# 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 estuaries and to quantify their export flux to the north Indian Ocean, 27 major and medium estuaries along the Indian coast were sampled during the discharge period. Significant variability in concentrations of DIC was observed within the Indian estuaries sampled (3.4 - 44.1mg $l^{-1}$) due to variations in the size of rivers, precipitation pattern and lithology in the catchments. Dilution with high precipitation (2500±500 mm) and exchange with ground waters of low DIC resulted in very low concentrations of DIC in the estuaries located in the southwest of India (6.6±2.1 mg $l^{-1}$) than the estuaries located in the southeast (36.3±6.3 mg $l^{-1}$), northwest (30.3±8.9 mg $l^{-1}$) and northeast (19.5±6.2 mg $l^{-1}$) of India. The stable isotopic composition of DIC ($\delta^{13}C_{DIC}$) indicates that DIC is largely contributed by weathering of silicate and carbonate minerals. The storage of water in dams/reservoirs and intrusion of marine waters appears to be responsible for the enriched $\delta^{13}C_{DIC}$ in the east-flowing rivers. It is estimated that the Indian monsoonal estuaries annually export ~10.4 Tg of DIC to the northern Indian Ocean, of which the major fraction (74%) enters into the Bay of Bengal and the remaining reaches to the Arabian Sea. This is consistent with the freshwater flux which is three times higher in the Bay of Bengal (~378 $km^3 yr^{-1}$) than the Arabian Sea (122 $km^3 yr^{-1}$). Despite the discharge from Indian monsoonal rivers account for only 1.3% of global freshwater discharge, they disproportionately export 2.5% of the total DIC export by the world major rivers and 9.4% of the Asian rivers to oceans. The yield of DIC (DIC export normalized by the catchment area of the river) was found to be higher in the SW estuaries (10.8±6.6 g m$^{-2}$ yr$^{-1}$) than the SE (5.8±2.3g m$^{-2}$ yr$^{-1}$), NE (8.6±5.7g m$^{-2}$ yr$^{-1}$) and NW (9.5±4.0 g m$^{-2}$ yr$^{-1}$) estuaries. Despite the SW estuaries export only 0.3 Tg yr$^{-1}$ of DIC, which is more than an order of magnitude lower than that of the export by the NE (4.2 Tg yr$^{-1}$), SE (3.5 Tg yr$^{-1}$) and NW (2.4 Tg yr$^{-1}$) estuaries., higher yield of DIC from the SW estuaries is attributed to intense precipitation (~3000 mm), favorable natural vegetation of tropical moist deciduous and tropical wet evergreen and semi evergreen forests, tropical wet climate, high soil organic carbon and the dominance of red loamy soils in catchments of the SW rivers. This study, therefore, revealed that significant variability of the hydrological (precipitation), lithological (bed rock and soils) and environmental (vegetation and climate) conditions in the catchments strongly controls the concentrations and yield of DIC from the Indian monsoonal estuaries.

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

## 1. Introduction

Dissolved inorganic carbon (DIC) is the major constituent of carbon species and accounts for ~38% of the total fluvial carbon transport to the global oceans (Meybeck, 1993; Cai, 2011; Jarvie et al., 2017). World major river systems export annually 33-400 Tg (1Tg=$10^{12}$g) of DIC to the global oceans (Ludwig et al., 1998; Mackenzie et al., 2004; Lerman et al., 2007). Chemical weathering of carbonate and silicate rocks and soils in the drainage basin are the major sources of DIC into rivers (Meybeck, 1987; Gaillardet et al., 1999, Dessert et al., 2001; Viers et al., 2007; Raymond et al., 2008; Tamooh et al., 2013). The DIC concentrations in the estuaries are largely influenced by (i) the hydrological (precipitation and runoff), lithological (type and dominance of rocks and soils) and environmental (temperature, climate and vegetation) conditions, (ii) anthropogenic activities (deforestation and land use change) in the catchment and (iii) physical and biological processes such as exchange with ground water (Finlay, 2003; Shin et al., 2011; Maher et al., 2013), atmosphere, autotrophic production and heterotrophic utilization of organic matter (McConnaughey et al., 1994; Abril et al., 2003; Finlay and Kendall, 2007, Hotchkiss et al., 2015; Zou, 2016) in rivers and estuaries. Weathering of carbonate and silicate rocks in the catchment, uptake of DIC by aquatic plants in rivers are the sinks for the atmospheric $CO_2$ (e.g. Berner et al., 1983; Raymond et al., 2008) while the oxidation of organic carbon is the source of $CO_2$ to the atmosphere. Due to human interferences, DIC fluxes from the world major rivers are found to increase dramatically in the last century (Cai, 2003; Raymond and Cole, 2003; Raymond et al., 2008; Ren et al., 2015). It has been noted that substantial alterations in the lateral transport of DIC from land to sea occurred after the industrialization (Regnier et al., 2013; Bauer et al., 2013). The increase in riverine DIC flux has a significant impact on the chemical composition (Williamson et al., 1994; Raymond and Cole, 2003; Findlay, 2010; Tank et al., 2010) and carbon budget in the coastal waters (Cole et al., 2007; Dhillon and Inamdar, 2013). The identification of major sources of DIC in the estuaries and quantification of their export fluxes to the coastal oceans are important in understanding the carbon cycling both in the regional as well global scales (Campeau et al., 2017).

Fluvial carbon fluxes from rivers in the tropical region ($30^{o}$ N to $30^{o}$S) are critical for global carbon budgets because they contribute significant fraction to the global riverine DIC (48-64%) and freshwater discharge (66.2%) to the world oceans despite they occupy only ~43% of the world's land area (Huang et al., 2012). Furthermore, humid tropical climate over the tropical region supports the export of fluvial carbon from the continental land masses than the other climates in the world (Meybeck 1993; Ludwig et al., 1998). However, the fluvial DIC fluxes from rivers in the tropical region, except a few large river systems, to the global ocean are unknown due to the paucity of data.

Numerous studies have been documented on DIC export flux from the world major rivers, for example, the Mississippi (Raymond and Cole, 2003; Raymond et al., 2008; Cai et al., 2008), Changjiang and Pearl (Cai et al., 2008), Congo (Wang et al., 2013) and large river systems in the world (e.g. Gaillardet et al., 1999; Raymond et al., 2013). Though some measurements were carried out on DIC in the Indian estuaries, for example, Mandovi and Zuari (Sarma et al., 2001), Godavari (Sarma et al., 2011), Cochin (Gupta et al.,2009; Bhavya et al., 2018), Hooghly (Mukhopadhyay et al., 2002; Samanta et al., 2015), Mahanadi (Pattanaik et al., 2017) and Chila lake, a brackish water estuarine system (Gupta et al., 2008), the focus was mainly on internal cycling of carbon and exchange at the air-water interface. Carbon export fluxes from the Chilka lake (Gupta et al., 2008) and Cochin estuary (Gupta et al., 2009) on east and west coast of India respectively were reported but their sources were not evaluated.

The stable isotopic composition of DIC ($\delta^{13}C_{DIC}$) is widely used to identify the major sources of DIC in the aquatic system (e.g. Singh et al., 2005; Tamooh et al., 2013; Samanta et al., 2015; Zou, 2016) due to distinct isotopic composition of different sources (Deines et al., 1974). The isotopic composition of DIC originated by dissolution of atmospheric $CO_2$ is about 0‰ (Coplen et al., 2002) whereas it is about -27 to -26‰ if the DIC is derived from oxidation of organic matter produced by $C_3$ plants (O'Leary, 1988). The $\delta^{13}C$ of DIC generated by soil $CO_2$ dissolved carbonic acid weathering of silicates is about -21 to -17‰ (Solomon and Cerling, 1987) while it is in the range of -10 to -9‰ for carbonate rocks because half of the carbon comes from carbonate rocks (0‰, Land, 1980) during weathering. The weathering of silicate and carbonate minerals yield $\delta^{13}C_{DIC}$ in the range of -8 to -7‰ and -4 to -3‰, respectively, if the carbonic acid formed by the dissolution of atmospheric $CO_2$. Despite distinct isotopic composition of DIC is expected for different sources, the identification of DIC sources is still challenging (Amiotte-Suchet et al., 1999; Campeau et al., 2017) due to isotopic fractionations associated with complex mixture of sources and processes such as photosynthesis (O'Leary, 1988; Finlay, 2004; Parker et al., 2005, 2010), respiration (Finlay, 2003; Waldron et al., 2007), DOC photo-oxidation (Opsahl and Zepp, 2001; Vahatalo and Wetzel, 2008), anaerobic metabolism (Waldron et al., 1999; Maher et al., 2015) and equilibration with atmospheric $CO_2$. We made an effort for the first time to identify the major sources of DIC in the Indian monsoonal estuaries and quantify their export fluxes to the north Indian Ocean. The main objectives of this study are to (i) identify the major sources and (ii) examine potential reasons responsible for DIC variability in the Indian monsoonal estuaries during the discharge (wet) period, and (iii) estimate the DIC export fluxes to the north Indian Ocean from the Indian monsoonal rivers.

## 2. Study region, sampling and methods

### 2.1 Study Area

The Indian peninsula bifurcates the north Indian Ocean into the Bay of Bengal and the Arabian Sea. Although these two basins occupy the same latitudinal belt, their oceanographic processes were reported to be remarkably different due to higher freshwater flux into the Bay of Bengal (1.63 x $10^{12}$ $m^3$ $yr^{-1}$) than Arabian Sea (0.3 x $10^{12}$ $m^3$ $yr^{-1}$; Subramanian, 1993; Gauns et al., 2005). The large freshwater influx leads to the formation of a strong vertical salinity stratification in the Bay of Bengal (Varkey et al., 1996) that prevents vertical mixing of nutrient rich sub-surface water with surface (Prasanna Kumar et al., 2004). As a result, the Bay of

Bengal is considered to be relatively less productive (Prasannakumar et al., 2002) than the adjacent Arabian Sea, which is one of the highly productive zones in the world (Madhupratap et al., 1996; Smith, 2001; Barber et al., 2001) due to injection of nutrients into surface through the seasonal upwelling and convective mixing (Shetye et al., 1994; Madhupratap et al., 1996; Muraleedharan and Prasannakumar, 1996).

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

## 2.2 Sample collection

Water samples were collected within the estuaries rather than from mid or upstream rivers to obtain reliable export fluxes of DIC to the coastal ocean. Further, to minimize the inter-annual variability in DIC concentrations, sampling was conducted in two different years and the mean is used for export flux estimations. Each estuary was sampled at 3 to 5 locations between the upper (head) and lower (mouth) estuaries in order to minimize the spatial variability in DIC concentrations, and the mean concentrations are used for flux estimates. Further, samples were collected in mid-stream of the estuary using a local mechanized boat to avoid the contamination from river banks.

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

## 2.3. Methods

Temperature and salinity at the sampling locations were measured using a conductivity-temperature-density (CTD) profiling system (Sea Bird Electronics, SBE 19 plus, United States of America). Concentration of DO was determined by a Winkler's method (Carritt and Carpenter, 1966) using an auto titrator (Metrohm, Switzerland) with potentiometric end point detection. The analytical precision of the method was ±0.07% (RSD). Dissolved oxygen saturation is computed following formulations given by Garcia and Gordon (1992). DIC concentrations in water samples were measured at our Institute laboratory using Coulometer (UIC Inc., USA) connected to an automatic sub-sampling system. Based on the repeated analysis of samples and standards, the precision of the method was ±0.02 mg $l^{-1}$. The certified reference materials (CRM) supplied by Dr. A.G. Dickson, Scripps Institute of Oceanography, USA and internal standards were used to test the accuracy of our DIC measurements and it was found to be within ± 0.2 to 0.3%. The stable carbon isotopic composition of DIC in the water was measured on Gas Bench coupled with isotope ratio mass spectrometer (EA-IRMS-Delta V, Finnigan,Germany). 50 ml air-tight bottles with rubble septa were filled with 0.5 ml of high purity ortho-phosphoric acid and purged with high purity helium. About 1 ml of water sample is injected to the bottle and incubated at constant temperature of 50°C for 12 hours. The $CO_2$ extracted into the head space is injected to the IRMS through gas bench. The results are expressed relative to conventional standards, that is, pee dee belemnite (PDB) limestone for carbon (Coplen, 1996) as δ values, defined as:

$$\delta R = [(Xsample–Xstandard)/Xstandard)\ x10^{3}]\ ‰$$

where R refers to $^{13}C$ and X stands for $^{13}C/^{12}C$. The high-purity tank of $CO_2$ was used as working standard for carbon. These gases were calibrated with IAEA standards. Standard deviation on 20 aliquots of the same sample was lower than 0.05‰ for $\delta^{13}C$. Chlorophyll-*a* (Chl-*a*) on the filter was extracted into di-methyl formamide (DMF) and measured the extract fluorometrically using a spectrofluorophotometer (Varian Eclipse, Varian Electronics., UK) following Suzuki and Ishimaru (1990). Annual mean discharge data of the rivers was taken from Meybeck and Ragu (1995, 1996), Central Water Commission, New Delhi (2006, 2012) and Kumar et al. (2005). Catchment area of the rivers was obtained from Water Resources Information System of India (WRIS, www.india-wris.nrsc.gov.in). Soil organic carbon data was taken from Kishwan et al. (2009) and Sreenivas et al. (2016), and the rainfall data was obtained from Soman and Kumar (1990). Dissolved organic carbon (DOC) data for the Indian estuaries was taken from Krishna et al. (2015)

Total export flux of DIC from each river was estimated by multiplying the mean concentrations of DIC in an estuary with the annual discharge. Spatial variability of DIC concentrations in estuaries was minimized to a large extent by collecting samples from head to mouth of the estuary while the inter-annual variability by collecting samples during discharge periods of two years. However, variability in DIC concentrations within the discharge period results in some uncertainties in our estimations of DIC export fluxes. Time series measurements in the Godavari estuary (our unpublished results) revealed that the variability in DIC concentrations within the discharge period is up to 10%. Therefore, the error associated with our DIC flux estimates may be about 10%. DIC fluxes normalized by catchment area (yield) were calculated by dividing the total DIC export flux of the river by its catchment area.

## 3. Results

### *3.1. Hydrographic characteristics*

Surface water temperature was higher in the estuaries located on the east coast (mean 30.9±1.2$^{o}$C) than the west coast (27.3±1.5$^{o}$C) of India. Salinity varied broadly from near zero

(0.1) to 28.8 during the study period. Relatively higher salinities (>20) were recorded by the medium estuaries, which receives relatively lower freshwater discharge from the upstream river, for example, Nagavali (28.8), Vaigai (24.6) and Rushikulya (20.7). Mean salinities were lower in the west-flowing NW (0.1±0.02) and SW (2.1±2.8) estuaries than the east-flowing SE (9.5±7.8) and NE (8.5±11) estuaries. Dissolved oxygen saturation varied from as low as 63% to as high as 105%, with a mean saturation of 90±11% in the estuaries sampled. The SW estuaries recorded slightly lower DO saturation (82±7%) than the NE (89±15%), NW (93±3%) and SE (96±11%) estuaries. Chlorophyll-*a* (Chl-*a*) concentrations varied broadly from 0.8 to 7.5 mg $m^{-3}$, with relatively higher mean concentrations in the SE (4.7±2.5 mg $m^{-3}$) followed by the SW (2.8±0.7 mg $m^{-3}$) estuaries. On the other hand, relatively low Chl-*a* was observed in the medium (2.6±1.3 mg $m^{-3}$) than in the major estuaries (3.2±2.1 mg $m^{-3}$).

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

DIC concentrations in the Indian monsoonal estuaries widely varied from 3.4 (Bharathappuzha) to 44.1 mg $l^{-1}$ (Vellar), with a significant spatial variability (Fig. 2). More than five times higher mean concentrations were observed in the SE (36.3±6.3 mg $l^{-1}$) and NW estuaries (30.3±8.9 mg $l^{-1}$) than in the SW (6.6±2.1 mg $l^{-1}$) and NE estuaries (19.5±6.2 mg $l^{-1}$). DIC concentrations were found to be similar in the major (22.7±13.6 mg $l^{-1}$) and medium (21.1±13.2 mg $l^{-1}$) estuaries (homoscedastic Student's t-test; p=0.76). The $\delta^{13}C_{DIC}$ varied from -13.0 to 2.5‰, with a significant spatial variability (Fig. 3) in the estuaries sampled. Relatively depleted $\delta^{13}C_{DIC}$ values were observed in the west flowing estuaries of NW (-11.1±2.3‰) and SW (-7.4±1.9‰) than the east flowing estuaries of NE (-3.5±2.8‰) and SE (-2.7±5.2‰) regions of India.

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

Annual export flux of DIC to the coastal ocean from individual estuaries varied broadly from 0.01 Tg (Chalakudi) to as high as 2.3 Tg (Krishna). The NE estuaries export higher DIC flux (4.2 Tg $yr^{-1}$) followed by the SE (3.5 Tg $yr^{-1}$) and NW estuaries (2.4 Tg $yr^{-1}$). In contrast, the SW estuaries recorded the lowest export flux of 0.3 Tg $yr^{-1}$ which is an order of magnitude lower than that of the export flux by other estuaries (Fig. 2). The Indian monsoonal estuaries together export about 10.4 Tg $yr^{-1}$ of DIC to the northern Indian Ocean, of which 7.7 Tg (74%) enters into the Bay of Bengal and the remaining into the Arabian Sea (2.7 Tg). The estuaries Krishna (2.3 Tg $yr^{-1}$), Godavari (1.5 Tg $yr^{-1}$) and Haldia (1.2 Tg $yr^{-1}$) together responsible for the transport of 65% of total riverine DIC export to the Bay of Bengal. The yield of DIC ranged from 2.7 (Bharathappuzha) to 21.6 g $m^{-2}$ $yr^{-1}$ (Mandovi), excluding the exceptionally high yield of 113.4 g $m^{-2}$ $yr^{-1}$ from Haldia estuary. The west flowing rivers to the Arabian Sea are characterized by relatively higher yield of DIC (mean 10.4±5.6 g $m^{-2}$ $yr^{-1}$) than the east flowing rivers to the Bay of Bengal (7.3±4.6 g $m^{-2}$ $yr^{-1}$). Among the estuaries sampled, the SW and SE estuaries recorded higher (10.8±6.6 g $m^{-2}$ $yr^{-1}$) and lower (5.8±2.3 g $m^{-2}$ $yr^{-1}$) yields of DIC respectively whereas intermediate values were noticed in the NW (9.5±4.0 g $m^{-2}$ $yr^{-1}$) and NE (8.6±5.7g $m^{-2}$ $yr^{-1}$) estuaries.

## 4. Discussion

Hydrographic characteristics of the Indian monsoonal estuaries during the study (discharge) period were described elsewhere (Sarma et al., 2012, 2014; Krishna et al., 2015). Strong flow from upstream rivers due to heavy precipitation over the catchment makes most of the estuaries less saline (near zero) during the study period, except the medium estuaries, Nagavali, Vaigai and Rushikulya. No vertical salinity stratification was observed in all estuaries sampled during the study period and it is consistent with earlier observations in Godavari and Mandovi estuaries (Vijith et al., 2009; Sridevi et al., 2015). This is the unique feature of the Indian estuaries as strong stratification occurs in the European and American estuaries following discharge (Christopher et al., 2002). This difference is mainly caused by high discharge in shorter period in the Indian than other estuaries in the world (Vijith et al., 2009).

## 4.1 Distribution and sources of DIC in the Indian monsoonal estuaries

Mean DIC concentration found in this study (21.9±13.2 mg $l^{-1}$) is similar to those observed earlier in the Indian estuaries such as Ganga-Brahmaputra and Hooghly (Singh et al., 2005, Samanta et al., 2015), and in estuaries elsewhere in the world, for example York, Yangtze, Seri and Xi etc (Raymond and Bauer, 2000, Cai et al., 2008, Ishikawa et al., 2015; Zou, 2016) (Table 1). The DIC concentrations in the Indian estuaries are higher than those found in some of the Asian rivers of tropical region (12.7 mg $l^{-1}$, Huang et al., 2012) and the global mean (10.3 mg $l^{-1}$, Meybeck and Vorosmarty, 1999) (Table 1), but lower than those reported in the rivers draining into the Gulf of Trieste (N Adriatic; 37-66 mg $l^{-1}$, Tamse et al., 2014) (Table 1). Among the estuaries sampled along the Indian coast, the SW estuaries are characterized by significantly lower mean concentrations of DIC (6.6±2.1 mg $l^{-1}$) than the SE (36.3±6.3 mg $l^{-1}$), NE (19.5±6.2 mg $l^{-1}$) and NW (30.3±8.9 mg $l^{-1}$) estuaries (Table 2). This could be due to considerable spatial variations in the (i) hydrological, lithological and environmental conditions in the catchments and (ii) in-stream physical and biogeochemical processes.

### *4.1.1. The impact of hydrological conditions*

The SW region of India receives the highest amount of precipitation during the SW monsoon (2500±500 mm) than the SE (400±50 mm), NE (1000±200 mm) and NW (750±250 mm) regions of India (Table 2) (Soman and Kumar, 1990). The intense precipitation in the SW region is expected to cause higher weathering rates and therefore higher DIC (e.g., Gupta et al., 2011), but lower DIC concentrations were found in the SW estuaries. This is attributed to the influence of dilution because the catchment area normalized volume of discharge was found to be higher in the SW estuaries (1.71 $m^3$ $m^{-2}$) than in the SE (0.17 $m^3$ $m^{-2}$), NE (0.6 $m^3$ $m^{-2}$) and NW (0.32$m^3$ $m^{-2}$) estuaries. About three times higher catchment area normalized discharge might have diluted DIC concentrations in the SW estuaries. A strong negative correlation between precipitation in the catchment and DIC concentration in estuaries ($r^2$= -0.89, p<0.001; Fig. 4a) also suggest that DIC concentration in Indian estuaries are rather controlled by the intensity of precipitation over the catchment. Dilution of DIC by heavy precipitation in the SW region can also be seen from relatively depleted $\delta^{13}C_{DIC}$ values (-7.4±1.9‰) in the SW estuaries because the shorter residence time of soil water depletes the $\delta^{13}C_{DIC}$ due to preferential dissolution of $^{12}CO_2$ over $^{13}CO_2$ (Amiotte-Suchet et al., 1999).

Since many of the hydrological processes are largely dependent on the size of the river and its catchment area, these two factors may govern the concentrations of DIC in estuaries. The lower concentrations of DIC in the SW estuaries may possibly due to smaller catchment area as SW rivers are small, both in terms of discharge (46 $km^3$ $yr^{-1}$) and catchment area (total catchment area: 0.02 M $km^2$), than that of SE, NE and NW rivers (Table 2). The concentrations of DIC in the Indian estuaries showed a significant positive relationship with catchment area ($r^2$=0.76; p<0.001; Fig. 4b) and a negative relationship with volume of discharge ($r^2$=-0.57; p<0.001; Fig. 4c) only in the medium estuaries (discharge: <150 $m^3 s^{-1}$), suggesting that an area of catchment and magnitude of discharge controls DIC concentrations largely in the medium estuaries rather than in the major estuaries. It could be due to the influence of in-stream processes as the major rivers are long compared to the medium rivers.

Mixing with seawater and exchange of submarine ground water also influence DIC concentrations in the estuaries. Since this study was conducted during the SW monsoon, many of the estuaries are filled with freshwater (salinity >1) due to maximum discharge during this period. On the other hand, higher salinities (>20) were observed in some medium estuaries, namely, Rushikulya, Nagavali and Vaigai recorded higher salinities (>20) due to low flow from upstream river. A strong positive correlation was found between $\delta^{13}C_{DIC}$ and salinity (Fig. 4d; $r^2=0.71$, $p<0.001$), suggesting that DIC in the Indian estuaries is also influenced by the intrusion of marine waters particularly in medium estuaries. The $\delta^{13}C_{DIC}$ values were found to be >0‰ in Rushikulya, Nagavali and Vaigai estuaries (0.1, 0.7 and 2.5‰ respectively) suggesting that major contribution of DIC in these estuaries is from intrusion of marine water.

As found in many estuaries over the world, submarine groundwater discharge is found to contribute up to 52% of DIC in the Godavari estuary (Rengarajan and Sarma, 2015) due to higher concentrations of DIC by 3 to 4 times in in the ground water than estuary. The measured DIC concentrations in ground waters along the entire Indian coast suggest relatively lower concentrations in the SW (mean 32±19 mg $l^{-1}$) than the SE, NE and NW regions of India (Table 2) during discharge period (Dr. BSK Kumar, personal communication). Exchange of SW estuaries with ground water with relatively lower DIC concentrations might have possibly yielded low DIC concentrations. Nevertheless it is difficult to ascertain the impact of ground water exchange yielded low DIC in the SW estuaries due to lack of submarine ground water discharge rates.

### *4.1.2. The impact of in-stream processes*

Since the Indian monsoonal estuaries have been reported to be a source of $CO_2$ to the atmosphere during the discharge period (Sarma et al., 2001, 2011, 2012; Gupta et al., 2008, 2009; Bhavya et al., 2018), the DIC input from dissolution of atmospheric $CO_2$ can be ruled out. $CO_2$ release due to heterotrophic decomposition of organic matter adds significant amount of DIC to the Indian estuaries during this period as enhanced bacterial respiration rates were reported in the Indian estuaries (Sarma et al., 2011; 2012). A fairly good positive correlation between DIC and DOC concentrations ($r^2$=0.34, $p<0.01$; Fig. 4e), except few medium estuaries, suggests that DIC addition through microbial degradation of organic matter seems to be possible source in the Indian estuaries. A positive correlation between $\delta^{13}C_{DIC}$ and DOC was observed, with different slope for NW estuaries ($r^2$=0.43, $p<0.01$; Fig. 4f), confirming that oxidation of organic matter may be one of the major DIC sources in the Indian monsoonal estuaries. Similar relationship was also observed in the Xi river (Zou et al., 2016). The range of $\delta^{13}C_{DIC}$ (-13.0 to 2.5‰) in the Indian monsoonal estuaries is distinctly enriched than that of the $\delta^{13}C$ of DIC derived from decomposition of terrestrial $C_3$ plant derived organic matter (-27 to -26‰, O'Leary, 1988; Fig. 5), suggesting that DIC might have been contributed from decomposition of terrestrial $C_4$ plants (-17 to -13‰, Krishna et al., 2015) and weathering of silicate and carbonate rocks. In addition, if weathering occurs due to dissolution of silicate and carbonate rocks due to atmospheric $CO_2$, the $\delta^{13}C_{DIC}$ yields -8 to -7‰ and -4 to -3‰ respectively. On the other hand, the $\delta^{13}C_{DIC}$ would be -10 to -9‰ and -21 to -17‰ (Solomon and Cerling, 1987) if the dissolution of silicate and carbonate rocks occurs due to soil $CO_2$ respectively. As discussed above, flux of $CO_2$ from atmosphere to river cannot be expected due to super-saturation of riverine $CO_2$, weathering of silicate and carbonate rocks by dissolution of soil $CO_2$ may be possible. Though isotopic composition of $\delta^{13}C_{DIC}$ derived from decomposition of $C_4$ plants and weathering due to soil $CO_2$ are similar and difficult to separate, Sarma et al. (2014) measured isotopic composition of $\delta^{13}C_{POC}$ and found that >90% of the POC is contributed by $C_3$ plants. Hence possible contribution of DIC through decomposition of $C_4$ plants may be negated.

Significant negative correlation between chlorophyll-*a* and DIC ($r^2$=-0.44, $p<0.01$; Fig. 6a), except few SE estuaries where elevated phytoplankton biomass (Chl-a: >5 mg $m^{-3}$) was recorded, suggesting that autotrophic removal of DIC may be possible sink in the Indian monsoonal estuaries during the study period. This process would enrich $\delta^{13}C_{DIC}$ of residual DIC due to preferential removal of $^{12}CO_2$ over $^{13}CO_2$ during photosynthesis. A positive relationship was observed between $\delta^{13}C_{DIC}$ and Chl-a in the Indian estuaries ($r^2$=0.50; $p<0.01$), suggesting that biological removal of DIC enriched $\delta^{13}C_{DIC}$. In contrast, heterotrophic decomposition of organic matter (respiration) depletes $\delta^{13}C_{DIC}$ due to release of $^{12}CO_2$ over $^{13}CO_2$ during this process. Due to lack of respiration rates data, we could not able to evaluate its influence. Nevertheless, the dissolved oxygen saturation stores the net effect of biological production and heterotrophic respiration. In order to confirm the net biological influence on $\delta^{13}C_{DIC}$, the same is correlated with DO saturation and found significant positive correlation ($r^2$=0.50, $p<0.01$; Fig. 6b), (depleted $\delta^{13}C_{DIC}$ values at low DO saturation), except NW estuaries, which recorded depleted $\delta^{13}C_{DIC}$ (<-10.0‰) confirming that biological processes enriched $\delta^{13}C_{DIC}$ in the Indian monsoonal estuaries. $CO_2$ out gassing due to heterotrophic decomposition of organic matter and equilibrium with atmospheric $CO_2$ results in the enrichment of $\delta^{13}C_{DIC}$ in reservoirs/dams and stored water bodies (Shin et al., 2011; Brunet et al., 2005; Bouvillion et al., 2009; Zeng et al., 2011; Tamooh et al., 2013). As many of the east flowing river (e.g. Godavari, Krishna and Cauvery etc) were dammed at many locations for domestic, industrial and irrigation purposes., relatively enriched $\delta^{13}C_{DIC}$ in these estuaries might have been influenced by storage of water besides sources of DIC A significant positive correlation between DIC concentrations and $\delta^{13}C_{DIC}$ ($r^2$=0.76; $p<0.001$; Fig. 6c), excluding the positive $\delta^{13}C_{DIC}$ values, indicate that significant contribution of DIC is from oxidation of organic carbon in dams/reservoirs or stored water bodies. Therefore, DIC in the Indian estuaries are contributed by weathering of silicate and carbonate rocks due to soil $CO_2$, biological production, organic matter decomposition and exchange of $CO_2$ to the atmosphere.

### *4.1.3. The impact of catchment lithology*

Spatial distribution of bedrock and soils over the Indian subcontinent shows that Narmada and Tapti rivers in the NW India and upper reaches of Godavari and Krishna rivers drain over the igneous rocks (Deccan traps) while the other rivers flow over the metamorphic rocks (Pre-Cambrian), which are the predominant rock type in south India. However, Haldia and lower reaches of the SE rivers drain over the sedimentary rocks (Geological Survey of India, https://www.gsi.gov.in). Though higher chemical weathering rates were reported in the Deccan Trap basalts (Das et al., 2005; Singh et al., 2005), higher DIC concentrations were also observed in estuaries draining over the metamorphic rocks, suggesting that other factors may also be governing the concentrations of DIC, than the bedrocks in the catchment. The broad range of $\delta^{13}C_{DIC}$ found in this study (-13.0 to 2.5‰) also indicates that DIC contribution is from variable sources such as weathering of carbonate and silicate rocks by carbonic acid derived from dissolution of soil $CO_2$ (-10 to -9‰ and -21 to -17‰ respectively, Solomon and Cerling, 1987), decomposition of organic matter and marine water (0 to 2‰) (Fig. 5).

Spatial distribution of soils shows that lateritic soils, which are poor in lime and silicate, occupied the catchment of the SW rivers. Chemical weathering rates are relatively lower in the lateritic than the non-lateritic soils and the consumption of atmospheric/soil $CO_2$ through silicate weathering is lower by ~2 times in the former than the latter (Boeglin and Probst, 1998). The upper reaches of the east flowing rivers (NE and SE) drain over the lime-poor red and yellow soils, while lower reaches drain predominantly the lime-rich alluvial soils. Upper reaches of Krishna and Godavari also drain over the lime-rich black soils. The dominance of lateritic soils, which are relatively less susceptible to chemical weathering than the non-lateritic soils in the catchments of the SW rivers could be possible reason for lower DIC concentrations in SW estuaries. The enriched $\delta^{13}C_{DIC}$ in the SW estuaries (-7.4±1.9‰) may also be due to less contribution of DIC from lateritic soils as these soils are poor in lime (-10 to -9‰) and silicate (-21 to -17‰) and less susceptible to chemical weathering rates.

## 4.2 Total DIC export by the Indian monsoonal rivers to the north Indian Ocean

Indian monsoonal rivers annually export ~10.4 Tg of DIC to the north Indian Ocean. Nearly three fourth of this amount (7.7 Tg) reaches to the Bay of Bengal while the remaining into the Arabian Sea. This is consistent with the higher magnitude of freshwater discharge to the Bay of Bengal (378 $km^3\ yr^{-1}$) from the catchment area of about 0.96 M $km^2$ than the Arabian Sea (122 $km^3\ yr^{-1}$ from the catchment area of 0.23 M $km^2$). The total DIC export by the Indian monsoonal estuaries (10.4 Tg $yr^{-1}$) is only 2.5% of the total DIC export by the world major rivers (400 Tg $yr^{-1}$), and 9.4% of the export by the Asian rivers (111 Tg $yr^{-1}$; Huang et al., 2012). The DIC export from the Indian estuaries is far less than the DIC export by the American (61.4 Tg $yr^{-1}$) and African (17.7 Tg $yr^{-1}$) rivers and major rivers draining to the tropical Atlantic from South America and Africa (53 Tg $yr^{-1}$, Araujo et al. 2014). It is mainly due to the fact that freshwater discharge from the Indian monsoonal rivers is very low (~500 $km^3\ yr^{-1}$) compared to the American (11,799 $km^3\ yr^{-1}$) and African (3,786 $km^3\ yr^{-1}$) rivers. However, the Indian monsoonal rivers are exporting disproportionately higher DIC to the north Indian Ocean because they account for only 1.3% of the global river discharge but export 2.5% of the global riverine DIC to the oceans. Though American and African rivers account for 30% and 10% of the global river discharge, they export only 15% and 4.4% of global riverine DIC to oceans, respectively. Higher DIC fluxes from the tropical regions are mainly attributed to the favourable climatic conditions, lithology and land use cover (Huang et al., 2012) in this region for higher dissolution as higher weathering rates of silicate and carbonate minerals were reported in the drainage basins of the Indian rivers (Das et al., 2005; Gurumurty et al., 2012; Pattanaik et al., 2013)

Krishna et al. (2015) reported that Indian monsoonal estuaries export 2.32 Tg $yr^{-1}$ of dissolved organic carbon (DOC) to the north Indian Ocean. The total fluvial dissolved carbon flux (DIC+DOC) would be 12.7 Tg $yr^{-1}$ in which DIC flux contributed up to ~81% and it is consistent with earlier reports elsewhere in the world, for example, the British rivers (80%, Jarvie et al., 2017). Since the catchment area of the Indian monsoonal rivers ranged widely from as low as 0.001 M $km^2$ to as high as 0.313 M $km^2$, the export fluxes of DIC were normalized with the catchment area of the river (yield) in order to examine various factors controlling the lateral DIC export to the north Indian Ocean.

### 4.3 Yield of DIC from the Indian monsoonal rivers

The yield (export flux normalized by catchment area) of DIC found in this study (mean 8.7±5.2 g $m^{-2}$ $yr^{-1}$) is similar those found earlier in the rivers from tropical region of the Asian continent, but significantly higher than those reported from tropical region of the American and African continents (Table 3) (Huang et al., 2012). The SW estuaries annually export relatively lower DIC to the north Indian Ocean (0.3 Tg) due to their low volume of discharge (46 $km^3$ $yr^{-1}$) and relatively smaller catchment area (0.02 M $km^2$) than the SE, NE and NW estuaries (Table 2

& 3), in contrast, the higher yield of DIC was found in the former (10.8±6.6 g $m^{-2}$ $yr^{-1}$) than the latter (Table 3). DIC yield showed a significant positive correlation with the volume of discharge ($r^2$=0.67, p<0.001; Fig. 6d) in medium estuaries and no such relationship was found in the major estuaries. Significant negative relationships were observed between DIC yield and catchment area in the medium ($r^2$ = -0.49, p<0.001; Fig. 6e) and major estuaries ($r^2$ = -0.43, p<0.001; Fig. 6f). This suggests that high precipitation over small catchments increases DIC yield because the dense precipitation increases the extraction of DIC from soils and rocks in their catchment. Therefore, high precipitation (2500±500mm) over the small catchment (0.02 M $km^2$) could have increased DIC yield from the SW estuaries. A strong linear relationship between the yield of DIC and the intensity of precipitation ($r^2$=0.64, p<0.001 Fig. 6g) confirms that dense precipitation increases the export yield of DIC from SW estuaries.

Existing natural vegetation of tropical moist deciduous and tropical wet evergreen and semi evergreen forests in the SW region could also have increased DIC yield from the SW estuaries as this vegetation favors the export fluxes of DIC. The drainage basins of the Indian monsoonal rivers are largely under the tropical dry and wet climate except the SW rivers, Narmada and Tapti. The rivers Narmada and Tapti are under the arid and semiarid climate while the SW rivers are under the tropical wet climate which was also reported to facilitate the riverine export of material from drainage basin to the coastal ocean.

Sreenivas et al. (2016) and Krishwan et al. (2009) found that the soil organic and inorganic carbon contents in the surface (100cm) soils in the catchment of SW rivers were higher and lower, respectively, than the catchments of the SE, SW and NE rivers (Table 2). This indicates that more dissolution of soil carbonates by acidic conditions formed by release of $CO_2$ through decomposition of soil organic carbon in catchments of the SW rivers. Hence, the higher soil organic carbon in the catchment of the SW than the SE, NE and NW rivers (Kishwan et al., 2009; Sreenivas et al., 2016) could have elevated the yield of DIC from SW estuaries through dissolution of soil carbonates. A significant linear correlation between soil organic carbon content and DIC yield in this study ($r^2=0.65$, $p<0.001$; Fig. 6h) confirms that strong influence of soil organic carbon content in the catchment on DIC yield from the Indian monsoonal rivers. The basin scale studies are required for comprehensive understanding of the influence of environmental and anthropogenic factors on DIC export fluxes from the Indian monsoonal rivers.

## 5. Summary

In order to examine the spatial variability in the sources and distribution of dissolved inorganic carbon (DIC) in the Indian monsoonal estuaries, and to estimate the riverine export fluxes of DIC to the north Indian Ocean, we sampled a total of 27 major and medium estuaries along the Indian coast during wet period. An order of magnitude variability was found in DIC concentrations among the estuaries sampled (3.4 - 44.1mg $l^{-1}$), with a lower mean concentration of 6.6±2.1 mg $l^{-1}$ in estuaries located in the SW region of India. It is attributed to significant spatial variability in the size of rivers, precipitation pattern and lithology in their catchments. Magnitude of discharge, catchment area and in-stream processes appears to be the controlling factors for concentration and yield of DIC in the medium estuaries rather than the major estuaries. This is probably due to a significant spatial variability in lithology and hydro-geological and environmental conditions in the catchments. Indian monsoonal estuaries annually export ~10.4 Tg of DIC to the north Indian Ocean, of which 7.7 Tg enters in to the Bay of Bengal while the Arabian Sea receives only 2.7 Tg. It is mainly attributed to the volume of river discharge as the former receives ~378 $km^3$ $yr^{-1}$ while the latter receives only 122 $km^3$ $yr^{-1}$ from the Indian monsoonal rivers. The range of $\delta^{13}C_{DIC}$ found in this study suggests that major contribution of DIC is from weathering of silicate and carbonate minerals by carbonic acid formed by dissolution of soil $CO_2$. However, relatively enriched $\delta^{13}C_{DIC}$ in the east-flowing river estuaries indicated the storage of water in dams/reservoirs and intrusion of marine waters. Dense rainfall and higher soil organic carbon content in the catchment of SW rivers than in the catchment of the other rivers resulted in higher yield of DIC from the former than the latter.

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## 7. Data Availability

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

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## Figure captions

**Figure 1:** Map showing the study region. Estuaries of the rivers sampled in this study were indicated by solid black line.

**Figure 2:** Concentration (mg $l^{-1}$), export flux (Tg $yr^{-1}$) and yield (g $m^{-2}$ $yr^{-1}$) of dissolved inorganic carbon (DIC) in the Indian monsoonal estuaries. Estuaries geographically located in the northeastern (NE), southeastern (SE), southwestern (SW) and northwestern (NW) regions of India were also shown. Estuaries draining into the Bay of Bengal and the Arabian Sea were also provided

**Figure 3:** Spatial variability in stable carbon isotopes of dissolved inorganic carbon ($\delta^{13}C_{DIC}$, ‰) in the Indian monsoonal estuaries during the study period.

**Figure 4:** (a) Correlation between mean DIC concentration and precipitation in the four regions (NE, SE, SW and NW) of India. Relationship of DIC concentrations with (b) catchment area and (c) discharge volume of rivers in the medium estuaries. (d) Correlation between $\delta^{13}C_{DIC}$ and salinity in the in the Indian monsoonal estuaries during the study period.

**Figure 5:** A schematic showing the range of $\delta^{13}C$ values of dissolved inorganic carbon (DIC) derived from various sources. Different physical and biogeochemical processes influencing the $\delta^{13}C$ of DIC were also shown. The forward arrow (⇨) indicates enrichment while the reverse arrow (⇦) indicates depletion in the $\delta^{13}C$ of DIC

**Figure 6:** Significant relationships between (a) chlorophyll-a and concentration of dissolved inorganic carbon (DIC), (b) $\delta^{13}C_{DIC}$ and dissolved oxygen (DO) saturation and (c) $\delta^{13}C_{DIC}$ and concentrations of DIC in the Indian monsoonal estuaries during the study period. The relationships of DIC yield from medium estuaries with (d) volume of discharge and (e) catchment area of the rivers. (f) Correlation between the yield of DIC and catchment area of the rivers in the major estuaries. Relationships of DIC yield from the Indian monsoonal estuaries with (g) precipitation and (h) soil organic carbon in the four regions (NE, SE, SW and NW) of India.

## Table captions

**Table 1:** Mean or range of concentrations of dissolved inorganic carbon (DIC, mg $l^{-1}$) in the Indian monsoonal estuaries and elsewhere in the world.

**Table 2:** Total catchment area (million square kilometre), annual discharge volume ($km^3$) and export flux (Tg $yr^{-1}$) of the estuaries located in the NE, SE, SW and NW regions of India. Mean (±SD) values of concentration, $\delta^{13}C$ and yield of DIC in estuaries of these four regions were given. Annual mean rainfall (mm) and soil organic carbon content (ton $ha^{-1}$) in surface soils of these regions were also shown. Mean (±SD) concentrations of DIC in the ground waters of these four regions were also provided.

**Table 3:** Export flux (Tg $yr^{-1}$) and yield (gC $m^{-2}$ $yr^{-1}$) of dissolved inorganic carbon (DIC) from the Indian monsoonal rivers and from the rivers elsewhere in the world.

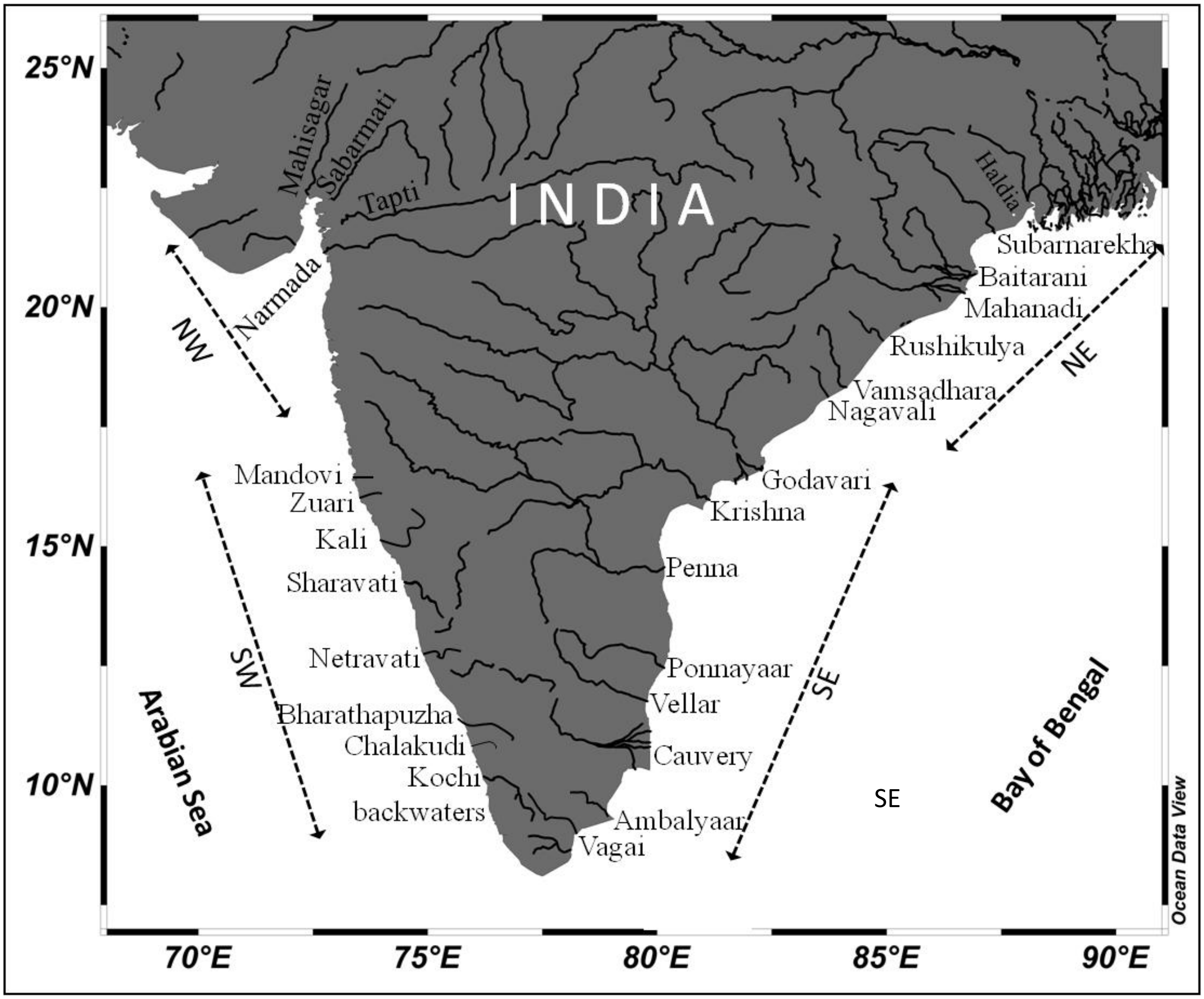

25°N
20°N
15°N
10°N
70°E
75°E
80°E
85°E
90°E
INDIA
Mahisagar
Sabarmati
Tapti
Narmada
Haldia
Subarnarekha
Baitarani
Mahanadi
Rushikulya
Vamsadhara
Nagavali
Godavari
Krishna
Penna
Ponnayaar
Vellar
Cauvery
Ambalyaar
Vagai
Mandovi
Zuari
Kali
Sharavati
Netravati
Bharathapuzha
Chalakudi
Kochi
backwaters
NW
SW
NE
SE
SE
Arabian Sea
Bay of Bengal
Ocean Data View

Fig.1:

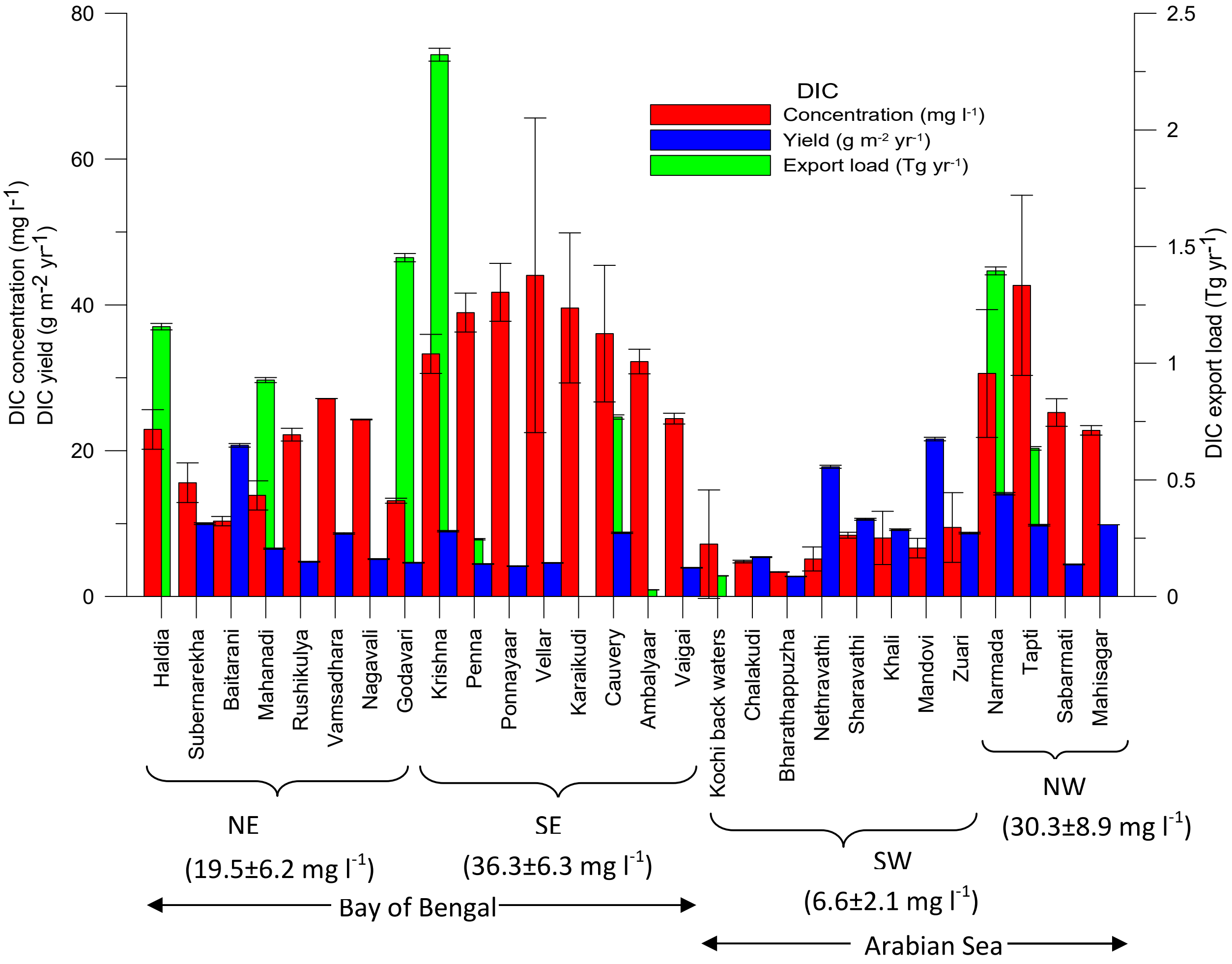

DIC
Concentration (mg l-1)
Yield (g m-2 yr-1)
Export load (Tg yr-1)
DIC concentration (mg l-1)
DIC yield (g m-2 yr-1)
DIC export load (Tg yr-1)
0
20
40
60
80
0
0.5
1
1.5
2
2.5
Haldia
Subernarekha
Baitarani
Mahanadi
Rushikulya
Vamsadhara
Nagavali
Godavari
Krishna
Penna
Ponnayaar
Vellar
Karaikudi
Cauvery
Ambalyaar
Vaigai
Kochi back waters
Chalakudi
Bharathappuzha
Nethravathi
Sharavathi
Khali
Mandovi
Zuari
Narmada
Tapti
Sabarmati
Mahisagar
NE
(19.5±6.2 mg l-1)
SE
(36.3±6.3 mg l-1)
SW
(6.6±2.1 mg l-1)
NW
(30.3±8.9 mg l-1)
Bay of Bengal
Arabian Sea

Fig. 2

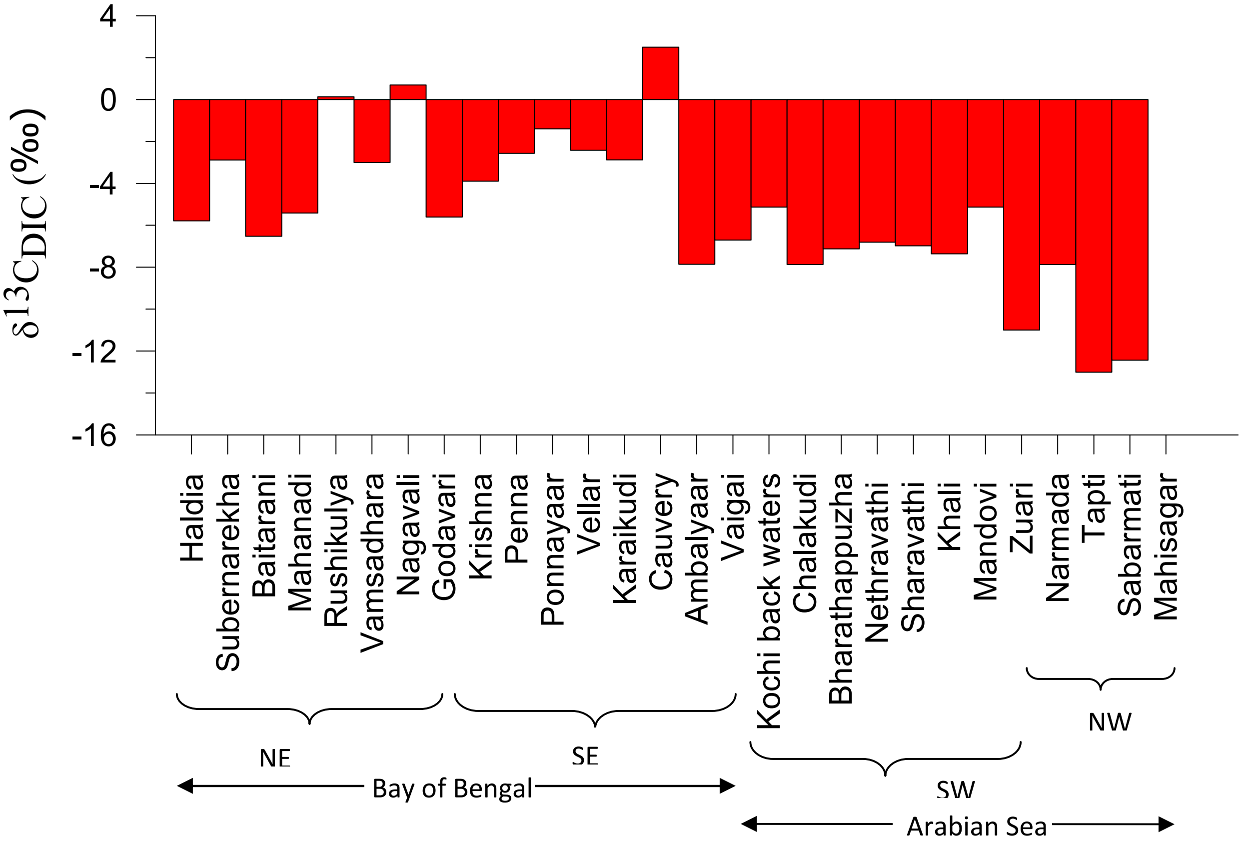

4
0
-4
-8
-12
-16
δ13CDIC (‰)
Haldia
Subernarekha
Baitarani
Mahanadi
Rushikulya
Vamsadhara
Nagavali
Godavari
Krishna
Penna
Ponnayaar
Vellar
Karaikudi
Cauvery
Ambalyaar
Vaigai
Kochi back waters
Chalakudi
Bharathappuzha
Nethravathi
Sharavathi
Khali
Mandovi
Zuari
Narmada
Tapti
Sabarmati
Mahisagar
NE
SE
SW
NW
Bay of Bengal
Arabian Sea

Fig. 3:

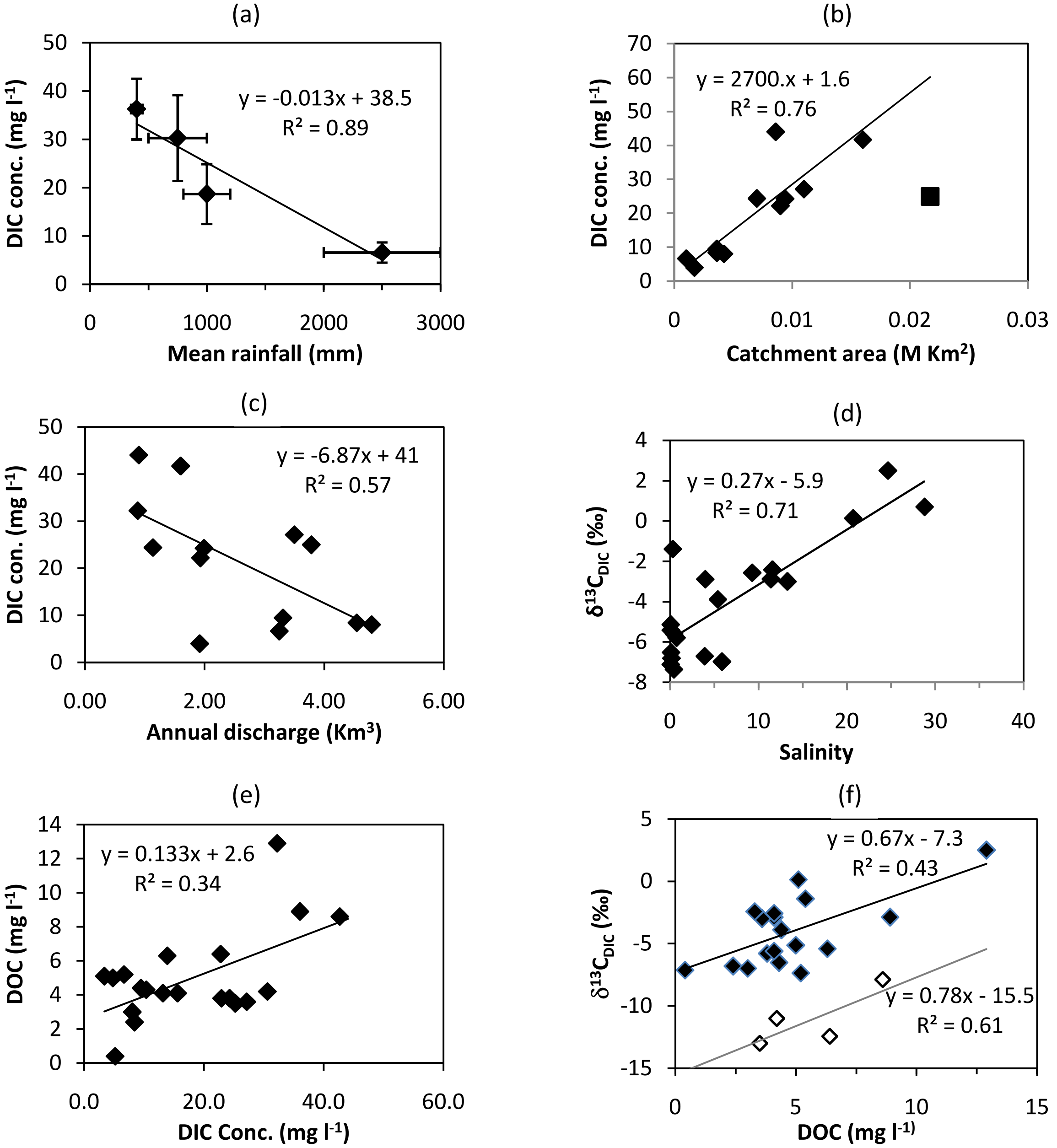
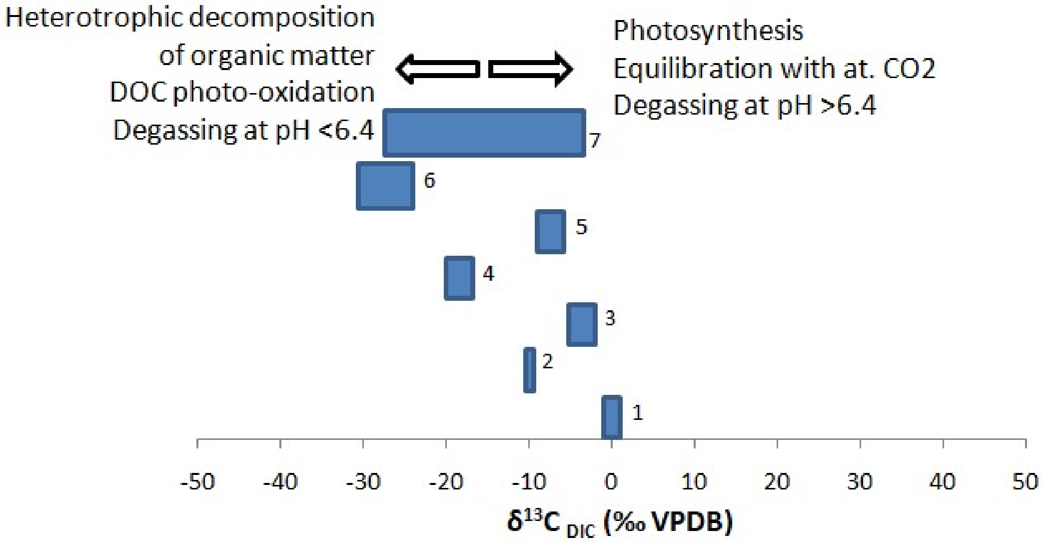

(a)
y = -0.013x + 38.5
R² = 0.89
DIC conc. (mg l-1)
Mean rainfall (mm)
0
1000
2000
3000
0
10
20
30
40
50
(b)
y = 2700.x + 1.6
R² = 0.76
DIC conc. (mg l-1)
Catchment area (M Km2)
0
0.01
0.02
0.03
0
10
20
30
40
50
60
70
(c)
y = -6.87x + 41
R² = 0.57
DIC con. (mg l-1)
Annual discharge (Km3)
0.00
2.00
4.00
6.00
0
10
20
30
40
50
(d)
y = 0.27x - 5.9
R² = 0.71
δ13CDIC (‰)
Salinity
0
10
20
30
40
-8
-6
-4
-2
0
2
4
(e)
y = 0.133x + 2.6
R² = 0.34
DOC (mg l-1)
DIC Conc. (mg l-1)
0.0
20.0
40.0
60.0
0
2
4
6
8
10
12
14
(f)
y = 0.67x - 7.3
R² = 0.43
y = 0.78x - 15.5
R² = 0.61
δ13CDIC (‰)
DOC (mg l-1)
0
5
10
15
-15
-10
-5
0
5

Fig. 4



1: DIC derived from dissolution of atmospheric $CO_2$ / natural carbonates
2: weathering of carbonate rocks by carbonic acid derived from dissolution of soil $CO_2$
3: weathering of carbonate rocks by carbonic acid derived from dissolution of atmospheric $CO_2$
4. Weathering of silicate rocks by carbonic acid derived from dissolution of soil $CO_2$
5. Weathering of silicate rocks by carbonic acid derived from dissolution of atmospheric $CO_2$
6. Heterotrophic decomposition of organic matter derived from terrestrial C3/aquatic plants
7. Typical range of $\delta^{13}C_{DIC}$ (‰) in river water

Fig. 5

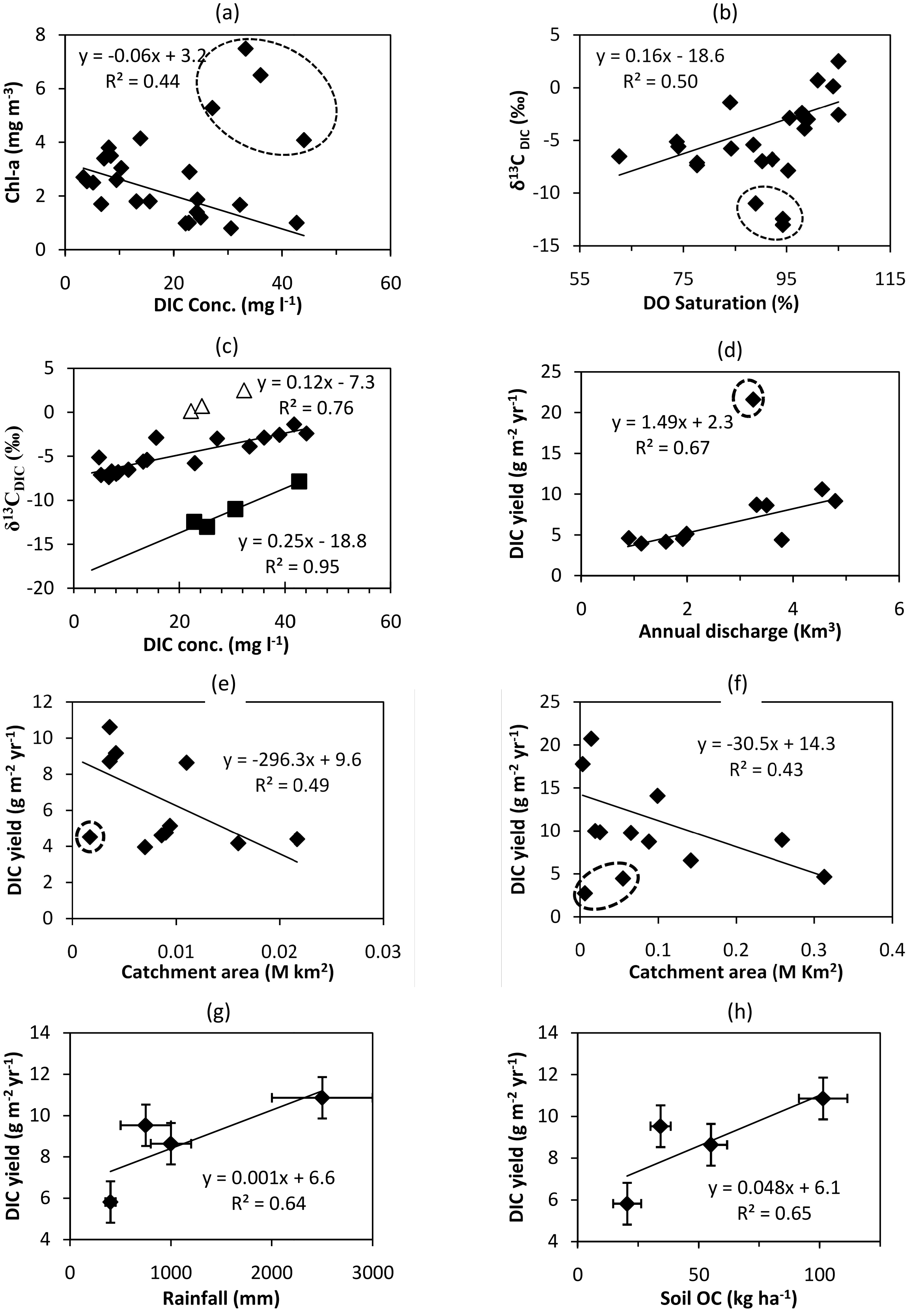

(a)
y = -0.06x + 3.2
R² = 0.44
Chl-a (mg m⁻³)
DIC Conc. (mg l⁻¹)
0
2
4
6
8
0
20
40
60
(b)
y = 0.16x - 18.6
R² = 0.50
δ¹³C DIC (‰)
DO Saturation (%)
5
0
-5
-10
-15
55
75
95
115
(c)
y = 0.12x - 7.3
R² = 0.76
y = 0.25x - 18.8
R² = 0.95
δ¹³C DIC (‰)
DIC conc. (mg l⁻¹)
5
0
-5
-10
-15
-20
0
20
40
60
(d)
y = 1.49x + 2.3
R² = 0.67
DIC yield (g m⁻² yr⁻¹)
Annual discharge (Km³)
0
5
10
15
20
25
0
2
4
6
(e)
y = -296.3x + 9.6
R² = 0.49
DIC yield (g m⁻² yr⁻¹)
Catchment area (M km²)
0
2
4
6
8
10
12
0
0.01
0.02
0.03
(f)
y = -30.5x + 14.3
R² = 0.43
DIC yield (g m⁻² yr⁻¹)
Catchment area (M Km²)
0
5
10
15
20
25
0
0.1
0.2
0.3
0.4
(g)
y = 0.001x + 6.6
R² = 0.64
DIC yield (g m⁻² yr⁻¹)
Rainfall (mm)
4
6
8
10
12
14
0
1000
2000
3000
(h)
y = 0.048x + 6.1
R² = 0.65
DIC yield (g m⁻² yr⁻¹)
Soil OC (kg ha⁻¹)
4
6
8
10
12
14
0
50
100

Fig. 6:

| S. No. | Mean DIC conc. (mg $l^{-1}$) | River | Reference |
|---|---|---|---|
| 1 | 23 | Ganga-Brahmaputra | Singh et al., 2005 |
| 2 | 22 | Hooghly | Samanta et al., 2015 |
| 3 | 15 | Mahanadi | Pattanaik et al., 2017 |
| 4 | 6-21 | York river estuary | Raymond and Bauer, 2000 |
| 5 | 28 | Yangtze river | Cai et al., 2008 |
| 6 | 4 - 43 | British rivers | Jarvie et al., 2017 |
| 7 | 18 - 22 | Seri, central Japan | Ishikawa et al., 2015 |
| 8 | 9 - 30 | Red river, Vietnam | Quynh et al., 2016 |
| 9 | 18 - 46 | Xi river, southwest China | Zou, 2016 |
| 10 | 37 - 66 | rivers draining into the Gulf of Trieste | Tamse et al., 2014 |
| 11 | 10.3 | Global mean | Meybeck and Vorosmarty, 1999 |
| 12 | 12.7 | Asian rivers in tropical region | Huang et al., 2012 |
| 13 | 3.4 to 44 | Indian estuaries | Present study |

Table 1

| S. No. | Region of India | Total catchment area (M km$^2$) | Annual Discharge (km$^3$ ) | Mean±SD of DIC conc. (mg l$^{-1}$) | Mean±SD DIC yield (g m$^{-2}$yr$^{-1}$) | Annual DIC export flux (Tg) | Mean±SD $\delta^{13}C_{DIC}$ (‰) | Mean (±SD) annual rainfall (mm) | Mean±SD GW DIC (mg l$^{-1}$)* | Soil OC (ton ha$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | NE | 0.53 | 276 | 19.5±6.2 | 8.6±5.7 | 4.2 | -3.5±2.8 | 1000±200 | 92±31 | 55 |
| 2 | SE | 0.45 | 102 | 36.3±6.3 | 5.8±2.3 | 3.5 | -2.7±5.2 | 400±50 | 106±56 | 20 |
| 3 | SW | 0.02 | 46 | 6.6±2.1 | 10.8±6.6 | 0.3 | -7.4±1.9 | 2500±500 | 32±19 | 101 |
| 4 | NW | 0.21 | 75 | 30.3±8.9 | 9.5±4.0 | 2.4 | -11.1±2.3 | 750±250 | 84±54 | 34 |

*data has been taken from Dr. BSK Kumar, personnel communication.

Table 2

| S. No. | Rivers | DIC export flux (Tg yr$^{-1}$) | DIC yield (gC m$^{-2}$ yr$^{-1}$) | Reference |
|---|---|---|---|---|
| 1 | World major rivers | 385 | 2.58 | Meybeck and Vorosmarty, 1999 |
| 2 | Asian rivers | 111 | 9.79 | Huang et al., 2012 |
| 3 | American rivers | 61.4 | 3.3 | Huang et al., 2012 |
| 4 | African rivers | 17.7 | 0.63 | Huang et al., 2012 |
| 5 | Rivers draining to the tropical Atlantic from South America and Africa | 53 | - | Araujo et al. 2014 |
| 6 | Tropical rivers | 210 | 3.3 | Huang et al., 2012 |
| 7 | Indian monsoonal rivers* | 10.4 | 8.7 | Present study |

Table 3