

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

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10 **Abstract.** Rivers are an important source of dissolved inorganic carbon (DIC) to the adjacent  
11 coastal waters. In order to examine the spatial variability in the distribution and major  
12 sources of DIC in the Indian monsoonal rivers and to quantify their export flux to the north  
13 Indian Ocean, 27 major and medium rivers were sampled during the discharge period.  
14 Significant spatial variability of DIC concentrations (3.4 – 73.6 mg l<sup>-1</sup>) was observed and it is  
15 attributed to spatial variations in the precipitation pattern, size of rivers, pollution, and  
16 lithology of the catchments. The stable isotopic composition of bulk DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) indicates  
17 that predominant contribution of DIC is from chemical weathering of carbonate and silicate  
18 minerals by soil CO<sub>2</sub>. As the in-stream processes significantly alter the  $\delta^{13}\text{C}_{\text{DIC}}$  in rivers, two  
19 different graphical mixing model techniques, Keeling plot and Miller-Tans plot, were used to  
20 approximate the  $\delta^{13}\text{C}$  of DIC source. Least square linear regression models of both Keeling  
21 and Miller-Tans plots approximated the similar  $\delta^{13}\text{C}$  of DIC source (-2.0 and -3.0‰  
22 respectively). Further, the  $\delta^{13}\text{C}$  of CO<sub>2</sub> was approximated in order to filter the influence of  
23 pH and DIC speciation on the measured  $\delta^{13}\text{C}_{\text{DIC}}$ . Our results indicated that DIC in the Indian  
24 rivers is contributed by chemical weathering of carbonate minerals, but largely influenced by  
25 autotrophic production in rivers from the southeast region and heterotrophic decomposition  
26 of organic matter in the other Indian monsoonal rivers. It is estimated that the Indian  
27 monsoonal rivers annually export ~10.3 Tg of DIC to the northern Indian Ocean, of which  
28 the major fraction (75%) enters into the Bay of Bengal and the remaining reaches to the  
29 Arabian Sea. This is consistent with the freshwater flux which is three times higher to the

30 Bay of Bengal ( $\sim 378 \text{ km}^3 \text{ yr}^{-1}$ ) than to the Arabian Sea ( $122 \text{ km}^3 \text{ yr}^{-1}$ ). Despite discharge  
31 from the Indian monsoonal rivers account for only 1.3% of the global freshwater discharge,  
32 they disproportionately export 2.5% of the total DIC export by the world major rivers.  
33 Despite rivers from the SW region of India export an order of magnitude lower DIC ( $0.3 \text{ Tg}$   
34  $\text{yr}^{-1}$ ) than the rivers from other regions of India, the highest yield of DIC was found in the  
35 former and it is attributed to intense precipitation ( $\sim 3000 \text{ mm}$ ), favorable natural vegetation  
36 of tropical moist deciduous and tropical wet evergreen and semi evergreen forests, tropical  
37 wet climate, high soil organic carbon and the dominance of red loamy soils in catchments of  
38 the rivers from SW region. Our study demonstrates that significant spatial variability of the  
39 hydrological, lithological and environmental conditions in the catchments and in-stream  
40 processes (autotrophic production and heterotrophic decomposition of organic matter)  
41 strongly controls the DIC in the Indian monsoonal rivers.

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

## 44 **1. Introduction**

45 Dissolved inorganic carbon (DIC) is one of the major constituent of carbon species in  
46 rivers. DIC in rivers mainly originates from the geogenic (weathering of carbonate and  
47 silicate rocks) and biogenic (decomposition of organic matter in soils) sources (Meybeck,  
48 1987; Mook and Tan, 1991; Gaillardet et al., 1999, Dessert et al., 2001; Viers et al., 2007;  
49 Raymond et al., 2008; Tamooh et al., 2013). The former consumes atmospheric carbon  
50 dioxide ( $\text{CO}_2$ ) while the latter releases  $\text{CO}_2$  fixed by the terrestrial plants. In addition to these  
51 major sources in the catchment, DIC is also contributed by various physical and biological  
52 processes within the rivers. For instance, heterotrophic decomposition of organic matter,  
53 photo-oxidation of dissolved organic carbon (DOC), autotrophic respiration and dissolution  
54 of atmospheric  $\text{CO}_2$  contribute DIC to rivers. On the other hand, autotrophic production by

55 aquatic plants (photosynthesis) and evasion of CO<sub>2</sub> to atmosphere with draw DIC from rivers.  
56 All these processes in the catchments and within the rivers are strongly coupled to  
57 atmospheric CO<sub>2</sub> because they act as either sink or source of atmospheric CO<sub>2</sub> (e.g. Berner  
58 et al., 1983; Mook and Tan, 1991; Gaillardet et al., 1999; Raymond et al., 2008). The DIC in  
59 rivers and its export to the coastal oceans is thus intimately linked to the global carbon cycle  
60 (Campeau et al., 2017)

61 Riverine export fluxes of DIC to coastal regions of the world oceans have been  
62 estimated on the global (Gaillardet et al., 1999; Raymond et al., 2013) and regional scales  
63 (Richey et al., 2002; Wallin et al., 2013; Crawford et al., 2014; Campeau et al., 2014; Kocio  
64 et al., 2015) to understand the component of DIC in the global carbon budget. Annual export  
65 flux of DIC from the world major river systems to the global ocean has been estimated as  
66 ~327 - 385 Tg (1Tg=10<sup>12</sup>g) (Ludwig et al., 1998; Meybeck and Vorosmarty, 1999). However,  
67 many of the regional studies on DIC export fluxes were limited only to the major river  
68 systems (e.g. Gaillardet et al., 1999; Raymond et al., 2013), for example, the Mississippi  
69 (Raymond and Cole, 2003; Raymond et al., 2008; Cai et al., 2008), Changjiang and Pearl  
70 (Cai et al., 2008) and Congo (Wang et al., 2013) rivers etc. Regional studies on the riverine  
71 export fluxes of DIC are very important for the global carbon cycle and budget as the export  
72 fluxes are largely dependent on the hydrological, lithological and environmental conditions,  
73 which are highly variable on the regional scales. However, DIC measurements are still  
74 lacking in several medium rivers from different regions of the world in general and Asia in  
75 particular.

76 Studies on the sources and export fluxes of DIC from the Indian rivers are very  
77 limited. Though DIC measurements were conducted in some Indian estuaries, for example,  
78 Mandovi and Zuari (Sarma et al., 2001), Godavari (Sarma et al., 2011), Cochin (Gupta et al.,  
79 2009; Bhavya et al., 2018), Hooghly (Mukhopadhyay et al., 2002; Samanta et al., 2015),

80 Mahanadi (Pattanaik et al., 2017) and Chilka (Gupta et al., 2008; Muduli et al., 2013), they  
81 were confined only to the internal cycling of DIC and exchange of CO<sub>2</sub> at the air-water  
82 interface, but not focused on the sources and export fluxes of DIC. The major sources of DIC  
83 in the Indian rivers remain unclear, except only a couple of rivers, Krishna (Das et al., 2005;  
84 Laskar et al., 2014) and Ganges (Samanta et al., 2015). Further, the quantity of annual DIC  
85 export by the Indian rivers to the coastal regions is unknown. Here, we made an attempt to  
86 understand the major sources of DIC in the Indian monsoonal rivers (Fig. 1) using  $\delta^{13}\text{C}_{\text{DIC}}$  as  
87 a potential tracer, and to estimate the riverine export flux of DIC to the north Indian Ocean  
88 from the Indian subcontinent.

89 The stable isotopic composition of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) is widely used to identify the major  
90 sources of DIC in the aquatic systems (e.g. Singh et al., 2005; Tamoooh et al., 2013; Samanta  
91 et al., 2015; Zou, 2016). The isotopic composition of DIC originated by dissolution of  
92 atmospheric CO<sub>2</sub> is about 0‰ (Coplen et al., 2002) whereas it is about -27 to -26‰ if the  
93 DIC is derived from oxidation of organic matter produced by C<sub>3</sub> plants (O’Leary, 1988). The  
94  $\delta^{13}\text{C}$  of DIC generated by carbonic acid (formed by soil CO<sub>2</sub> dissolution) weathering of  
95 silicates is about -21 to -17‰ (Solomon and Cerling, 1987) while it is in the range of -10 to -  
96 9‰ for carbonate rocks because half of the carbon comes from carbonate rocks (0‰, Land,  
97 1980) during weathering. The weathering of silicate and carbonate minerals yield  $\delta^{13}\text{C}_{\text{DIC}}$  in  
98 the range of -8 to -7‰ and -4 to -3‰, respectively, if the carbonic acid formed by the  
99 dissolution of atmospheric CO<sub>2</sub>. Though the  $\delta^{13}\text{C}$  of DIC derived from different sources is  
100 well separable (Deines et al., 1974), the isotopic fractionation by in-stream physical and  
101 biological processes alters the  $\delta^{13}\text{C}$  of DIC source (Fig. 2). For example, photosynthesis and  
102 equilibration with atmospheric CO<sub>2</sub> enriches (O’Leary, 1988; Finlay, 2004; Parker et al.,  
103 2005, 2010) while the heterotrophic decomposition of organic matter and photo-oxidation of  
104 dissolved organic carbon depletes the  $\delta^{13}\text{C}$  of DIC (Opsahl and Zepp, 2001; Finlay, 2003;

105 Waldron et al., 2007; Vahatalo and Wetzel, 2008) (Fig. 2). Of these processes, equilibrium  
106 with atmospheric CO<sub>2</sub> is of less significance because rivers are generally in disequilibrium  
107 with atmospheric CO<sub>2</sub> (Raymond et al., 2013) and emit CO<sub>2</sub> to atmosphere due to  
108 oversaturation (Oquist et al., 2009; Campeau et al., 2017). Nevertheless, the influence of  
109 internal processes within the rivers must be considered while interpreting the δ<sup>13</sup>C<sub>DIC</sub> results  
110 for identification of DIC sources. The main objectives of this study are to (i) identify the  
111 major sources of DIC in the Indian monsoonal rivers, (ii) estimate the export flux and yield of  
112 DIC to the north Indian Ocean and (iii) examine the major processes in the catchments and  
113 within the rivers controlling DIC in the Indian monsoonal rivers.

## 114 **2. Study region, sampling and methods**

### 115 **2.1 Study Area**

116 The Indian peninsula bifurcates the north Indian Ocean into the Bay of Bengal and the  
117 Arabian Sea. Although these two basins occupy the same latitudinal belt, their  
118 oceanographic processes were reported to be remarkably different due to higher freshwater  
119 flux into the Bay of Bengal ( $1.63 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ ) than to the Arabian Sea ( $0.3 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ ;  
120 Subramanian, 1993; Gauns et al., 2005). The large freshwater influx leads to the formation  
121 of a strong vertical salinity stratification in the Bay of Bengal (Varkey et al., 1996) that  
122 prevents vertical mixing of nutrient rich sub-surface water with the surface (Prasanna Kumar  
123 et al., 2004). As a result, the Bay of Bengal is considered to be relatively less productive  
124 (Prasannakumar et al., 2002) than the adjacent Arabian Sea, which is one of the highly  
125 productive zones in the world (Madhupratap et al., 1996; Smith, 2001; Barber et al., 2001)  
126 due to injection of nutrients into the surface through the seasonal upwelling and convective  
127 mixing (Shetye et al., 1994; Madhupratap et al., 1996; Muraleedharan and Prasannakumar,  
128 1996).

129 Discharge from the Indian monsoonal rivers is largely fed by the monsoon induced  
130 precipitation over the Indian subcontinent, which receives >80% of its annual rainfall during  
131 the southwest (SW) monsoon period (June-September) (Soman and Kumar, 1990). Though  
132 some amount of rainfall occurs during the northeast (NE) monsoon (December-March), it  
133 does not generate discharge as it will be stored within the dam reservoirs for domestic,  
134 industrial and irrigation purposes. Discharge from the Indian monsoonal rivers mainly occurs  
135 during the SW monsoon season (Vijith et al., 2009; Sridevi et al., 2015) hence, these rivers  
136 are called as monsoonal rivers. Since the major portion of the annual freshwater discharge  
137 occurs only during the SW monsoon, the entire estuary is filled with freshwater (Vijith et al.,  
138 2009; Sridevi et al., 2015) during this period. As discharge is small during the rest of the  
139 year, the discharge during the SW monsoon (wet period) is considered to be equivalent to the  
140 annual discharge of the monsoonal rivers. Based on rainfall intensity, forest cover, vegetation  
141 and soil type in the catchment, rivers sampled in the present study were categorized into 4  
142 groups, namely the northwest (NW), southwest (SW), southeast (SE) and northeast (NE)  
143 rivers of India (Fig. 1). The SW region of India is characterized by the intense rainfall during  
144 SW monsoon (~3000 mm) following the NE (1000-2500 mm), SE (300-500 mm) and NW  
145 (200-500 mm) regions of India (Soman and Kumar, 1990). The SW rivers drain red loamy  
146 soils while the NW rivers drain black soils. Except the major rivers Godavari and Krishna,  
147 all the rivers reaching Bay of Bengal (NE and SE rivers) drain red loamy and alluvial soils in  
148 their upper and lower catchments respectively. The Godavari and Krishna rivers drain black  
149 soils in their upper catchment whereas red loamy and alluvial soils in their middle and lower  
150 catchments respectively (Geological Survey of India; www.gsi.gov.in). Based on discharge,  
151 the monsoonal rivers in this study were divided into two types, namely, the major ( $>150 \text{ m}^3 \text{ s}^{-1}$ )  
152 and medium ( $<150 \text{ m}^3 \text{ s}^{-1}$ ) rivers.

## 153 **2.2 Sample collection**

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

161 *In-situ* measurements and sample collection were conducted in 27 rivers of the Indian  
162 subcontinent (Fig. 1) during the SW monsoon season of the years, 2011 and 2014. Surface  
163 water samples at each location were collected for phytoplankton biomass (Chl-*a*), DIC and  
164 dissolved oxygen (DO). Samples for DIC were collected in air-tight crimp-top glass bottles  
165 and added poison (mercuric chloride) to arrest the biological activity. DO analysis was  
166 carried out at a temporary shore laboratory set up for sample processing after the completion  
167 of sampling on each day. Water samples were filtered through GF/F (nominal pore size of  
168 0.7 $\mu$ m) under moderate vacuum and stored in liquid nitrogen for Chl-*a* analysis.

169

170

### 171 **2.3. Methods**

172 Temperature and salinity at the sampling locations were measured using a  
173 conductivity-temperature-density (CTD) profiling system (Sea Bird Electronics, SBE 19 plus,  
174 United States of America). Concentration of DO was determined by a Winkler's method  
175 (Carritt and Carpenter, 1966) using an auto titrator (Metrohm, Switzerland) with  
176 potentiometric end point detection. The analytical precision of the method was  $\pm 0.07\%$   
177 (RSD). Dissolved oxygen saturation is computed following formulations given by Garcia and  
178 Gordon (1992). DIC concentrations in water samples were measured at our Institute

179 laboratory using Coulometer (UIC Inc., USA) connected to an automatic sub-sampling  
180 system. Based on the repeated analysis of samples and standards, the precision of the method  
181 was  $\pm 0.02 \text{ mg l}^{-1}$ . The certified reference materials (CRM) supplied by Dr. A.G. Dickson,  
182 Scripps Institute of Oceanography, USA and internal standards were used to test the accuracy  
183 of our DIC measurements and it was found to be within  $\pm 0.2$  to  $0.3\%$ . Potentiometric Gran  
184 titration method (Metrohm, Switzerland) was used for determination of pH and total  
185 alkalinity and followed the standard operating procedures given by Department of Energy  
186 (DOE) (1998).

187 The stable carbon isotopic composition of DIC in the water was measured on Gas  
188 Bench coupled with isotope ratio mass spectrometer (EA-IRMS-Delta V,  
189 Finnigan, Germany). 50 ml air-tight bottles with rubber septa were filled with 0.5 ml of high  
190 purity ortho-phosphoric acid and purged with high purity helium. About 1 ml of water sample  
191 is injected to the bottle and incubated at constant temperature of  $50^\circ\text{C}$  for 12 hours. The  $\text{CO}_2$   
192 extracted into the head space is injected to the IRMS through gas bench. The results are  
193 expressed relative to conventional standards, that is, Pee Dee belemnite (PDB) limestone for  
194 carbon (Coplen, 1996) as  $\delta$  values, defined as:

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

195  
196 where R refers to  $^{13}\text{C}$  and X stands for  $^{13}\text{C}/^{12}\text{C}$ . The high-purity tank of  $\text{CO}_2$  was used as  
197 working standard for carbon. These gases were calibrated with IAEA standards. Standard  
198 deviation on 20 aliquots of the same sample was lower than  $0.05\%$  for  $\delta^{13}\text{C}$ . Chlorophyll-*a*  
199 (Chl-*a*) on the filter was extracted into di-methyl formamide (DMF) and measured the extract  
200 fluorometrically using a spectrofluorophotometer (Varian Eclipse, Varian Electronics., UK)  
201 following Suzuki and Ishimaru (1990). Annual mean discharge data of the rivers was taken  
202 from Meybeck and Ragu (1995, 1996), Central Water Commission, New Delhi (2006, 2012)  
203 and Kumar et al. (2005). Catchment area of the rivers was obtained from Water Resources  
204



205 Information System of India (WRIS, [www.india-wris.nrsc.gov.in](http://www.india-wris.nrsc.gov.in)). Soil organic carbon data  
206 was taken from Kishwan et al. (2009) and Sreenivas et al. (2016), and the rainfall data was  
207 obtained from Soman and Kumar (1990). Dissolved organic carbon (DOC) data for the  
208 Indian rivers was taken from Krishna et al. (2015)

209 Total export flux of DIC from each river was estimated by multiplying the mean  
210 concentrations of DIC at near zero salinity (river end member) with the annual discharge.  
211 Spatial variability of DIC concentrations within the river was minimized to a large extent by  
212 collecting samples from 2 to 3 locations in each river while the inter-annual variability by  
213 collecting samples during discharge periods of two years. However, variability in DIC  
214 concentrations within the discharge period results in some uncertainties in our estimations of  
215 DIC export fluxes. Time series measurements in the Godavari estuary (our unpublished  
216 results) revealed that the variability in DIC concentrations within the discharge period is up to  
217 10%. Therefore, the error associated with our DIC flux estimates may be about 10%. DIC  
218 flux normalized by catchment area (yield) was calculated by dividing the total DIC export  
219 flux of the river by its catchment area.

## 220 **3. Results**

### 221 *3.1. Hydrographic characteristics*

222 Surface water temperatures were higher in rivers from the NE and SE regions (mean  
223  $30.9 \pm 1.2^\circ\text{C}$ ) than the rivers from SW and NW regions ( $27.3 \pm 1.5^\circ\text{C}$ ) of India. Dissolved  
224 oxygen saturation varied from as low as 63% to as high as 105%, with a mean saturation of  
225  $90 \pm 11\%$ . The rivers from SW region of India recorded more unsaturation of DO ( $82 \pm 7\%$ )  
226 than the rivers located in the NE ( $89 \pm 15\%$ ), NW ( $93 \pm 3\%$ ) and SE ( $96 \pm 11\%$ ) regions of India.  
227 Chlorophyll-*a* (Chl-*a*) concentrations varied broadly from 0.8 to 7.5 mg m<sup>-3</sup>, with relatively  
228 higher mean concentrations in rivers of the SE region ( $4.7 \pm 2.5$  mg m<sup>-3</sup>) followed by the SW

229 (2.8±0.7 mg m<sup>-3</sup>) regions of India. On the other hand, relatively low Chl-*a* was observed in  
230 the medium (2.6±1.3 mg m<sup>-3</sup>) than the major estuaries (3.2±2.1 mg m<sup>-3</sup>).

### 231 3.2 DIC concentrations and $\delta^{13}C_{DIC}$

232 DIC concentrations in the Indian monsoonal rivers widely varied from 3.4  
233 (Bharathapuzha) to 73.6 mg l<sup>-1</sup> (Vellar), with a significant spatial variability (Fig. 3a; Table  
234 1). Highest mean DIC concentration was observed in rivers of the SE region (37.4±6.3 mg l<sup>-1</sup>)  
235 while the lowest was found in the SW region (5.2±2.1 mg l<sup>-1</sup>) of India. Intermediate values  
236 were found in rivers of the NW (28.4±8.9 mg l<sup>-1</sup>) and NE (17.1±6.2 mg l<sup>-1</sup>) regions of India.  
237 DIC concentrations were found to be similar in the major (22.7±13.6 mg l<sup>-1</sup>) and medium  
238 (21.1±13.2 mg l<sup>-1</sup>) rivers (homoscedastic Student's t-test; p=0.76). Mean DIC concentration  
239 found in this study (21.4±16.3 mg l<sup>-1</sup>) is similar to those observed earlier in the major river  
240 systems of India (Brahmaputra; Singh et al., 2005) and elsewhere in the world, for example,  
241 British rivers (Jarvie et al., 2017) and Swedish rivers (Campeau et al., 2017). However, DIC  
242 concentrations in the present study are higher than the global mean DIC (10.3 mg l<sup>-1</sup>,  
243 Meybeck and Vorosmarty, 1999) (Table 1), but lower than those reported in the rivers  
244 draining into the Gulf of Trieste (N Adriatic; 37-66 mg l<sup>-1</sup>, Tamse et al., 2014).

245 The  $\delta^{13}C_{DIC}$  varied from -13.0 to -1.4‰, with a significant spatial variability (Fig. 3d;  
246 Table 1) in the rivers sampled. Relatively depleted  $\delta^{13}C_{DIC}$  values were observed in rivers of  
247 the NW region (-11.1±2.3‰) while enriched  $\delta^{13}C_{DIC}$  was found in rivers of the SE region (-  
248 3.5±2.3‰) of India (Fig. 3d). The  $\delta^{13}C_{DIC}$  values found in this study are well within the range  
249 of values reported earlier in rivers of India (Das et al., 2005) and elsewhere in the world, for  
250 example, Swedish streams (-27.6 to -0.6‰; Campeau et al., 2017) and rivers from Italy and  
251 Slovenia (-12.8 to -7.7‰, Tamse et al., 2014).

### 252 3.3. Export fluxes and yield of DIC

253 Annual export flux of DIC to the coastal ocean from the individual rivers varied  
254 broadly from 0.01 Tg (Chalakuudi) to as high as 2.33 Tg (Krishna) (Fig. 3b; Table 1). Among  
255 the rivers sampled, rivers of the NE region of India export higher DIC ( $6.52 \text{ Tg yr}^{-1}$ ) while  
256 the lowest was found from rivers of the SW region ( $0.24 \text{ Tg yr}^{-1}$ ) (Table 1). The Indian  
257 monsoonal rivers together export about  $10.32 \text{ Tg yr}^{-1}$  of DIC to the northern Indian Ocean, of  
258 which 7.81 Tg (75%) enters into the Bay of Bengal and the remaining into the Arabian Sea  
259 ( $2.51 \text{ Tg}$ ). The yield of DIC ranged from 2.8 (Bharathapuzha) to  $20.7 \text{ g m}^{-2} \text{ yr}^{-1}$  (Baitarani)  
260 (3c; Table 1), excluding the exceptionally high yield of  $119 \text{ g m}^{-2} \text{ yr}^{-1}$  from Haldia river. The  
261 mean yield was found to be more or less similar in rivers from all the four regions of India,  
262 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 ( $7.7 \text{ g m}^{-2} \text{ yr}^{-1}$ )  
263 regions. Despite the export flux of DIC is lowest from rivers of the SW region ( $0.24 \text{ Tg yr}^{-1}$ ),  
264 interestingly, the yield from rivers of this region is on par with (even slightly higher than) the  
265 other Indian monsoonal rivers (Table 1; Fig. 3b&c). Yields of DIC found in this study are  
266 similar to those found earlier in rivers elsewhere in the world (Huang et al., 2012).

## 267 **4. Discussion**

### 268 **4.1 Distribution of DIC in the Indian monsoonal rivers**

269 Distribution of DIC in the Indian monsoonal rivers showed large spatial variability,  
270 with the lowest values in rivers from the SW region of India (Fig. 3a). DIC concentrations in  
271 rivers are known to be influenced by the intensity of precipitation over the catchment, basin  
272 lithology (Giesler et al., 2013; Lofgren et al., 2014), length of the fluvial network (Hotchkiss  
273 et al., 2015) and in-stream physical and biological processes (Mook and Tan, 1991; Raymond  
274 et al., 2008). The spatial distribution of rainfall over the Indian subcontinent  
275 ([www.imd.gov.in](http://www.imd.gov.in)) shows that the SW region receives the highest annual rainfall ( $\sim 3000 \text{ mm}$ )  
276 than the rest of India (Soman and Kumar, 1990).

277           The intense precipitation over the SW region is expected to cause higher weathering  
278 rates and thus higher DIC in rivers (e.g., Gupta et al., 2011), but lower DIC concentrations  
279 were found in rivers of this region. It could be due to the influence of dilution because the  
280 dense precipitation over the small catchment area (Table 1) might have diluted DIC  
281 concentrations in rivers of this region. In order to understand the influence of the density of  
282 rainfall on DIC in rivers, we normalized the volume of discharge from the river with its  
283 catchment area. The catchment area normalized volume of discharge was found to be much  
284 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  
285 ( $0.6 \text{ m}^3 \text{ m}^{-2}$ ) and NW ( $0.32 \text{ m}^3 \text{ m}^{-2}$ ) regions of India. About three times higher catchment  
286 area normalized discharge might have diluted DIC concentrations in the rivers of the former  
287 region. A strong exponential decrease in DIC concentrations with increasing rainfall over the  
288 catchment ( $r^2= 0.72$ ,  $p<0.001$ ; Fig. 4a) also suggests that DIC concentration in the Indian  
289 rivers are strongly influenced by density of precipitation over the catchment.

290           Rivers of the SW region are relatively small in size, both in terms of catchment area  
291 (total catchment area:  $20 \times 10^3 \text{ km}^2$ ) and the length of the river (mean length: 126 km), than  
292 the rivers from other regions (SE, NE and NW) of India (Table 1). Since the contribution of  
293 DIC from in-stream processes, such as decomposition of organic matter, has been  
294 demonstrated to increase along the course of the fluvial network (Hotchkiss et al., 2015),  
295 possibly due to increase in the residence time of water (Catalan et al., 2016), the lowest DIC  
296 concentrations found in rivers from the SW region may also, at least partly, be due to their  
297 small size. Fairly good positive correlation between DIC concentrations and length of the  
298 rivers ( $r^2=0.38$ ,  $p<0.01$ ; Fig. 4b) also support this argument.

299           The major physical and biological processes controlling DIC concentrations in rivers  
300 are the exchange with atmospheric  $\text{CO}_2$ , autotrophic removal and heterotrophic addition of  
301 DIC. Since the Indian monsoonal estuaries have been reported to be a source of  $\text{CO}_2$  to the

302 atmosphere during the discharge period due to heterotrophic decomposition of organic matter  
303 (Sarma et al., 2001, 2011, 2012; Gupta et al., 2008, 2009; Bhavya et al., 2018), the DIC input  
304 from the dissolution of atmospheric CO<sub>2</sub> may be unlikely. On the other hand, organic matter  
305 decomposition is expected to add significant amount of DIC as enhanced bacterial respiration  
306 rates were reported during this period (Sarma et al., 2011; 2012). In contrast, significant  
307 negative correlation between chlorophyll-*a* and DIC ( $r^2=-0.44$ ,  $p<0.01$ ; Fig. 4c), except few  
308 SE rivers where elevated phytoplankton biomass (Chl-*a*:  $>5 \text{ mg m}^{-3}$ ) was recorded,  
309 suggesting that autotrophic removal of DIC is also significant in the Indian monsoonal rivers  
310 during the study period. A significant positive relationship was observed between the  $\delta^{13}\text{C}_{\text{DIC}}$   
311 and Chl-*a* ( $r^2=0.49$ ;  $p<0.01$ ; Fig. 4d), supporting this argument because preferential uptake of  
312  $^{12}\text{C}$  than  $^{13}\text{C}$  during photosynthesis leaves the residual DIC enriched in  $^{13}\text{C}$ . On the other  
313 hand,  $\delta^{13}\text{C}_{\text{DIC}}$  showed significant positive correlation with DO saturation ( $r^2=0.50$ ,  $p<0.01$ ;  
314 Fig. 4e) (depleted  $\delta^{13}\text{C}_{\text{DIC}}$  values at more under saturation of DO) and DOC concentrations  
315 ( $r^2=0.43$ ,  $p<0.01$ ; Fig. 4f) as was observed in the Xi river (Zou et al., 2016). Altogether,  
316 enriched  $\delta^{13}\text{C}_{\text{DIC}}$  are associated with higher DOC, less under saturation of DO and higher  
317 phytoplankton biomass (Chl-*a*) while the depleted  $\delta^{13}\text{C}_{\text{DIC}}$  are associated more under  
318 saturation of DO and less DOC. This suggests that both autotrophic removal and  
319 heterotrophic addition control DIC in the Indian rivers during the discharge period, with a  
320 considerable spatial variability. However, influence of these processes on DIC  
321 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  
322 also influenced by pollution, catchment lithology and outgassing of CO<sub>2</sub> (Shin et al., 2011;  
323 Brunet et al., 2005; Bouvillion et al., 2009; Zeng et al., 2011; Tamooh et al., 2013).  
324 Excluding Sabarmati and Mahisagar rivers, DIC concentrations showed fairly good linear  
325 relationship with population density over the catchment of the river ( $r^2=0.41$ ,  $p<0.01$ ; Fig.

326 4g), suggesting that considerable influence of pollution from the mega cities and industries on  
327 DIC in the Indian rivers.

328 Spatial distribution of soils shows that rivers of the NW region of India and upper  
329 reaches of Krishna and Godavari rivers drain the lime-rich black soils (Fig. 1) while rivers  
330 from the SW region drain red loamy soils. Whereas, the east-flowing rivers drain the lime-  
331 poor red sandy soils in the upper but lime-rich alluvial soils in the lower reaches (Fig.1).  
332 Lateritic soils, which are poor in lime and silicate, occupied the catchment of the rivers in the  
333 SW region of India. Relatively lower chemical weathering rates of the lateritic than the non-  
334 lateritic soils could be one of the reasons for the observed lower DIC concentration the rivers  
335 from SW region of India. A significant positive correlation was found between total  
336 alkalinity (TA) and  $\delta^{13}\text{C}_{\text{DIC}}$  ( $r^2=0.52$ ;  $p<0.01$ ; Fig. 4h), suggesting that significant contribution  
337 of DIC is from weathering of carbonate minerals in the catchment. Though the higher  
338 chemical weathering rates were reported for the Deccan Trap basalts (Das et al., 2005;  
339 Singh et al., 2005), which occupied the catchments of rivers of the NW region of India and  
340 upper reaches of Godavari and Krishna, higher DIC concentrations were also observed in  
341 rivers draining over the metamorphic rocks. This suggests that the influences of factors other  
342 than bedrock are also significant on the concentrations of DIC in the Indian rivers.

#### 343 **4.2 Major sources of DIC in the Indian monsoonal rivers**

344 Though, the  $\delta^{13}\text{C}_{\text{DIC}}$  is a promising tool to decipher the sources of DIC, its  
345 interpretation for source material identification in rivers is still challenging because multiple  
346 physical and biological processes within the rivers significantly alter the  $\delta^{13}\text{C}$  of DIC source.  
347 The influence of major in-stream processes on the  $\delta^{13}\text{C}_{\text{DIC}}$  must be separated before  
348 interpreting the results for major sources of DIC, failing which leads to erroneous  
349 conclusions. In order to identify and separate DIC sources, we used here two different  
350 graphical mixing model techniques, Keeling plot (Keeling, 1958; Pataki et al., 2003) and

351 Miller-Tans plots (Miller and Tans, 2003). These models approximate the hypothetical  $\delta^{13}\text{C}$   
352 of source material as an intercept (in Keeling plot) and slope (in Miller-Tans plot) of the least  
353 square linear regression equations (Pataki et al., 2003; Campeau et al., 2017). The deviations  
354 from the approximated  $\delta^{13}\text{C}$  of source can be interpreted to the influence of in-stream  
355 processes. Further, we approximated the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  using a set of enrichment factors of  
356 isotopic fractionation across the carbonate species (Zhang et al., 1995) in order to filter the  
357 impact of DIC speciation and pH on the bulk  $\delta^{13}\text{C}_{\text{DIC}}$  values. This approach has already  
358 been used by Quay et al. (1992), Mayorga et al. (2005) and recently by Campeau et al.  
359 (2017).

360 Significant negative relationships were observed in both Keeling plot ( $\delta^{13}\text{C}_{\text{DIC}}$  as a  
361 function of  $1/\text{DIC}$ ; Fig. 5a) and Miller-Tans plot ( $\delta^{13}\text{C}_{\text{DIC}}$  x DIC as a function of DIC; Fig.  
362 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  
363 rivers draining the Deccan Trap basalts. Both graphical mixing models, Keeling and Muller-  
364 Tans plots, approximated the similar  $\delta^{13}\text{C}$  of source material (-3.0‰ and -2.0‰ respectively;  
365 Fig. 5a&b), suggesting that weathering of carbonate minerals is the predominant source of  
366 DIC in the Indian monsoonal rivers rather than biogenic soil  $\text{CO}_2$ . Calculated  $\delta^{13}\text{C}$  of  $\text{CO}_2$   
367 ranged from -21.5 to -9.6‰ in the Indian rivers with a mean value of  $-13.0\pm 2.7\%$ . Calculated  
368  $\delta^{13}\text{C}$  of  $\text{CO}_2$  is linearly correlated with the measured  $\delta^{13}\text{C}_{\text{DIC}}$ , but correlation coefficient ( $r^2$ ) is  
369 only 0.51 (Fig. 5c), suggesting that significant spatial variability in the influence of in-stream  
370 processes on the  $\delta^{13}\text{C}_{\text{DIC}}$ . The Miller-Tans plot of  $\text{CO}_2$  ( $\delta^{13}\text{C}\text{-CO}_2$  x  $\text{CO}_2$  as a function of  
371  $\text{CO}_2$ ) showed highly significant linear regression model with a slope of -10.7‰ ( $r^2=0.97$ ;  
372  $p<0.001$ ; Fig. 5d). These results indicated that DIC in the Indian rivers is largely contributed  
373 by chemical weathering of carbonate and silicate minerals by soil  $\text{CO}_2$  (-10 to -9‰).  
374 Deviations of the measured  $\delta^{13}\text{C}_{\text{DIC}}$  (-13.0 to -1.4‰) from that of the approximated  $\delta^{13}\text{C}$  of  
375 DIC source (-3.0 to -2.0‰) and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  (-10.7‰) could be due to the influence of in-

376 stream process. In more than 75% of the Indian rivers sampled, the deviation from the  $\delta^{13}\text{C}$  of  
377 DIC source is towards negative side (depletion) ( $\delta^{13}\text{C}_{\text{DIC}} < -3.0\text{‰}$ ), suggesting that  
378 heterotrophic decomposition of organic matter is the dominant process controlling DIC in  
379 these rivers. While, no (or very little) deviation was observed only in rivers from the SE  
380 region of India (mean  $\delta^{13}\text{C}_{\text{DIC}}$ :  $-3.1\text{‰}$ ) could be due to the competition between autotrophy,  
381 degassing and heterotrophy as these processes influences the  $\delta^{13}\text{C}_{\text{DIC}}$  in opposite directions  
382 (Fig. 2); the former two processes causes enrichment while the latter depletes  $\delta^{13}\text{C}_{\text{DIC}}$ .  
383 Relatively higher phytoplankton biomass (mean Chl-a:  $4.6 \text{ mg m}^{-3}$ ) and less unsaturation of  
384 DO (98.7%) was observed in these rivers compared to the mean of the rest of the Indian  
385 rivers ( $2.4 \text{ mg m}^{-3}$  and 87.5% respectively), suggesting that autotrophy is one of the dominant  
386 processes controlling DIC in rivers from the SE region of India. Total number of dams on the  
387 rivers from this (SE) region (mean 155, Table 1) is not significantly higher from that of the  
388 mean of total number of dams on the Indian rivers sampled (mean 135) , suggesting that  
389 degassing due to storage of water may not be the dominant process responsible for  
390 enrichment in  $\delta^{13}\text{C}_{\text{DIC}}$  of these rivers.

#### 391 **4.3 Total DIC export by the Indian monsoonal rivers to the north Indian Ocean**

392 Indian monsoonal rivers annually export  $\sim 10.3 \text{ Tg}$  of DIC to the north Indian Ocean.  
393 Nearly three fourth of this amount ( $7.8 \text{ Tg}$ ) reaches to the Bay of Bengal while the remaining  
394 into the Arabian Sea. This is consistent with the higher magnitude of freshwater discharge to  
395 the Bay of Bengal ( $378 \text{ km}^3 \text{ yr}^{-1}$ ) from the catchment area of about  $970 \times 10^3 \text{ km}^2$  than the  
396 Arabian Sea ( $122 \text{ km}^3 \text{ yr}^{-1}$  from the catchment area of  $244 \times 10^3 \text{ km}^2$ ). The total DIC export by  
397 the Indian monsoonal rivers ( $10.3 \text{ Tg yr}^{-1}$ ) is far less than the DIC export by the American  
398 ( $61.4 \text{ Tg yr}^{-1}$ ) and African ( $17.7 \text{ Tg yr}^{-1}$ ) rivers and major rivers draining to the tropical  
399 Atlantic from South America and Africa ( $53 \text{ Tg yr}^{-1}$ , Araujo et al. 2014). It is mainly due to  
400 the fact that freshwater discharge from the Indian monsoonal rivers is very low ( $\sim 500 \text{ km}^3 \text{ yr}^{-1}$ )



401 <sup>1</sup>) compared to the American (11,799 km<sup>3</sup> yr<sup>-1</sup>) and African (3,786 km<sup>3</sup> yr<sup>-1</sup>) rivers. However,  
402 the Indian monsoonal rivers are exporting disproportionately higher DIC because they  
403 account for only 1.3% of the global river discharge but export 2.5% of the global riverine  
404 DIC export to the oceans (400 Tg yr<sup>-1</sup>). Though American and African rivers account for  
405 30% and 10% of the global river discharge, they export only 15% and 4.4% of global riverine  
406 DIC to oceans, respectively. Disproportionately higher DIC flux from the Indian rivers could  
407 be due to relatively higher weathering rates of silicate and carbonate minerals in their  
408 drainage basins (Das et al., 2005; Gurumurthy et al., 2012; Pattanaik et al., 2013). Higher DIC  
409 fluxes from the tropical regions are mainly attributed to the favourable climatic conditions,  
410 lithology and land use cover (Huang et al., 2012) of this region for higher dissolution.

411 Krishna et al. (2015) reported that Indian monsoonal rivers export 2.32 Tg yr<sup>-1</sup> of  
412 dissolved organic carbon (DOC) to the north Indian Ocean. The total fluvial dissolved carbon  
413 flux (DIC+DOC) would be 12.6 Tg yr<sup>-1</sup> in which DIC flux contributed up to ~81%. The  
414 predominance of DIC has also been found in rivers elsewhere in the world, for example, the  
415 British rivers (Jarvie et al., 2017) and high altitude Swedish rivers (Campeau et al., 2017).  
416 Since the catchment area of the Indian monsoonal rivers ranged widely from as low as 1x10<sup>3</sup>  
417 km<sup>2</sup> to as high as 313x10<sup>3</sup> km<sup>2</sup>, the export fluxes of DIC were normalized with the catchment  
418 area of the river (yield) in order to examine various factors controlling the DIC export to the  
419 north Indian Ocean.

#### 420 **4.4 Yield of DIC from the Indian monsoonal rivers**

421 The yield of DIC found in this study (mean 8.7±5.2 g m<sup>-2</sup> yr<sup>-1</sup>) is close to those found  
422 in rivers from the tropical region of Asia, but significantly higher than those reported from  
423 tropical region of the American and African continents (Huang et al., 2012). The yield was  
424 highest (8.8±5.6 g m<sup>-2</sup> yr<sup>-1</sup>) in rivers from the SW region of India, despite they export  
425 relatively lower DIC (0.3 Tg yr<sup>-1</sup>) due to their low volume of discharge (46 km<sup>3</sup> yr<sup>-1</sup>) and

426 relatively smaller catchment ( $20 \times 10^3 \text{ km}^2$ ) than the rivers from SE, NE and NW regions of  
427 India (Table 1. DIC yield showed a significant positive correlation with the volume of  
428 discharge ( $r^2=0.67$ ,  $p<0.001$ ; Fig. 6a) in medium rivers and no such relationship was found in  
429 the major rivers. Significant negative relationship was observed between DIC yield and  
430 catchment area of river ( $r^2 = -0.49$ ,  $p<0.001$ ; Fig. 6b and  $r^2 = -0.43$ ,  $p<0.001$ ; Fig. 6c for  
431 medium and major rivers respectively), suggesting the smaller rivers export more DIC per  
432 unit area of catchment compared to the major river systems, and thus inclusion of DIC data  
433 from medium rivers in the world significantly alters the global estimations of DIC. A fairly  
434 good linear relationship between the yield of DIC and the intensity of precipitation ( $r^2=0.43$ ,  
435  $p<0.01$  Fig. 6d) was observed only in the rivers which receives  $>2000\text{mm}$  of annual mean  
436 precipitation. Higher precipitation over the catchment increases the yield of DIC because the  
437 dense precipitation enhances the extraction of DIC from soils and rocks in their catchment  
438 Therefore, high precipitation ( $\sim 3000 \text{ mm}$ ) over the small catchment ( $20 \times 10^3 \text{ km}^2$ ) could have  
439 increased DIC yield from the rivers of SW region of India.

440 Sreenivas et al. (2016) and Krishwan et al. (2009) found that the soil organic and  
441 inorganic carbon contents in the surface (100cm) soils in the catchment of rivers in the SW  
442 region were higher and lower, respectively, than the catchments of the rivers from SE, SW  
443 and NE region of India. Decomposition of soil organic matter releases excess  $\text{CO}_2$  and, the  
444 increase in soil  $\text{CO}_2$  leads to the formation of acidic conditions in soils. This would increase  
445 the DIC yield by more dissolution of soil carbonates and chemical weathering of carbonate  
446 and silicate rocks (Zou et al., 2016). A significant linear correlation was found between soil  
447 organic carbon content and DIC yield in this study ( $r^2=0.65$ ,  $p<0.001$ ; Fig. 6e), suggesting  
448 that higher soil organic carbon in the catchment of the rivers from SW region could have  
449 elevated the yield of DIC from rivers of this region. The basin scale studies are, however,

450 required for comprehensive understanding of the influence of environmental and  
451 anthropogenic factors on export fluxes and yield of DIC from the Indian monsoonal rivers.

## 452 **5. Summary**

453 In order to examine the spatial variability in the sources and distribution of dissolved  
454 inorganic carbon (DIC) in the Indian monsoonal rivers, and to estimate their export fluxes of  
455 DIC to the north Indian Ocean, we sampled a total of 27 major and medium rivers during  
456 wet period. An order of magnitude variability was found in DIC concentrations among the  
457 rivers sampled (3.4 - 73.6 mg l<sup>-1</sup>), with a lower mean concentration of 6.6±2.1 mg l<sup>-1</sup> in rivers  
458 located in the SW region of India. It is attributed to significant spatial variability in the size  
459 of rivers, precipitation pattern, pollution and lithology in their catchments. The approximated  
460 δ<sup>13</sup>C of DIC source from the Keeling and Miller-Tans plots (-2.0 and -3.0‰ respectively)  
461 and, the calculated δ<sup>13</sup>C of CO<sub>2</sub> which filters the influence of pH and DIC speciation,  
462 suggested that DIC in the Indian rivers is mainly originated from chemical weathering of  
463 carbonate minerals, but largely affected by autotrophic production in rivers from the  
464 southeast region of India and heterotrophic decomposition of organic matter in rivers from  
465 other regions of India. Indian monsoonal rivers together export ~10.3 Tg yr<sup>-1</sup> of DIC to the  
466 north Indian Ocean, of which 7.8 Tg yr<sup>-1</sup> enters in to the Bay of Bengal while the Arabian Sea  
467 receives only 2.5 Tg yr<sup>-1</sup>. It is mainly attributed to the volume of river discharge as the  
468 former receives ~378 km<sup>3</sup> yr<sup>-1</sup> while the latter receives only 122 km<sup>3</sup> yr<sup>-1</sup> from the Indian  
469 monsoonal rivers. Dense rainfall and higher soil organic carbon content in the catchment of  
470 rivers from the SW region than in the catchment of the other Indian rivers resulted in highest  
471 yield of DIC from the former than the latter.

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## 482 **7. Data Availability**

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

485

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## 900 **Figure captions**

901

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

906

907 **Figure 2:** Schematic diagram showing the  $\delta^{13}\text{C}$  of different end members of dissolved  
908 inorganic carbon (DIC) sources. Various major processes influencing the  $\delta^{13}\text{C}$  of DIC  
909 ( $\delta^{13}\text{C}_{\text{DIC}}$ ) within the rivers were also shown. Black arrows ( and ) indicates the  
910 direction of change in  $\delta^{13}\text{C}_{\text{DIC}}$  due to the influences different in-stream process mentioned  
911 against arrows.

912

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

919

920 **Figure 4:** (a) Exponential decrease and (b) linear increase of dissolved inorganic carbon  
921 (DIC) concentrations with increasing the rainfall over the catchment and length of the river  
922 respectively. (c) Inverse and (d) linear relationships of chlorophyll-a (Chl-a) with  
923 concentrations and  $\delta^{13}\text{C}$  of DIC respectively. Significant linear relationships of  $\delta^{13}\text{C}$  of DIC  
924 with (e) dissolved oxygen (DO) saturation and (f) dissolved organic carbon (DOC)  
925 concentration. Linear relationships observed between (g) DIC concentrations and population  
926 density in the catchment and (h) total alkalinity and  $\delta^{13}\text{C}$  of DIC in the Indian monsoonal  
927 rivers during the study period. Ovals with dashed line indicate that outliers which were not  
928 included in the regression equations. Rivers of the northwest region of India showed linear  
929 relationships as shown by other Indian rivers but with a different slope (Fig. f-h)

930

931 **Figure 5:** Least square linear regression models of (a)  $\delta^{13}\text{C}_{\text{DIC}}$  as a function of  $1/\text{DIC}$   
932 (Keeling plot) and (b)  $\delta^{13}\text{C}_{\text{DIC}} \times \text{DIC}$  as a function of DIC concentrations (Millte-Tans plot) in  
933 the Indian monsoonal rivers. (c) Linear relationship between calculated  $\delta^{13}\text{C}$  of  $\text{CO}_2$  and the  
934 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  
935 function of  $\text{CO}_2$  concentration in the Indian monsoonal rivers.

936

937 **Figure 6:** Significant relationships dissolved inorganic carbon (DIC) yield with (a) river  
938 discharge in medium estuaries, (b) catchment areas of the medium rivers, (c) catchment areas

939 of the major rivers, (d) rainfall over the catchment of all the rivers sampled and (e) soil  
940 organic carbon (OC) content in catchments of the Indian monsoonal rivers studied. Since the  
941 data on soil OC is not available for each watershed (e) was plotted using the available soil  
942 OC data on regional scale (NW, SW, SE and NE regions of India), Hence, it contains only  
943 four points.

944

#### 945 **Table captions**

946

947 **Table 1:** Catchment area, discharge, length and elevation of each river and, annual mean  
948 rainfall, number of dams and population density in each watershed of the Indian monsoonal  
949 rivers sampled. Concentrations, export fluxes and yields of dissolved inorganic carbon (DIC)  
950 and its stable isotopes ( $\delta^{13}\text{C}_{\text{DIC}}$ ) of Indian rivers were given. Measured pH and calculated  
951  $\delta^{13}\text{C}$  of  $\text{CO}_2$  from isotopic fractionation factors across DIC speciation were also provided.

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River name	Catchment area (x10 <sup>3</sup> km <sup>2</sup> )	Annual Discharge (km <sup>3</sup> )	Length (km)	Population (No. km <sup>-2</sup> )	No. of major Dams	Elevation (m)	Rain-fall (mm)	pH	DIC Conc. (mg l <sup>-1</sup> )	DIC export flux (Tg yr <sup>-1</sup> )	DIC yield (g m <sup>-2</sup> yr <sup>-1</sup> )	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	Cal. $\delta^{13}\text{C-CO}_2$ (‰)
<b>West flowing rivers (Arabian Sea)</b>													
MAHISAGAR	34.8	11.0	580	507	138	500	785	7.3	22.8	0.3	7.2	-12.4	-21.5
SABARMATI	21.7	3.8	371	1702	62	1173	787	7.2	24.6	0.1	4.3	-13.0	-
TAPTI	65	14.9	724	208	375	752	888	7.1	35.6	0.5	8.2	-7.9	-16.4
NARMADA	99	45.6	1312	184	281	1317	1120	7.5	30.6	1.4	14.1	-11.0	-
ZUARI	1	3.2	34	92	3	-	3500	7.0	4.8	0.0	4.4	-5.1	-13.2
MANDOVI	3.6	3.3	81	62	2	600	3500	6.5	4.5	0.0	14.5	-7.4	-13.6
KHALI	4.2	4.8	184	111	6	600	3200	7.2	5.7	0.0	6.5	-7.0	-15.5
SHARAVATHI	3.6	4.5	128	109	3	700	4000	6.5	8.4	0.0	10.6	-6.8	-13.1
NETRAVATHI	3.2	11.1	103	103	-	1000	3923	6.3	5.1	0.1	17.8	-7.1	-12.4
BHARATHAPUZHA	6.2	5.1	209	-	13	1964	2500	6.0	3.4	0.0	2.8	-7.9	-11.6
CHALAKUDY	1.7	1.9	144	-	6	1250	3600	6.3	4.8	0.0	5.4	-5.1	-10.3
<b>East flowing rivers (Bay of Bengal)</b>													
VAIGAI	7	1.1	258	499	2	1200	850	-	26.0	0.0	4.2	-7.9	-
AMBALAYAAR	-	0.9	-	-	-	-	-	8.6	32.2	0.0	-	-	-
CAUVERY	88	21.3	800	393	122	1341	1075	7.5	40.5	0.9	9.8	-2.9	-11.8
VELLAR	8.6	0.9	210	457	3	900	980	7.4	73.6	0.1	7.7	-2.4	-11.1
PONNAIYAR	16	1.6	396	291	4	900	969	7.4	43.4	0.1	4.3	-1.4	-10.3
PENNA	55	6.3	597	186	61	1439	510	8.3	37.1	0.2	4.3	-2.6	-11.9
KRISHNA	259	69.8	1300	260	736	1903	784	8	33.5	2.3	9.0	-3.9	-
GODAVARI	313	110.5	1465	193	978	1067	1300	-	13.1	1.5	4.6	-5.6	-9.6
NAGAVALI	9.4	2.0	256	150	4	1300	1000	-	15.5	0.0	3.3	-	-13.1
VAMSADHARA	11.0	3.5	254	130	3	370	1400	8.2	27.2	0.1	8.6	-3.0	-12.4
RUSIKULYA	9.0	1.9	175	360	13	1000	1000	-	19.8	0.0	4.2	-	-
MAHANADI	141.6	66.9	858	282	280	890	1406	6.9	13.3	0.9	6.3	-5.4	-13.2
BAITARANI	14.2	28.5	414	324	8	900	1450	6.0	10.3	0.3	20.7	-6.5	-10.2
SUBARNALEKHA	29.2	12.4	395	338	12	600	1800	8.0	13.6	0.2	5.8	-2.9	-12.0
HYADRI	10.2	50.5		191				7.1	24.1	1.2	-	-5.8	-14.0

Table 1

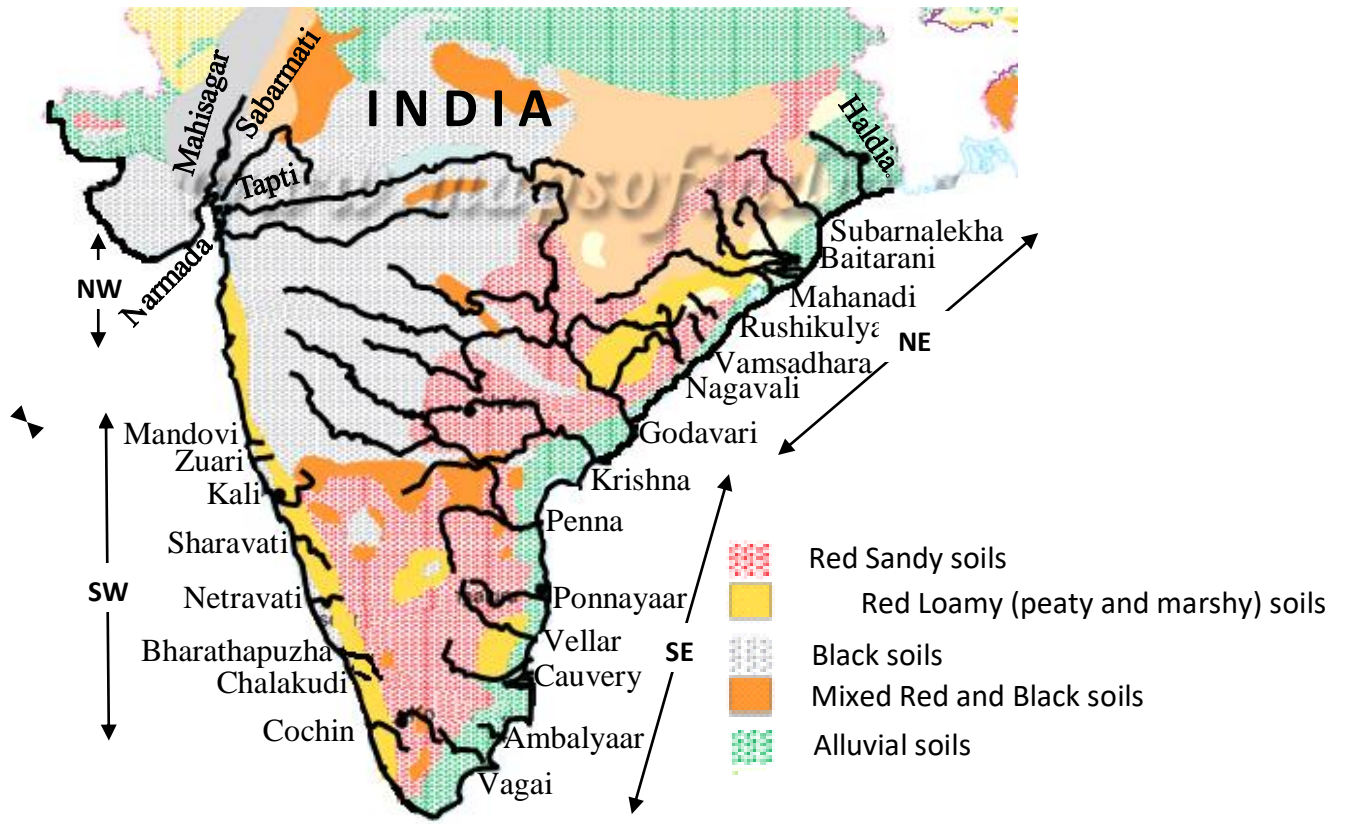
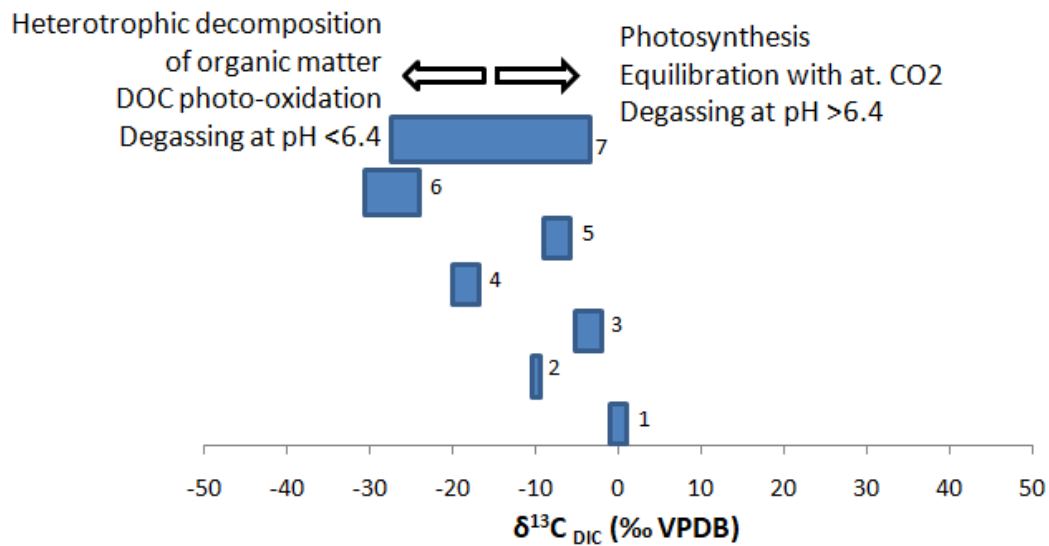


Fig.1





- 1: DIC derived from dissolution of atmospheric CO<sub>2</sub> / natural carbonates
- 2: weathering of carbonate rocks by carbonic acid derived from dissolution of soil CO<sub>2</sub>
- 3: weathering of carbonate rocks by carbonic acid derived from dissolution of atmospheric CO<sub>2</sub>
- 4: Weathering of silicate rocks by carbonic acid derived from dissolution of soil CO<sub>2</sub>
- 5: Weathering of silicate rocks by carbonic acid derived from dissolution of atmospheric CO<sub>2</sub>
- 6: Heterotrophic decomposition of organic matter derived from terrestrial C3/aquatic plants
- 7: Typical range of  $\delta^{13}\text{C}_{\text{DIC}}$  (‰) in river water

Fig. 2

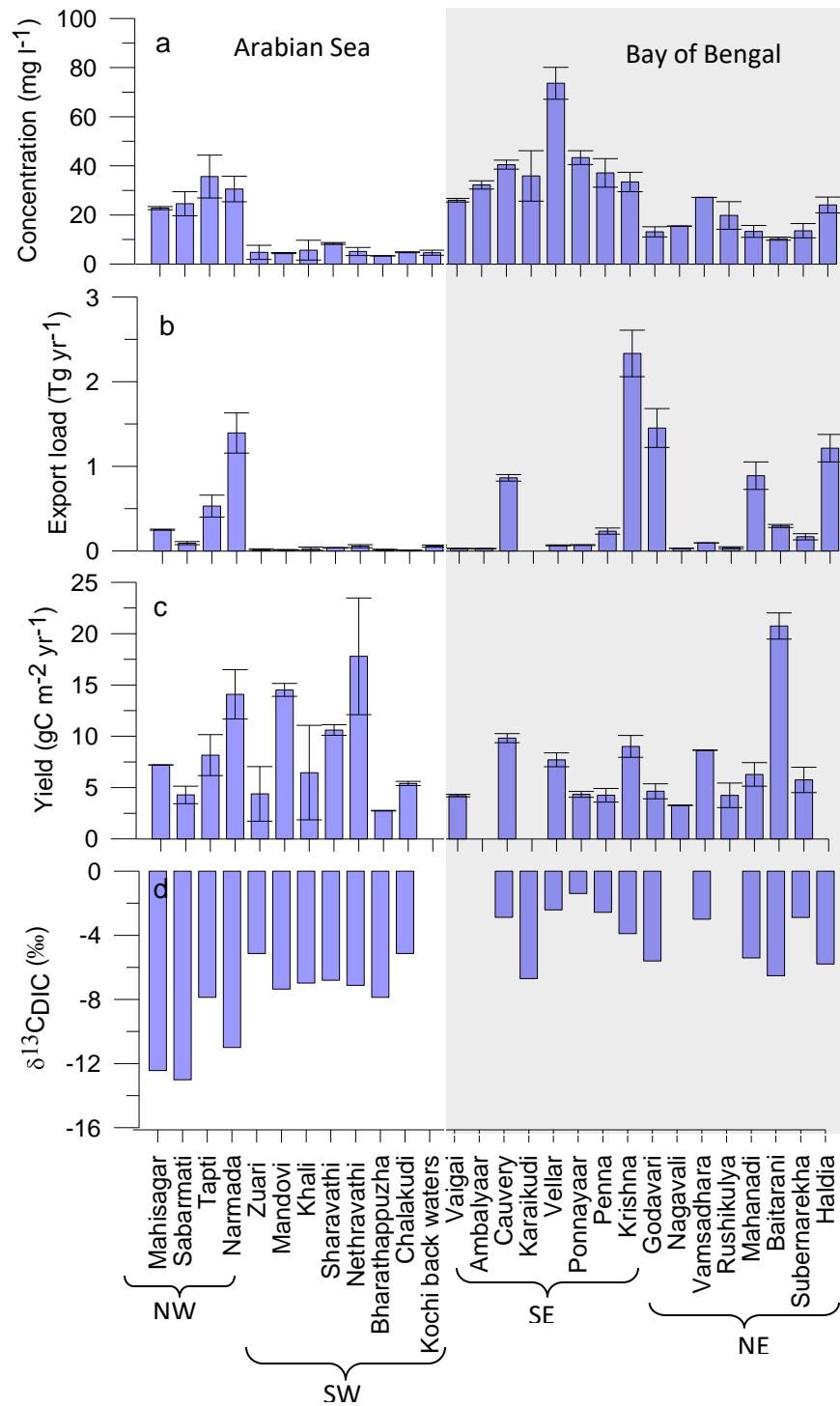


Fig. 3

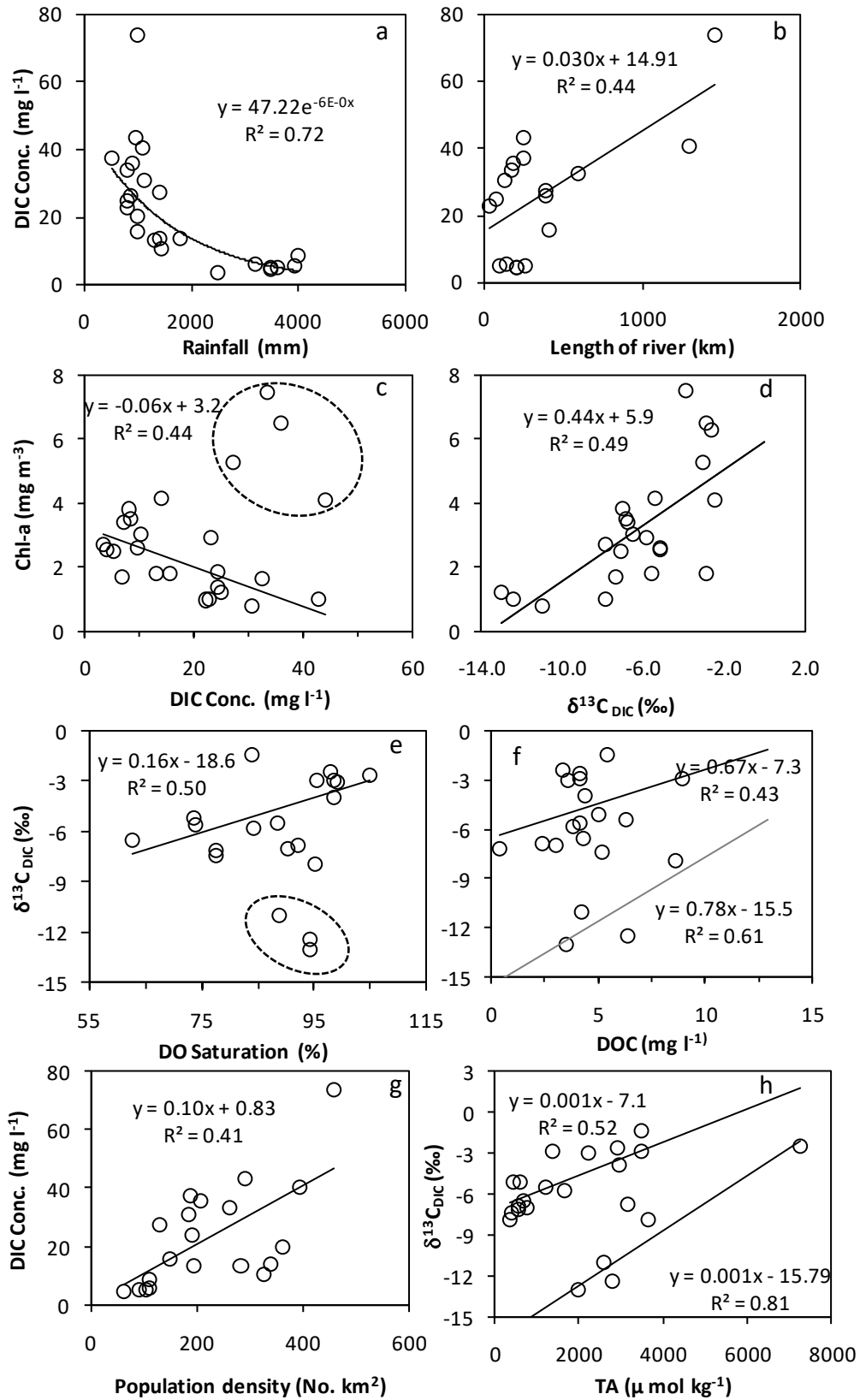


Fig. 4

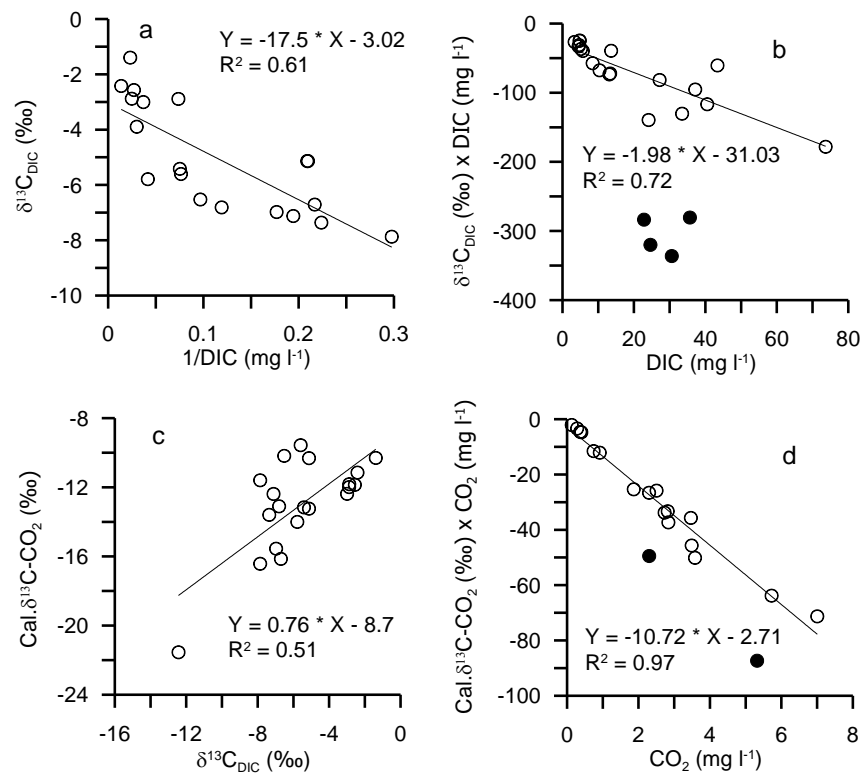


Fig. 5

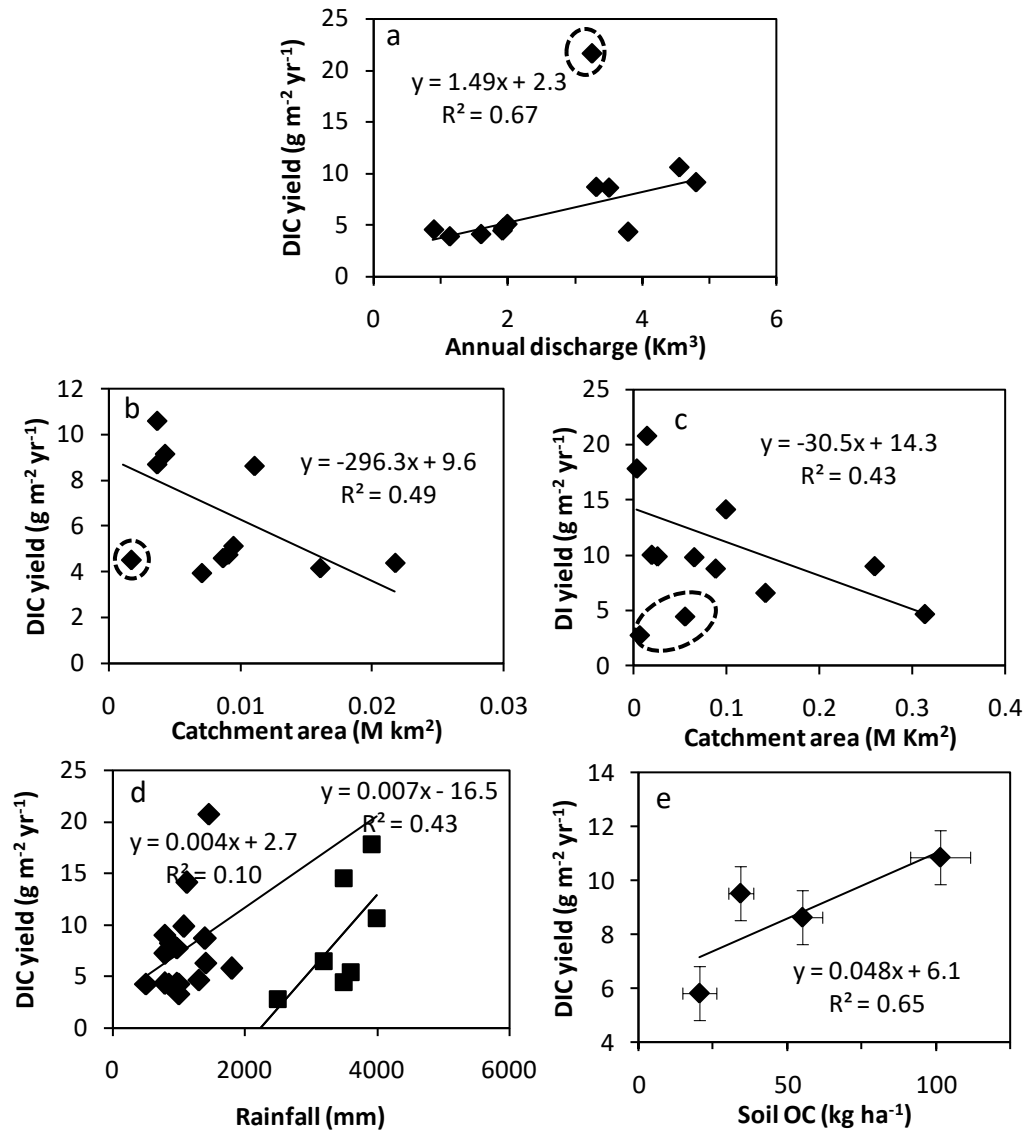


Fig. 6: