On the other
319 hand, organic matter decomposition is expected to add significant amount of DIC as
320 enhanced bacterial respiration rates were reported during this period (Sarma et al., 2011;
321 2012). In contrast, significant negative correlation between chlorophyll-*a* and DIC ($r^2=-0.44$,
322 $p<0.01$; Fig. 4c), except few SE rivers where elevated phytoplankton biomass (Chl-*a*: >5 mg
323 m^{-3}) was recorded, suggesting that autotrophic removal of DIC is also significant in the
324 Indian monsoonal rivers during the study period. A significant positive relationship was
325 observed between the $\delta^{13}C_{DIC}$ and Chl-*a* ($r^2=0.49$; $p<0.01$; Fig. 4d), supporting this argument
326 because preferential uptake of ^{12}C than ^{13}C during photosynthesis leaves the residual DIC
327 enriched in ^{13}C . On the other hand, $\delta^{13}C_{DIC}$ showed significant positive correlation with DO
328 saturation ($r^2=0.50$, $p<0.01$; Fig. 4e) (depleted $\delta^{13}C_{DIC}$ values at more under saturation of DO)
329 and DOC concentrations ($r^2=0.43$, $p<0.01$; Fig. 4f) as was observed in the Xi river (Zou et al.,
330 2016). Altogether, enriched $\delta^{13}C_{DIC}$ are associated with higher DOC, less under saturation of

331 DO and higher phytoplankton biomass (Chl-a) while the depleted $\delta^{13}\text{C}_{\text{DIC}}$ are associated more
332 under saturation of DO and less DOC. This suggests that both autotrophic removal and
333 heterotrophic addition control DIC in the Indian rivers during the discharge period, with a
334 considerable spatial variability. However, influence of these processes on DIC
335 concentrations is difficult to separate with this bulk $\delta^{13}\text{C}_{\text{DIC}}$ data set, as the $\delta^{13}\text{C}_{\text{DIC}}$ in rivers is
336 also influenced by pollution, catchment lithology and outgassing of CO_2 (Shin et al., 2011;
337 Brunet et al., 2005; Bouvillion et al., 2009; Zeng et al., 2011; Tamooh et al., 2013).
338 Excluding Sabarmati and Mahisagar rivers, DIC concentrations showed fairly good linear
339 relationship with population density over the catchment of the river ($r^2=0.41$, $p<0.01$; Fig.
340 4g), suggesting that considerable influence of pollution from the mega cities and industries on
341 DIC in the Indian rivers.

342 Spatial distribution of soils shows that rivers of the NW region of India and upper
343 reaches of Krishna and Godavari rivers drain the lime-rich black soils (Fig. 1) while rivers
344 from the SW region drain red loamy soils. Whereas, the east-flowing rivers drain the lime-
345 poor red sandy soils in the upper but lime-rich alluvial soils in the lower reaches (Fig.1).
346 Lateritic soils, which are poor in lime and silicate, occupied the catchment of the rivers in the
347 SW region of India. Relatively lower chemical weathering rates of the lateritic than the non-
348 lateritic soils could be one of the reasons for the observed lower DIC concentration the rivers
349 from SW region of India. A significant positive correlation was found between total
350 alkalinity (TA) and $\delta^{13}\text{C}_{\text{DIC}}$ ($r^2=0.52$; $p<0.01$; Fig. 4h), suggesting that significant contribution
351 of DIC is from weathering of carbonate minerals in the catchment. Though the higher
352 chemical weathering rates were reported for the Deccan Trap basalts (Das et al., 2005;
353 Singh et al., 2005), which occupied the catchments of rivers of the NW region of India and
354 upper reaches of Godavari and Krishna, higher DIC concentrations were also observed in

355 rivers draining over the metamorphic rocks. This suggests that the influences of factors other
356 than bedrock are also significant on the concentrations of DIC in the Indian rivers.

357 **4.2 Major sources of DIC in the Indian monsoonal rivers**

358 Though, the $\delta^{13}\text{C}_{\text{DIC}}$ is a promising tool to decipher the sources of DIC, its
359 interpretation for source material identification in rivers is still challenging because multiple
360 physical and biological processes within the rivers significantly alter the $\delta^{13}\text{C}$ of DIC source.
361 The influence of major in-stream processes on the $\delta^{13}\text{C}_{\text{DIC}}$ must be separated before
362 interpreting the results for major sources of DIC, failing which leads to erroneous
363 conclusions. In order to identify and separate DIC sources, we used here two different
364 graphical mixing model techniques, Keeling plot (Keeling, 1958; Pataki et al., 2003) and
365 Miller-Tans plots (Miller and Tans, 2003). These models approximate the hypothetical $\delta^{13}\text{C}$
366 of source material as an intercept (in Keeling plot) and slope (in Miller-Tans plot) of the least
367 square linear regression equations (Pataki et al., 2003; Campeau et al., 2017). The deviations
368 | from the approximated $\delta^{13}\text{C}$ of source can be interpreted ~~to~~as the influence of in-stream
369 processes. Further, we approximated the $\delta^{13}\text{C}$ of CO_2 using a set of enrichment factors of
370 isotopic fractionation across the carbonate species (Zhang et al., 1995) in order to filter the
371 impact of DIC speciation and pH on the bulk $\delta^{13}\text{C}_{\text{DIC}}$ values. This approach has already
372 been used by Quay et al. (1992), Mayorga et al. (2005) and recently by Campeau et al.
373 (2017).

374 Significant negative relationships were observed in both Keeling plot ($\delta^{13}\text{C}_{\text{DIC}}$ as a
375 function of $1/\text{DIC}$; Fig. 5a) and Miller-Tans plot ($\delta^{13}\text{C}_{\text{DIC}} \times \text{DIC}$ as a function of DIC ; Fig.
376 5b) ($r^2=0.61$, $p<0.01$ and $r^2=0.72$, $p<0.01$ respectively) of DIC in the Indian rivers, except the
377 rivers draining the Deccan Trap basalts. Both graphical mixing models, Keeling and Muller-
378 Tans plots, approximated the similar $\delta^{13}\text{C}$ of source material (-3.0‰ and -2.0‰ respectively;
379 Fig. 5a&b), suggesting that weathering of carbonate minerals is the predominant source of

380 DIC in the Indian monsoonal rivers rather than biogenic soil CO₂. Calculated δ¹³C of CO₂
381 ranged from -21.5 to -9.6‰ in the Indian rivers with a mean value of -13.0±2.7‰. Calculated
382 δ¹³C of CO₂ is linearly correlated with the measured δ¹³C_{DIC}, but correlation coefficient (r²) is
383 only 0.51 (Fig. 5c), suggesting that significant spatial variability in the influence of in-stream
384 processes on the δ¹³C_{DIC}. The Miller-Tans plot of CO₂ (δ¹³C-CO₂ x CO₂ as a function of
385 CO₂) showed highly significant linear regression model with a slope of -10.7‰ (r²=0.97;
386 p<0.001; Fig. 5d). These results indicated that chemical weathering of carbonate and silicate
387 minerals by soil CO₂ (-10 to -9‰) is the major source of DIC in the Indian rivers. ~~is largely~~
388 ~~contributed by~~ ~~chemical weathering of carbonate and silicate minerals by soil CO₂ (-10 to~~
389 ~~9‰)~~. Deviations of the measured δ¹³C_{DIC} (-13.0 to -1.4‰) from that of the approximated
390 δ¹³C of DIC source (-3.0 to -2.0‰) and δ¹³C of CO₂ (-10.7‰) could be due to the influence
391 of in-stream process. In more than 75% of the Indian rivers sampled, the deviation from the
392 δ¹³C of DIC source is towards negative side (depletion) (δ¹³C_{DIC} < -3.0‰), suggesting that
393 heterotrophic decomposition of organic matter is the dominant process controlling DIC in
394 these rivers. While, no (or very little) deviation was observed only in rivers from the SE
395 region of India (mean δ¹³C_{DIC}: -3.1‰) could be due to the competition between autotrophy,
396 degassing and heterotrophy as these processes influences the δ¹³C_{DIC} in opposite directions
397 (Fig. 2); the former two processes causes enrichment while the latter depletes δ¹³C_{DIC}.
398 Relatively higher phytoplankton biomass (mean Chl-a: 4.6 mg m⁻³) and less under-saturation
399 of DO (98.7%) was observed in these rivers compared to the mean of the rest of the Indian
400 rivers (2.4 mg m⁻³ and 87.5% respectively), suggesting that autotrophy is one of the dominant
401 processes controlling DIC in rivers from the SE region of India. Total number of dams on the
402 rivers from this (SE) region (mean 155, Table 1) is not significantly higher from that of the
403 mean of total number of dams on the Indian rivers sampled (mean 135) , suggesting that

404 degassing due to storage of water may not be the dominant process responsible for
405 enrichment in $\delta^{13}\text{C}_{\text{DIC}}$ of these rivers.

406 **4.3 Total DIC export by the Indian monsoonal rivers to the north Indian Ocean**

407 Indian monsoonal rivers annually export ~ 10.3 Tg of DIC to the north Indian Ocean.
408 Nearly three fourth of this amount (7.8 Tg) reaches to the Bay of Bengal while ~~the remaining~~
409 ~~into~~ the Arabian Sea receives only one fourth (2.5 Tg). This is consistent with the higher
410 magnitude of freshwater discharge to the Bay of Bengal ($378 \text{ km}^3 \text{ yr}^{-1}$) from the catchment
411 area of about $970 \times 10^3 \text{ km}^2$ than the Arabian Sea ($122 \text{ km}^3 \text{ yr}^{-1}$ from the catchment area of
412 $244 \times 10^3 \text{ km}^2$). The total DIC export by the Indian monsoonal rivers (10.3 Tg yr^{-1}) is ~~far~~
413 ~~less~~lower than the DIC export by the American (61.4 Tg yr^{-1}) and African (17.7 Tg yr^{-1})
414 rivers and major rivers draining to the tropical Atlantic from South America and Africa (53
415 Tg yr^{-1} , Araujo et al. 2014). It is mainly due to the fact that freshwater discharge from the
416 Indian monsoonal rivers is very low ($\sim 500 \text{ km}^3 \text{ yr}^{-1}$) compared to the American ($11,799 \text{ km}^3$
417 yr^{-1}) and African ($3,786 \text{ km}^3 \text{ yr}^{-1}$) rivers. However, the Indian monsoonal rivers are exporting
418 disproportionately higher DIC because they account for only 1.3% of the global river
419 discharge but export 2.5% of the global riverine DIC export to the oceans (400 Tg yr^{-1}).
420 Though American and African rivers account for 30% and 10% of the global river discharge,
421 they export only 15% and 4.4% of global riverine DIC to oceans, respectively.
422 Disproportionately higher DIC flux from the Indian rivers could be due to relatively higher
423 weathering rates of silicate and carbonate minerals in their drainage basins (Das et al., 2005;
424 Gurumurthy et al., 2012; Pattanaik et al., 2013). Higher DIC fluxes from the tropical regions
425 are mainly attributed to the favourable climatic conditions, lithology and land use cover
426 (Huang et al., 2012) of this region for higher dissolution.

427 Krishna et al. (2015) reported that Indian monsoonal rivers export 2.32 Tg yr^{-1} of
428 dissolved organic carbon (DOC) to the north Indian Ocean. The total fluvial dissolved carbon

429 flux (DIC+DOC) would be 12.6 Tg yr⁻¹ in which DIC flux contributed up to ~81%. The
430 predominance of DIC has also been found in rivers elsewhere in the world, for example, the
431 British rivers (Jarvie et al., 2017) and high altitude Swedish rivers (Campeau et al., 2017).
432 Since the catchment area of the Indian monsoonal rivers ranged widely from as low as 1x10³
433 km² to as high as 313x10³ km², the export fluxes of DIC were normalized with the catchment
434 area of the river (yield) in order to examine various factors controlling the DIC export to the
435 north Indian Ocean.

436 **4.4 Yield of DIC from the Indian monsoonal rivers**

437 The yield of DIC found in this study (mean 8.7±5.2 g m⁻² yr⁻¹) is close to those found
438 in rivers from the tropical region of Asia, but significantly higher than those reported from
439 tropical region of the American and African continents (Huang et al., 2012). The yield was
440 highest (8.8±5.6 g m⁻² yr⁻¹) in rivers from the SW region of India, despite they export
441 relatively lower DIC (0.3 Tg yr⁻¹) due to their low volume of discharge (46 km³ yr⁻¹) and
442 relatively smaller catchment (20x10³ km²) than the rivers from SE, NE and NW regions of
443 India (Table 1. DIC yield showed a significant positive correlation with the volume of
444 discharge (r²=0.67, p<0.001; Fig. 6a) in medium rivers and no such relationship was found in
445 the major rivers. Significant negative relationship was observed between DIC yield and
446 catchment area of river (r² = -0.49, p<0.001; Fig. 6b and r² = -0.43, p<0.001; Fig. 6c for
447 medium and major rivers respectively), suggesting the smaller rivers export more DIC per
448 unit area of catchment compared to the major river systems, and thus inclusion of DIC data
449 from medium rivers in the world significantly alters the global estimations of DIC. A fairly
450 good linear relationship between the yield of DIC and the intensity of precipitation (r²=0.43,
451 p<0.01 Fig. 6d) was observed only in the rivers which receives >2000mm of annual mean
452 precipitation. Higher precipitation over the catchment increases the yield of DIC because the
453 dense precipitation enhances the extraction of DIC from soils and rocks in their catchment

454 Therefore, high precipitation (~3000 mm) over the small catchment ($20 \times 10^3 \text{ km}^2$) could have
455 increased DIC yield from the rivers of SW region of India.

456 Sreenivas et al. (2016) and Krishwan et al. (2009) found that the soil organic and
457 inorganic carbon contents in the surface (100cm) soils in the catchment of rivers in the SW
458 region were higher and lower, respectively, than the catchments of the rivers from SE, SW
459 and NE region of India. Decomposition of soil organic matter releases excess CO_2 and, the
460 increase in soil CO_2 leads to the formation of acidic conditions in soils. This would increase
461 the DIC yield by more dissolution of soil carbonates and chemical weathering of carbonate
462 and silicate rocks (Zou et al., 2016). A significant linear correlation was found between soil
463 organic carbon content and DIC yield in this study ($r^2=0.65$, $p<0.001$; Fig. 6e), suggesting
464 that higher soil organic carbon in the catchment of the rivers from SW region could have
465 elevated the yield of DIC from rivers of this region. The basin scale studies are, however,
466 required for comprehensive understanding of the influence of environmental and
467 anthropogenic factors on export fluxes and yield of DIC from the Indian monsoonal rivers.

468 **5. Summary**

469 In order to examine the spatial variability in the sources and distribution of dissolved
470 inorganic carbon (DIC) in the Indian monsoonal rivers, and to estimate their export fluxes of
471 DIC to the north Indian Ocean, we sampled a total of 27 major and medium rivers during
472 wet period. An order of magnitude variability was found in DIC concentrations among the
473 rivers sampled ($3.4 - 73.6 \text{ mg l}^{-1}$), with a lower mean concentration of $6.6 \pm 2.1 \text{ mg l}^{-1}$ in rivers
474 located in the SW region of India. It is attributed to significant spatial variability in the size
475 of rivers, precipitation pattern, pollution and lithology in their catchments. The approximated
476 $\delta^{13}\text{C}$ of DIC source from the Keeling and Miller-Tans plots (-2.0 and -3.0% respectively)
477 and, the calculated $\delta^{13}\text{C}$ of CO_2 ~~which filters the influence of pH and DIC speciation,~~
478 suggested that DIC in the Indian rivers is mainly originated from chemical weathering of

479 carbonate minerals, but largely affected by autotrophic production in rivers from the
480 southeast region of India and heterotrophic decomposition of organic matter in rivers from
481 other regions of India. Indian monsoonal rivers together export $\sim 10.3 \text{ Tg yr}^{-1}$ of DIC to the
482 north Indian Ocean, of which 7.8 Tg yr^{-1} enters in to the Bay of Bengal while the Arabian Sea
483 receives only 2.5 Tg yr^{-1} . It is mainly attributed to the volume of river discharge as the
484 former receives $\sim 378 \text{ km}^3 \text{ yr}^{-1}$ while the latter receives only $122 \text{ km}^3 \text{ yr}^{-1}$ from the Indian
485 monsoonal rivers. Dense rainfall and higher soil organic carbon content in the catchment of
486 rivers from the SW region than in the catchment of the other Indian rivers resulted in highest
487 yield of DIC from the former than the latter.

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490

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498 **7. Data Availability**

499 The data set used in the current study can be obtained from the corresponding author by an e-
500 mail request.

501

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940 **Figure captions**

941

942 **Figure 1:** Map showing the study region. Rivers sampled in this study were indicated by
943 solid black line. Distribution of soils in catchments of the Indian monsoonal rivers sampled
944 was also shown. Rivers draining the four regions, i.e., northwest (NW), southwest (SW),
945 southeast (SE) and northeast (NE) were shown by solid black arrows.

946

947 **Figure 2:** Schematic diagram showing [the typical range of the \$\delta^{13}\text{C}\$ of different sources of](#)
948 [end-members of dissolved inorganic carbon \(DIC\) sources in rivers.](#) Various major processes
949 influencing the $\delta^{13}\text{C}$ of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) within the rivers were also shown. [Hollow black](#)
950 [arrows \(\$-\leftarrow\$ and \$\rightarrow-\$ \)](#) indicates the direction of change in $\delta^{13}\text{C}_{\text{DIC}}$ due to the influences
951 different in-stream process mentioned against arrows.

952

953 **Figure 3:** Spatial variability in concentration (mg l^{-1} ; 3a), export flux (Tg yr^{-1} ; 3b) and yield
954 ($\text{g m}^{-2} \text{yr}^{-1}$; 3c) of dissolved inorganic carbon (DIC) and its stable isotopes ($\delta^{13}\text{C}_{\text{DIC}}$, 3d) in the
955 Indian monsoonal rivers studied. Rivers geographically located in the northwest (NW),
956 southwest (SW), southeast (SE) and northeast (NE) regions of India were also shown. Rivers
957 draining into the Bay of Bengal (east-flowing rivers) were shown by gray shade while rivers
958 draining into the Arabian Sea (west-flowing) were shown by no shade.

959

960 **Figure 4:** (a) Exponential decrease and (b) linear increase of dissolved inorganic carbon
961 (DIC) concentrations with increasing the rainfall over the catchment and length of the river
962 respectively. (c) Inverse and (d) linear relationships of chlorophyll-a (Chl-a) with
963 concentrations and $\delta^{13}\text{C}$ of DIC respectively. Significant linear relationships of $\delta^{13}\text{C}$ of DIC
964 with (e) dissolved oxygen (DO) saturation and (f) dissolved organic carbon (DOC)
965 concentration. Linear relationships observed between (g) DIC concentrations and population
966 density in the catchment and (h) total alkalinity and $\delta^{13}\text{C}$ of DIC in the Indian monsoonal
967 rivers during the study period. Ovals with dashed line indicate [the](#) outliers which were not
968 included in the regression equations. Rivers of the northwest region of India showed linear
969 relationships as shown by [the](#) other Indian rivers but with a different slope (Fig. f-h)

970

971 **Figure 5:** Least square linear regression models of (a) $\delta^{13}\text{C}_{\text{DIC}}$ as a function of $1/\text{DIC}$
972 (Keeling plot) and (b) $\delta^{13}\text{C}_{\text{DIC}} \times \text{DIC}$ as a function of DIC concentrations (Miller-Tans plot)
973 in the Indian monsoonal rivers. (c) Linear relationship between calculated $\delta^{13}\text{C}$ of CO_2 and
974 the measured $\delta^{13}\text{C}_{\text{DIC}}$ and (d) Miller-Tans linear regression model of $\delta^{13}\text{C}-\text{CO}_2 \times \text{CO}_2$ as a
975 function of CO_2 concentration in the Indian monsoonal rivers.

976

977 **Figure 6:** Significant relationships [of](#) dissolved inorganic carbon (DIC) yield with (a) river
978 discharge in medium estuaries, (b) catchment areas of the medium rivers, (c) catchment areas
979 of the major rivers, (d) rainfall over the catchment of all the rivers sampled and (e) soil

980 organic carbon (OC) content in catchments of the Indian monsoonal rivers studied. Since the
981 data on soil OC is not available for each watershed (e) was plotted using the available soil
982 OC data on regional scale (NW, SW, SE and NE regions of India), Hence, it contains only
983 four points.

984

985 **Table captions**

986

987 **Table 1:** Catchment area, discharge, length and elevation of each river and, annual mean
988 rainfall, number of dams and population density in each watershed of the Indian monsoonal
989 rivers sampled. Concentrations, export fluxes and yields of dissolved inorganic carbon (DIC)
990 and its stable isotopes ($\delta^{13}\text{C}_{\text{DIC}}$) of Indian rivers were given. Measured pH and calculated
991 $\delta^{13}\text{C}$ of CO_2 from isotopic fractionation factors across DIC speciation were also provided.

992 Rivers located in the northern region (north of 16°N) of India were shown by the shaded
993 (grey) area. Of these rivers, Mahisagar, Sabarmati, Tapti and Narmada are located in the
994 northwestern (NW) region whereas, rivers from Godavari to Hyadri are located in the
995 northeastern (NE) region of India.

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