

Fluxes of dissolved organic carbon and nitrogen to the Northern Indian Ocean from the Indian monsoonal rivers

M.S.Krishna^{1*}, V.R. Prasad¹, V.V.S.S. Sarma¹, N.P.C. Reddy¹, K.P.J. Hemalatha², Y.V. Rao³

¹*CSIR-National Institute of Oceanography, Regional Centre, Visakhapatnam, India – 530017*

²*Department of Microbiology, Andhra University, Visakhapatnam, India - 530003*

³*Department of Botany, Andhra University, Visakhapatnam – 530003*

* Corresponding author- E-mail: moturi@nio.org (M.S.Krishna); Phone: 91 891 2539180

Abstract

Dissolved organic carbon (DOC) and nitrogen (DON) were measured in 27 major and medium monsoonal estuaries along the Indian coast during southwest monsoon in order to understand the spatial variability in their concentrations and fluxes to the northern Indian Ocean. A strong spatial variability (~20-fold) in DOC and DON was observed in the Indian monsoonal estuaries due to variable characteristics of the catchment area and volume of discharge. It is estimated that the Indian monsoonal estuaries transport $\sim 2.37 \pm 0.47$ Tg ($1\text{Tg} = 10^{12}$ g) of DOC and $\sim 0.41 \pm 0.08$ Tg of DON during wet period to the northern Indian Ocean. The Bay of Bengal receives three times higher DOC and DON (1.82 and 0.30 Tg, respectively) than the Arabian Sea (0.55 and 0.11 Tg). Catchment area normalized fluxes of DOC and DON were found to be higher in the estuaries located in the southwestern than the estuaries from other regions of India. It was attributed to relatively higher soil organic carbon, biomass carbon and heavy rainfall in catchment areas of the rivers from the former region. It has been noticed that neither catchment area nor discharge volume of the river controls the fluxes of DOC and DON to the northern Indian Ocean. Since the total load of DOC and DON is strongly linked to the volume of discharge, alterations in the freshwater discharge due to natural or anthropogenic activities may have significant influence on organic matter fluxes to the Indian coastal waters and its impact on microbial food web dynamics needs further evaluation.

Keywords: dissolved organic carbon, nitrogen fluxes, Indian rivers, Bay of Bengal, Arabian Sea, northern Indian Ocean

1. Introduction

Rivers are the major source of organic matter (OM) to the coastal environment [Onstad *et al.*, 2000; Sanchez-Vidal *et al.*, 2013] as they transport OM derived from vascular plants and soils through discharge. Terrestrial OM derived from continental land masses is one of the major energy sources to aquatic and marine organisms [Sedell *et al.* 1989; Wang *et al.* 2014]. In addition, transformation of organic carbon (OC) in the rivers releases carbon dioxide (CO₂) to the atmosphere [Regnier *et al.*, 2013; Raymond *et al.*, 2013; van Geldern *et al.*, 2015]. On the global scale, world major rivers transport a total carbon of 900 Tg yr⁻¹ (Tg=10¹²g) to coastal ocean besides a net CO₂ emission of 1200 Tg C yr⁻¹ to the atmosphere [Battin *et al.*, 2009] due to transformation of organic carbon (OC) by heterotrophic activity during transportation to coastal regions [e.g. Thorp and Delong, 2002; Bianchi, 2011]. Dissolved organic nitrogen (DON), an important constituent of the dissolved organic matter (DOM), also support autotrophic growth as an alternative source of nutrient [Townshed and Thomas, 2002; Bronk *et al.* 2007] and also heterotrophic bacteria [Veuger *et al.*, 2004; Purvina *et al.*, 2010] under nutrient depleted conditions. Therefore, riverine transport of OM not only influences the global carbon cycle but also the food web dynamics in the freshwater and coastal ecosystems [Caffrey, 2004]. Net annual input of dissolved OC (DOC) and particulate OC (POC) to the coastal oceans was estimated to be ~210 and 170 Tg yr⁻¹ respectively by the world major rivers [Ludwig *et al.*, 1996]. Leaching of DOM from soils, terrestrial plant debris and leaf litter in the catchment is the major terrestrial source of DOC and DON to rivers, which subsequently enters into the marine environment *via* estuaries.

Numerous studies have been conducted on variations in concentrations of OM and their fluxes to the global oceans from major rivers [Meybeck, 1982, Huang *et al.*, 2012; Alvarez-Cobelas *et al.*, 2012] and estimated that ~210 to 250 Tg of DOC is transported annually to the world oceans [Hedges and Keil, 1995; Ludwig *et al.*, 1996]. The dynamics of DOM was relatively better understood in several major rivers draining into the Atlantic [e.g. Richey *et al.*, 1990; Moreira-Turcq *et al.*, 2003], Pacific [Zhang *et al.*, 2014] and Arctic [Opsahl *et al.*, 1999; Lobbes *et al.*, 2000; Raymond *et al.*, 2007] oceans, whereas the studies on rivers draining to the Indian Ocean are rather scarce [Hansell, 2009]. Studies have been carried out in the major rivers, such as Ganga-Brahmaputra [Ludwig *et al.*, 1996; Galy *et al.*, 2007], Indus [Ludwig *et al.*, 1996], Irrawaddy [Bird *et al.*, 2008] and Godavari [Gupta *et al.*, 1997; Balakrishna and Probst, 2005; Balakrishna *et al.*, 2006]. Despite knowing the fact that fluvial transport of carbon from small rivers is considered to be equally important in the OM cycling [Lauerwald *et al.* 2012], intensive studies involving several medium size rivers are warranted.

Hence, an attempt has been made here for the first time to examine the spatial variations in DOC and DON in the monsoonal estuaries, and their fluxes to the northern Indian Ocean during discharge period. The objectives of our study are to (i) understand the spatial variability in DOC and DON in the estuaries along the Indian coast, (ii) estimate the transport load and fluxes of DOC and DON to the northern Indian Ocean and (iii) identify the key factors controlling riverine fluxes of DOC and DON to the Indian coastal waters during discharge period.

2. Material and methods

2.1 Site description

Northern Indian Ocean is unique with reference to its geography as it is land locked in the north, west and east by southeast Asia and African land masses and opened to the Indian Ocean in the south. It is divided into two basins, the Arabian Sea (north western Indian Ocean) and the Bay of Bengal (north eastern Indian Ocean), by the Indian subcontinent with contrasting oceanographic features [e.g. *Gauns et al.*, 2005]. The Arabian Sea has been recognized as one of the most productive zones [*Bhattathiri et al.*, 1996; *Barber et al.*, 2001] in the world due to strong upwelling and convective mixing [*Madhupratap et al.*, 1996; *Muraleedhran and Prasannakumar*, 1996]. In contrast, the Bay of Bengal is traditionally considered to be less productive [*Prasannakumar et al.*, 2002] due to (i) strong stratification driven by freshwater discharge [*Varkey et al.*, 1996; *Sarma et al.*, 2013] and (ii) higher suspended sediment load [*Subramanian*, 1993] that limits the light availability [*Madhupratap et al.*, 2003] for phytoplankton growth. Major and minor monsoonal rivers draining into the Bay of Bengal and the Arabian Sea were shown in figure 1. The magnitude of discharge from all these rivers depends on spatial variations in rainfall over the catchment during SW monsoon (June-September). It has been noticed that the higher precipitation is received along the SW ($\sim 2500 \text{ m}^3 \text{ s}^{-1}$) followed NE ($\sim 2000 \text{ m}^3 \text{ s}^{-1}$) and SE ($\sim 200 \text{ m}^3 \text{ s}^{-1}$) coast of India. *Soman and Kumar* [1990] suggested that $\sim 90\%$ of annual precipitation occurs during SW monsoon (June – September), hence it represents the annual discharge from the Indian estuaries.

2.2 Sample collection

Samples were collected from 27 major and medium estuaries (Fig. 1) along the Indian coast (28 July-18 August, 2011) during southwest (SW) monsoon (June-September) when peak discharge occurs. As the loss of DOC in-river before exporting to estuaries and coastal ocean was reported to be significant [*Lauerwald et al.*, 2012], samples were collected from estuaries, which represent the net riverine input of DOC and DON to the coastal ocean. In order to minimize the spatial variability within the estuary, each estuary was sampled from mouth to upstream river at 3 to 5 locations, with a

distance of ~10 to 15 km between each station. As the depth of these rivers is shallow and no vertical stratification occurs during discharge period [Vijit *et al.*, 2009; Sridevi *et al.*, 2015], samples were collected only from surface. Mean annual discharge from individual rivers was collected from *Integrated Hydrological Data Book* [Central Water Commission 2006, 2012], *Indian Water Resources Society, Roorkee* [1996], *Meybeck and Ragu* [1995, 1996] and *Kumar et al.* [2005]. Freshwater discharge from the Indian estuaries in 2011 is normal since the precipitation over the Indian subcontinent during SW monsoon period (June-September) is normal (i.e., close to long term mean; www.imd.gov.in). Since the data on rainfall [Soman and Kumar, 1990], soil OC and biomass carbon [Kishwan *et al.*, 2009] in catchment area of each river is not available, the data was taken on regional (NE, SE, SW and NW regions of India) scales.

2.3 Methods

Temperature, salinity and depth were measured using a CTD system (Sea Bird Electronics, SBE 19 plus, USA). Samples for dissolved inorganic nutrients were collected in plastic bottles after filtering through 0.22 μm Isopore membrane filters (Millipore) and preserved with mercuric chloride to arrest biological activity. Nutrients were measured using auto analyzer following standard colorimetric method [Grashoff *et al.*, 1992]. Dissolved oxygen (DO) was measured using Winkler's titration method [Carritt and Carpenter, 1966] using potentiometric end point detection (Tritrindo autotitrator, Metrohm, Switzerland). The analytical precision for the method, expressed as standard deviation, was $\pm 0.07\%$. About 500 ml of sample was filtered through GF/F (nominal pore size: 0.7 μm) filter at a gentle vacuum and stored in liquid nitrogen for pigment analysis. At the shore laboratory, Chlorophyll-a (Chl-a) on the filter was extracted into N,N-dimethyl formamide (DMF) and fluorescence of the extract was measured using spectrofluorophotometer (Eclipse, Varian Electronics, UK) following *Suzuki and Ishimaru* [1990]. Total suspended matter (TSM) was determined by the weight difference between the dried 0.22 μm polycarbonate filters before and after filtering of 500 ml of water sample.

The DOC and total dissolved nitrogen (TDN) were determined by a high-temperature catalytic oxidation method using TOC analyzer (TOC-VCSH, Shimadzu, Japan) with ASI-V auto sampler. Non-dispersive Infra Red (NDIR) and chemiluminescence detectors were used for determination of DOC and TDN, respectively. This method is very efficient in oxidation of dissolved organics in water [Benner and Hedges, 1993; Spyres *et al.*, 2000]. Briefly, water samples (~60ml) were passed through pre-combusted (300°C; 6h) inline filters (GF/F; nominal pore size: 0.7 μm) into pre-acid-cleaned glass vials and added 10% phosphoric acid (0.5ml) for preservation. At the shore laboratory, samples were sparged with ultra pure oxygen (99.995%) to remove inorganic carbon as carbon

dioxide (CO₂). An aliquot of the treated water sample (50 µl) is then injected onto a combustion column. Non-purgeable organic carbon compounds are combusted and converted to CO₂, which is then detected by a NDIR while non-purgeable total dissolved nitrogen (TDN) compounds are converted to NO and detected by a photomultiplier. The DOC and TDN systems were calibrated using potassium hydrogen phthalate and potassium nitrate respectively. Reference seawater and blanks were checked regularly and the error associated with our analysis is ~5%. Blank values of 8-10 µMC were corrected for samples. Based on the repeated analyses of samples and standards, the precision of the instrument was ±2% and ±1.5% for DOC and TDN respectively.

DON was estimated by the subtraction of measured total dissolved inorganic nitrogenous nutrients (DIN; sum of nitrite, nitrate and ammonium) from that of the TDN. The disadvantage of this approach is that the accumulation of measurement errors in the final calculation of DON. The particulate organic carbon (POC) was measured by an elemental analyzer (Flash EA, Thermo) and their distribution pattern was discussed elsewhere [Sarma *et al.*, 2014]. Total transport load of DOC and DON from the individual monsoonal rivers was calculated by multiplying the mean concentration with the volume of discharge (km³). Monthly observations in the Godavari estuary for two years (2009 and 2010) and the discharge data collected from the dam at upstream river (Rajahmundry) revealed that a strong seasonal variability in total OC (TOC) concentrations, with a relatively higher concentrations during discharge period (mean 1063±81 µmol l⁻¹) than no discharge period (342±22 µmol l⁻¹). The variability in TOC concentrations within the discharge period was about ±20% and ±18% during years 2009 and 2010, respectively [Prasad, 2014]. Therefore, the errors associated with our estimations due to variability in concentrations of DOC and DON within the discharge period (June – September) and volume of river discharge can be up to ±20%. Catchment area normalized fluxes were determined by dividing the total load with that of the catchment area (km²) of the river.

4. Results

4.1. Hydrographic characteristics of the Indian estuaries during study period

Surface temperature varied between 25.51 and 33.52 °C, with relatively higher temperatures in the estuaries draining into the Bay of Bengal (mean 30.86±1.23°C) than the estuaries draining into the Arabian Sea (27.32±1.49°C). Salinity ranged from near zero (0.06) to 28.78 and higher salinities (>20) were observed in the minor estuaries, such as Nagavali (28.78), Vaigai (24.63) and Rushikulya (20.70), as they received relatively low fresh water discharge from the upstream river. Estuaries located in the northwestern (NW) part of India, such as Narmada, Tapi, Mahisagar and Sabarmati,

recorded elevated levels of suspended matter (mean $458 \pm 324 \text{ mg l}^{-1}$) than the other estuaries ($42 \pm 38 \text{ mg l}^{-1}$) except Godavari (691 mg l^{-1}) and Haldia (230 mg l^{-1}). Dissolved oxygen saturation varied between 62.6 and 105%, with a mean saturation of $89.9 \pm 11.4\%$ in the estuaries sampled. Chlorophyll-a (Chl-a) concentrations varied broadly from 0.8 to 10.7 mg m^{-3} , with relatively higher mean concentrations (4.7 mg m^{-3}) in the estuaries located in the southeastern (SE) coast of India that received lower discharge and suspended matter. Recently, *Sarma et al.* [2014] reported that the content of particulate organic carbon (POC) and nitrogen (PON) in Indian estuaries varied from 51 to $750 \text{ } \mu\text{mol l}^{-1}$ and 5.3 to $60.3 \text{ } \mu\text{mol l}^{-1}$, respectively during discharge period. Elemental C:N (POC:PON) ratios varied between 5.1 and 14.1, with a mean ratio of 8.7 ± 2.0 . Relatively higher concentration of dissolved inorganic nitrogen (DIN) and phosphorus (DIP) were observed in the estuaries of the major rivers (discharge: $>200 \text{ m}^3 \text{ s}^{-1}$) (35.8 ± 29.6 and $8.2 \pm 4.4 \text{ } \mu\text{mol l}^{-1}$ respectively) than the estuaries of minor rivers ($<200 \text{ m}^3 \text{ s}^{-1}$; 12.3 ± 9.2 and $5.6 \pm 3.6 \text{ } \mu\text{mol l}^{-1}$ respectively).

4.2 Concentrations and fluxes of DOC and DON

DOC and DON concentrations ranged from 33 to 1075 and 2.8 to $167 \text{ } \mu\text{mol l}^{-1}$, respectively (Fig. 2a; Table 1), with a large spatial variations among the Indian monsoonal estuaries. The mean DOC concentration in this study ($400 \pm 200 \text{ } \mu\text{mol l}^{-1}$) is similar to that of DOC concentrations found in the Amazon river ($372 \text{ } \mu\text{mol l}^{-1}$; Table 2), and relatively higher than those reported for many of the major rivers in the world (Table 2). However, it is lower than the DOC concentrations found in the rivers Mississippi, Congo and 16 rivers entering into the Bohai Sea (Table 2). Relatively higher concentrations of DOC were found in the polluted estuaries, such as Ambalyaar ($1079 \text{ } \mu\text{mol l}^{-1}$), Cauvery ($745 \text{ } \mu\text{mol l}^{-1}$) and Tapti ($716 \text{ } \mu\text{mol l}^{-1}$), than the other Indian estuaries studied (mean $341 \pm 107 \text{ } \mu\text{mol l}^{-1}$). Similarly, mean DON concentrations in the Indian estuaries ($42 \pm 21 \text{ } \mu\text{mol l}^{-1}$), except polluted estuaries which recorded elevated DON concentrations ($155 \pm 17 \text{ } \mu\text{mol l}^{-1}$), are within the range of reported values elsewhere in the world (Table 2). Except polluted rivers, ~20-fold variation in both DOC and DON concentrations were observed among the Indian estuaries. It could be due to a large variability in catchment area (1×10^3 to $313 \times 10^3 \text{ km}^2$) and volume of discharge (0.9 to 111 km^3) of the Indian monsoonal rivers. Among the monsoonal estuaries, relatively lower concentrations of DOC and DON (300 ± 142 and $24 \pm 18 \text{ } \mu\text{mol l}^{-1}$, respectively) were observed in the estuaries located in the SW coast of India.

Total transport load of DOC and DON by the individual rivers varied broadly from 3 to 453×10^9 and 0.2 to $85 \times 10^9 \text{ g}$, respectively (Fig. 2b) during discharge period. Total DOC load from the monsoonal rivers to the northern Indian Ocean was estimated as $\sim 2.37 \pm 0.47 \text{ Tg}$, which is significantly lower than that of the DOC load from major rivers in the world (Table 2). However, it is higher than the

DOC load from several rivers, such as Mackenzie (1.35 Tg yr^{-1}) and Nile (0.17 Tg yr^{-1}) [Ludwig *et al.*, 1996] (Table 2). Among the Indian monsoonal rivers, Godavari transports the highest DOC (0.45 Tg) and DON (0.09 Tg) to the northern Indian Ocean (Table 1) during discharge period. The total transport load of DOC ($2.37 \pm 0.47 \text{ Tg}$) and DON ($0.41 \pm 0.08 \text{ Tg}$) by the Indian monsoonal rivers to the northern Indian Ocean during discharge period is equivalent to about 1.0% and 4.1% of riverine input to the global oceans, respectively. The Bay of Bengal receives relatively higher amount of DOC ($1.82 \pm 0.36 \text{ Tg}$) and DON ($0.30 \pm 0.06 \text{ Tg}$) than Arabian Sea (0.54 ± 0.11 and $0.11 \pm 0.02 \text{ Tg}$ of DOC and DON respectively) as the former receives ~76% of the total discharge (378 km^3).

Catchment area normalized fluxes of DOC and DON were found to be in the range of 35 to $1903 \text{ gC m}^{-2} \text{ yr}^{-1}$ and 4.5 to $280 \text{ gN m}^{-2} \text{ yr}^{-1}$, respectively (Fig. 2c). The range of DOC fluxes in this study is well within the range of DOC fluxes ($0.1 - 5,695 \text{ gC m}^{-2} \text{ yr}^{-1}$) reported for 550 catchments worldwide [Alvarez-Cobelas *et al.*, 2012]. Except Baitarani and Haldia, mean DON flux from the Indian estuaries ($26.9 \pm 18.8 \text{ gN m}^{-2} \text{ yr}^{-1}$) is similar to that of the world-wide catchments ($< 50 \text{ gN m}^{-2} \text{ yr}^{-1}$) [Alvarez-Cobelas *et al.*, 2008] and the NEWS (Nutrient Export from Watersheds) model output of the global rivers ($0.2 - 47 \text{ gN m}^{-2} \text{ yr}^{-1}$) [Harrison *et al.*, 2005]. Exceptionally high fluxes of DOC ($1903 \text{ gC m}^{-2} \text{ yr}^{-1}$) and DON ($280 \text{ gN m}^{-2} \text{ yr}^{-1}$) were observed in the Haldia estuary compared to the other estuaries studied. Estuaries opened to the Arabian Sea from the southwest (SW) coast of India recorded relatively higher mean fluxes of DOC ($377 \pm 145 \text{ gC m}^{-2} \text{ yr}^{-1}$) and DON ($24 \pm 16 \text{ gN m}^{-2} \text{ yr}^{-1}$), while the lower fluxes ($86 \pm 71 \text{ gC m}^{-2} \text{ yr}^{-1}$ and $12 \pm 7 \text{ gN m}^{-2} \text{ yr}^{-1}$, respectively) were found in the SE estuaries opened to the Bay of Bengal. Relationships between different parameters and their controlling factors were provided in Table 3. Total transport load of DOC and DON showed strong linear relationship with that of catchment area of the rivers, whereas the catchment area normalized fluxes of DOC and DON showed no significant relationship with either catchment area or discharge volume of the river (Table 3).

5. Discussion

5.1 Hydrography of the Indian estuaries during SW monsoon

The annual discharge from the Indian estuaries was reported to be in the range of ~ 28 to $3505 \text{ m}^3 \text{ s}^{-1}$ [Sarma *et al.*, 2014]. This variation in discharge was largely controlled by the spatial variability in monsoonal precipitation over the Indian subcontinent and catchment area of the river. The south western India receives relatively higher rainfall followed by the northeast, southeast and northwest regions of India [Soman and Kumar, 1990]. Despite high concentrations of nutrients are available in

the Indian monsoonal estuaries during discharge period, phytoplankton biomass (Chl-a) was higher ($3.5 \pm 1 \text{ mg m}^{-3}$) in the estuaries of low discharge ($< 200 \text{ m}^3 \text{ s}^{-1}$) than the estuaries ($1.8 \pm 0.9 \text{ mg m}^{-3}$) of high discharge ($> 200 \text{ m}^3 \text{ s}^{-1}$) [Sarma *et al.*, 2014]. Instability of the water column due to high discharge and limited light availability to phytoplankton due to high suspended matter could have decreased in-situ primary production in the estuaries that received high discharge [Cloern *et al.*, 1985; Cloern and Jassby, 2012; Sin *et al.*, 2103; Sarma *et al.*, 2014] and contrasting conditions during low discharge period promotes in-situ production [Gupta *et al.*, 2008; Pednekar *et al.*, 2011; Acharyya *et al.*, 2012]. Sarma *et al.* [2014] demonstrated that spatial variations in biological processes in the Indian estuaries were mainly governed by the precipitation pattern over the Indian subcontinent and terrain characteristics that determines suspended load.

5.2 Concentrations of DOC and DON in the monsoonal estuaries

Relatively higher concentrations of DOC and DON were observed in this study than other major estuaries in the world, indicating that Indian monsoonal rivers are significant source of oceanic DOM. The major contributions of DOM could be from allochthonous sources, such as leaching of terrestrial OM from soils, debris of terrestrial plants, wood, and leaf litter in the catchment area [Bin and Longjun, 2011], domestic and industrial sewage, besides the input from autochthonous sources, such as phytoplankton [Carlson *et al.*, 1994; Bianchi *et al.*, 2004], bacteria and macrophytes [Bronk *et al.*, 1994; Diaz and Raimbault, 2000], autolysis of bacteria [Fuhrman, 1999], viral lysis of bacteria and phytoplankton [Wilhelm and Suttle, 1999; Middelboe and Jorgensen, 2006], zooplankton grazing and excretion [Berman and Bronk, 2003]. Huge amount of precipitation over the Indian subcontinent during SW monsoon washes out the terrestrial OM from the continental land masses to the rivers and subsequently to the estuaries. No relationship was observed for phytoplankton biomass (Chl-a) with neither DOC ($r^2=0.004$, $p=0.77$) nor DON ($r^2=0.2$, $p=0.54$) indicating that significant contribution of DOM from allochthonous sources. Though, Chl-a was lower in the more turbid and high discharge estuaries of the northern (north of 16°N) India than the less turbid and low discharge estuaries of the southern India, however, no such pattern was noticed for concentrations of DOC and DON. This suggests that variable contributions of DOM from allochthonous and autochthonous sources to the Indian estuaries. Based on stable isotopic composition of carbon and nitrogen of particulate OM (POM), Sarma *et al.* [2014] reported that POM was contributed predominantly by autochthonous sources (70-90%) in the southern and allochthonous sources (40-90%) in the northern estuaries. However, no isotopic studies were carried out on DOM to evaluate the possible sources to the Indian estuaries. In addition to the contribution of DOC from autochthonous and allochthonous sources, in-situ processes such as transformation of POC by heterotrophic activity to DOC [Fisher, 1977] also

influences the concentrations of DOC. The POC:DOC ratio can be used as a potential indicator for in-stream transformation of particulate organic matter [Alvarez-Cobelas *et al.*, 2012] as the ratio decreases with increasing the transformation of POC. The POC:DOC ratio was significantly higher in the northern estuaries (mean 1.0 ± 0.6) than that of the southern estuaries (0.4 ± 0.3), suggesting that significant transformation of POC in the latter estuaries. Strong inverse correlation between DOC and POC concentrations in the southern estuaries ($r^2=0.64$; $p<0.001$), except Ambalyaar and Cauvery where exceptionally higher DOC concentrations were observed, further confirms that significant transformation of POC in the southern estuaries. Relatively higher transformation of POC in the southern estuaries could be due to the predominance of autochthonous POM (70-90%; Sarma *et al.*, 2014] which is known to be easily bio-degradable. A significant linear correlation of DON with DOC ($r^2=0.61$, $p<0.001$; Fig. 3) suggests that dissolved pool of both organic C and N are rather coupled and similar mechanisms may be responsible for their production and/or transformation.

DON concentrations showed fairly good logarithmic relationship with that of the catchment area ($r=0.48$; $p=0.016$), while DOC showed no significant relationship ($r=0.20$; $p=0.336$). Such relationship with DON could be caused by significant use of nitrogen containing fertilizers, such as urea and diammonium phosphate, in agricultural fields, and the excess is washed into the rivers due to heavy rainfall. The logarithmic relationship between DON and catchment area could be due to dilution by the high volume of discharge from the rivers of larger catchment area (>0.2 million km^2) as the latter two displayed a strong linear relationship ($r^2=0.80$; $p<0.001$). Though, discharge is lower from the SW estuaries (1.9 - 12.3 km^3) due to small catchment area (1.0 - 6.2×10^3 km^2), relatively lower concentrations of DOC (mean: $305 \mu\text{mol l}^{-1}$) and DON ($21.1 \mu\text{mol l}^{-1}$) were observed in these estuaries than the other estuaries (mean 430 and $50.7 \mu\text{mol l}^{-1}$, respectively). It is attributed to intensity of rainfall since the SW part of India receives maximum rainfall during southwest monsoon (~ 3000 mm) than the NE (1000 - 2500 mm), SE (300 - 500 mm) and NW (200 - 500 mm) parts of India [Soman and Kumar, 1990]. The catchment area normalized volume of discharge confirms the dilution of DOC and DON in the SW estuaries as it is relatively higher in the estuaries of SW ($1.71 \text{ m}^3 \text{ m}^{-2}$) than the NE (0.6), SE (0.17) and NW (0.32) parts of India.

Transport load of DOC and DON showed a strong positive relationship with catchment area of the river ($r^2=0.77$, $p<0.001$, Fig. 4a and $r^2=0.77$, $p<0.001$, Fig. 4b, respectively; Table 3), suggesting that catchment area determines the transport load of DOM to the northern Indian Ocean. It could be due to leaching of OM from soils and vascular plant materials in the catchment. Alvarez-Cobelas *et al.* [2012] also found that DOC transport by the major rivers in the world is significantly controlled by catchment area of the river. Since the variability in catchment area of the Indian monsoonal rivers is

large (~300-fold; range: 0.001 - 0.313 million km²), the fluxes of DOC and DON were normalized with the catchment area of the river in order to examine the factors that govern the fluxes of DOC and DON. The catchment area normalized fluxes of DOC and DON (fluxes from unit area of the catchment) showed no significant correlation with either volume of discharge ($r^2=0.01$; $p=0.60$; $r^2=0.09$; $p=0.14$, respectively) or catchment area of the river ($r^2=0.05$, $p=0.30$; $r^2=0.01$, $p=0.68$, respectively; Table 3), suggesting that catchment area is not a governing factor for DOC and DON export fluxes from the Indian estuaries. *Ludwig et al.* [1996] also observed no significant relation between DOC flux and catchment area of the world rivers. Further, they reported that drainage intensity and soil OC content largely controlled the fluxes of DOC in the world rivers [*Ludwig et al.*, 1996]. Hydrological, environmental and climatic conditions and human interferences in the catchment are known to influence the riverine fluxes of DOC and DON to the coastal regions [e.g. *Clair et al.*, 1994; *Ludwig et al.*, 1996; *Aitkenhead and McDowell*, 2000; *Chapman et al.*, 2001; *Aitkenhead-Peterson et al.*, 2007; *Alvarez-Cobelas et al.*, 2012]. For instance, *Ferguson et al.* [2011] demonstrated that the export of dissolved carbon from Fly river, the largest river of Papua New Guinea, is primarily dependent on the rainfall intensity, and the export was higher during Austral summer when the river basin receives heavier rainfall. In drainage basins of the world major rivers, the basin area of 23.63x10⁶ km² under the tropical wet climate recorded a DOC flux of 90.24 Tg yr⁻¹ which is about three and half times higher than that of the DOC flux of 23.92 Tg yr⁻¹ recorded by the similar extent of area (22.93x10⁶ km²) under the tropical dry climate [*Ludwig et al.*, 1996].

In order to understand the influence of hydrological and environmental conditions on DOC fluxes from the Indian monsoonal estuaries, we examined the relationship of DOC flux with that of the rainfall [*Soman and Kumar*, 1990], soil OC and biomass carbon [*Kishwan et al.*, 2009]. DOC fluxes showed strong linear relationship with that of the mean annual rainfall ($r^2=0.87$; $p=0.06$; Fig. 5a), soil OC ($r^2=0.94$; $p=0.02$; Fig. 5b) and biomass carbon ($r^2=0.95$; $p=0.02$; Fig. 5c) in the regions, suggesting that strong impact of hydrological (rainfall) and environmental conditions (soil OC and biomass carbon) on fluxes of DOC to the coastal waters. Relatively higher fluxes of DOC from the SW estuaries could therefore be due to intense scouring of DOC from OC-rich soils (101.4 ton hec⁻¹) [*Kishwan et al.*, 2009] by heavy rainfall (~3000mm) [*Soman and Kumar*, 1990] in catchment areas of the SW rivers during discharge period. Nevertheless, further studies are required to understand the influence of climatic conditions (arid/semi-arid) and human interferences (land use change and deforestation) on DOC fluxes to the northern Indian Ocean from the Indian monsoonal estuaries.

5.3 Quality of DOC and DON in the Indian monsoonal estuaries

Elemental DOC:DON (C:N) ratios of DOM are potential indicators for the nutritional value of DOM and therefore, any shift in the C:N ratios of DOM from the Redfield ratio (C:N:P::106:16:1) [Redfield *et al.*, 1963] can be used as an indicator for the quality of substrate. The mean elemental C:N ratios in the Indian monsoonal estuaries (8.4 ± 3.8), except estuaries, such as Sharavati (68.6) and Zuari (94.1), are close to the Redfield ratio of 6.6. The DOC:DON ratios (8.4 ± 3.8) are also close to POC:PON ratios (8.7 ± 2) in the Indian monsoonal estuaries during SW monsoon [Sarma *et al.*, 2014]. Moreover, C:N ratios in the Indian estuaries (8.4 ± 3.8) are similar to those reported for biologically available fraction of DOM (BDOM) in the shallow coastal regions, Horsens Fjord (6 ± 5) and Darss Sill (7 ± 5) in Denmark [Lonborg and Sandergaard, 2009], and global coastal oceans (8.8 ± 4.4) [Lonborg and Alvarez-Salgado, 2012]. Further, C:N ratios in the Indian estuaries are significantly lower than those reported for recalcitrant (non-bioavailable) DOM in the Horsens Fjord, Denmark (16 ± 7) [Lonborg and Sandergaard, 2009], continental margins of the global oceans (17.8) [Lonborg and Alvarez-Salgado, 2012], Georges Bank, Middle Atlantic Bight, Hawaiian Ocean Time Series (17.4) [Hopkinson and Vallino, 2005] and terrestrial refractory DOM (29.6) [Meybeck, 1982]. These results indicate that the DOM in the Indian estuaries during the study period is potentially of high quality. This could be the reason for significant microbial modification during their transit to coastal ocean resulting in release of carbon dioxide from the Indian estuaries to the atmosphere [Sarma *et al.*, 2012]. However, more studies are required to quantify concentrations of BDOM to understand the impact of riverine DOC and DON on the ecosystem and biogeochemical processes in the Indian coastal waters.

6. Conclusion

The concentrations of DOC and DON were measured in 27 major and medium monsoonal estuaries along the Indian coast during discharge period to examine their fluxes to the northern Indian Ocean. Both DOC and DON concentrations showed strong spatial variability (~20-fold) during study period. Total transport load of DOC and DON to the northern Indian Ocean from the monsoonal rivers were estimated as 2.37 ± 0.47 and 0.41 ± 0.08 Tg, respectively, during discharge period. The major fraction of the DOC (77%; 1.82 Tg) and DON (73%; 0.30 Tg) load enters into the Bay of Bengal than to the Arabian Sea (0.55 and 0.11 Tg, respectively) as the former basin receives ~76% (378 km^3) of the total discharge from the monsoonal rivers. The catchment area normalized fluxes of DOC and DON were relatively higher in estuaries located in the SW coast of India than other estuaries. It could be due to scouring of DOC from OC-rich soils by heavy rainfall in catchment areas of the SW rivers during discharge period. This study suggests that hydrological (rainfall) and environmental

conditions (soil OC and biomass carbon) strongly influences the fluxes of DOC and DON rather than the volume of discharge and catchment area of the river. As the total transport load of DOC and DON by the Indian monsoonal rivers is strongly linked to the volume of discharge, any alterations in the freshwater discharge to coastal ocean due to human interferences may strongly affect the input of riverine DOC and DON to the Indian coastal waters which in-turn may have significant impact on coastal ecosystem.

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Figure captions:

Fig.1: Map showing the study region. Mean annual rainfall (mm) for 40 years (1941-90) was also shown (source: Indian Meteorological Department, New Delhi). Estuaries of the rivers sampled in this study were indicated by solid black line.

Fig.2: Spatial distribution of (a) concentrations in $\mu\text{mol l}^{-1}$, (b) transport load in ($\times 10^9\text{g}$) and (c) catchment area normalized fluxes ($\text{g m}^{-2}\text{ yr}^{-1}$) of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in the Indian monsoonal estuaries.

Fig.3: Relationship between dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations in the Indian monsoonal estuaries during SW monsoon

Fig.4: Correlation between (a) total transport load of dissolved organic carbon (DOC) and catchment area (b) total transport load of dissolved organic nitrogen (DON) and catchment area of the Indian monsoonal rivers

Fig. 5: Relationship of DOC fluxes from estuaries located in the northeast (NE), southeast (SE), southwest (SW) and northwest (NW) regions of India with that of the (a) mean rainfall (mm), (b) soil organic carbon (tones hec^{-1}) and (c) biomass carbon (tones hec^{-1}) in the regions.

Table captions:

Table 1: Name of the monsoonal estuary along with its catchment area (million km^2) and mean annual volume of discharge (km^3) sampled in this study. Concentrations of dissolved organic carbon (DOC; $\mu\text{mol l}^{-1}$) and dissolved organic nitrogen (DON; $\mu\text{mol l}^{-1}$), transport loads of DOC ($\times 10^9\text{g yr}^{-1}$) and DON ($\times 10^9\text{g yr}^{-1}$) and catchment area normalized fluxes of DOC ($\text{g m}^{-2}\text{yr}^{-1}$) and DON ($\text{g m}^{-2}\text{yr}^{-1}$) to the northern Indian Ocean were provided. Elemental DOC:DON ratios were also shown.

Table2: Concentrations of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) ($\mu\text{mol l}^{-1}$) in the world major rivers. Annual transport loads of DOC (Tg yr^{-1}) from the few major rivers in the world were also given.

Table 3: Correlation coefficients for linear relationship of concentrations ($\mu\text{mol l}^{-1}$), transport load ($\times 10^9\text{g yr}^{-1}$) and catchment area normalized fluxes ($\text{g m}^{-2}\text{ yr}^{-1}$) of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) with the catchment area of the river (million km^2) and volume of discharge (km^3) of the Indian monsoonal rivers.

Fig.1

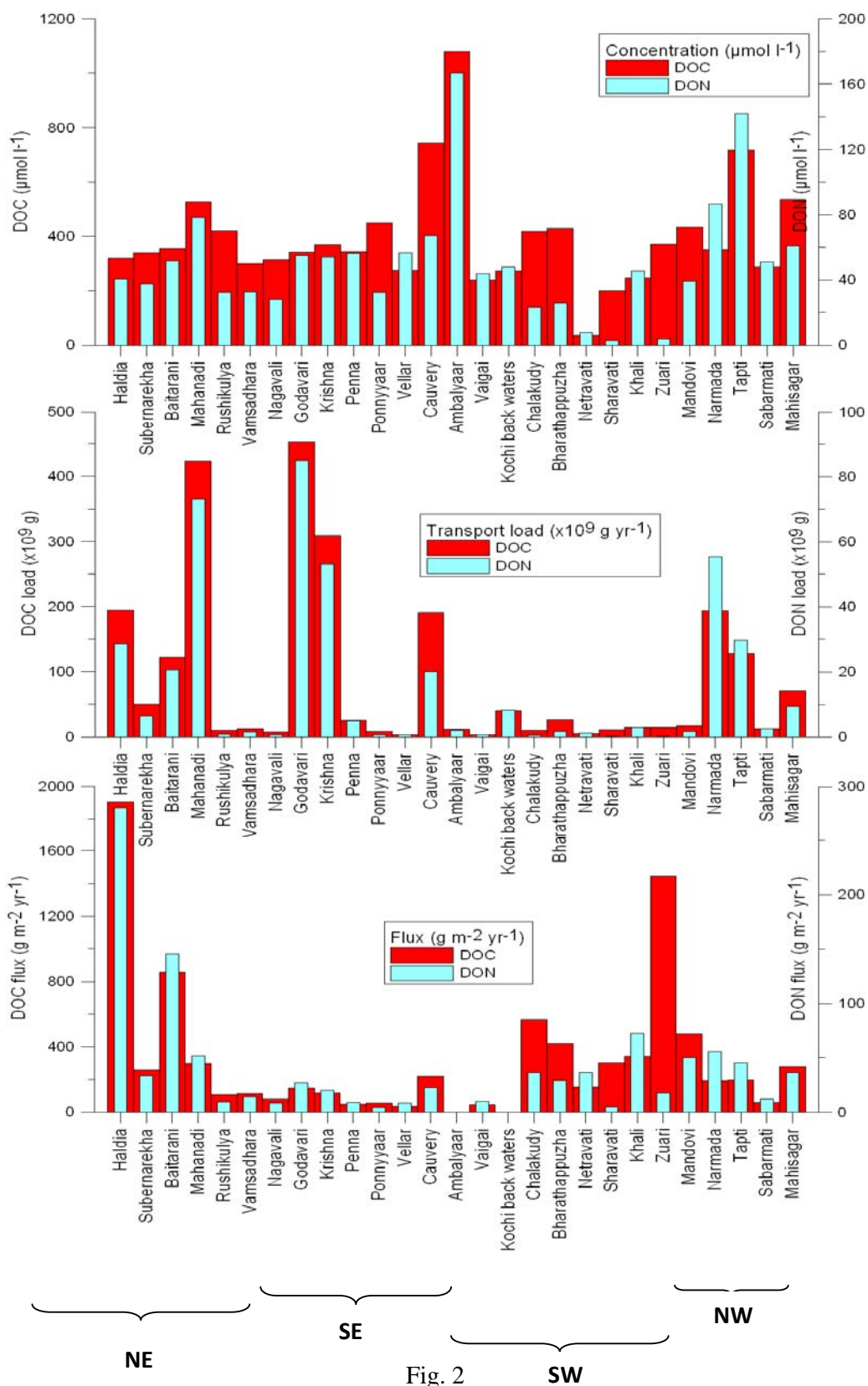


Fig. 2

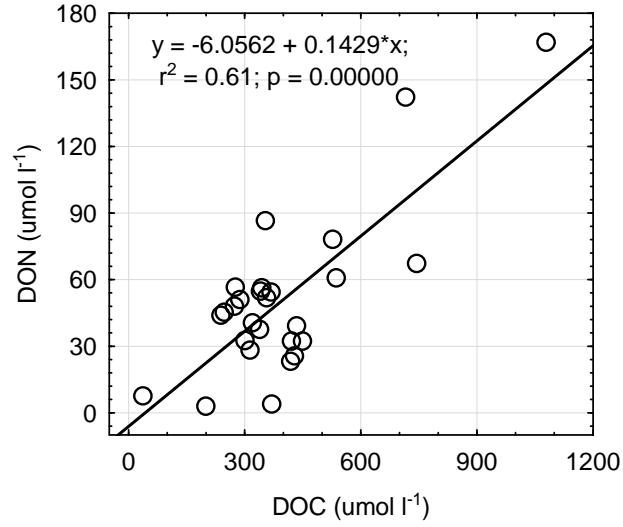


Fig. 3

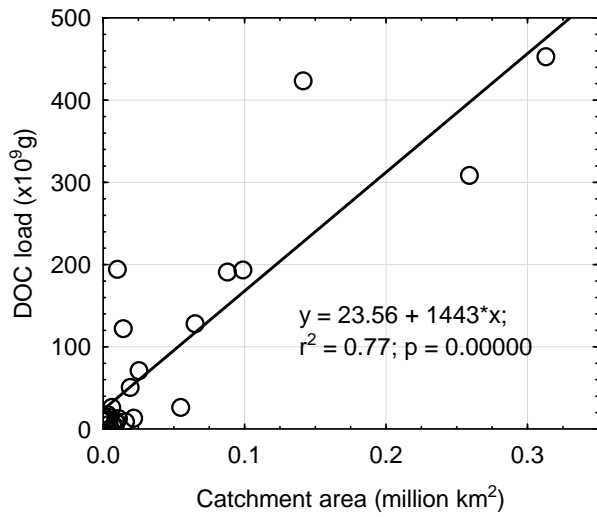


Fig. 4a

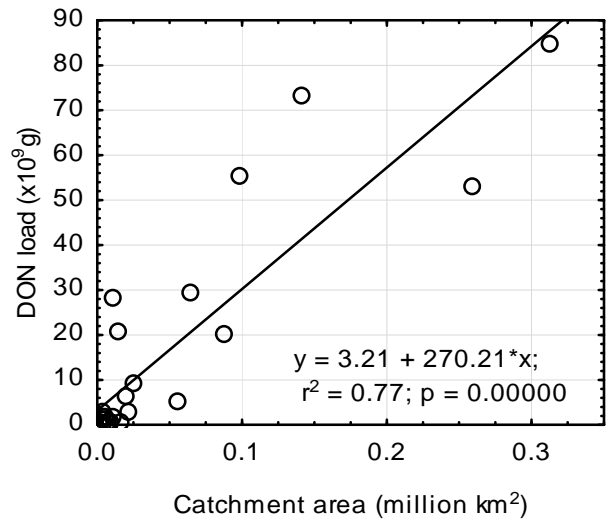


Fig. 4b

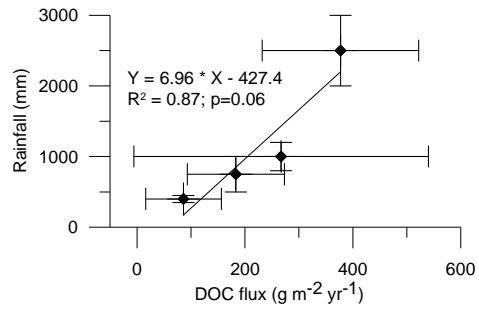


Fig. 5a

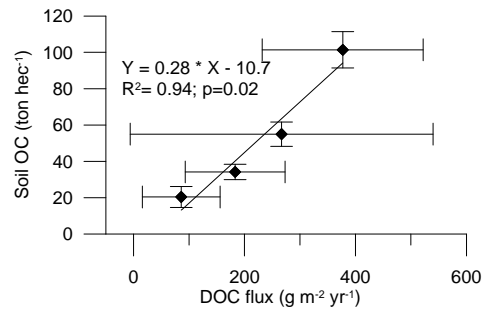


Fig. 5b

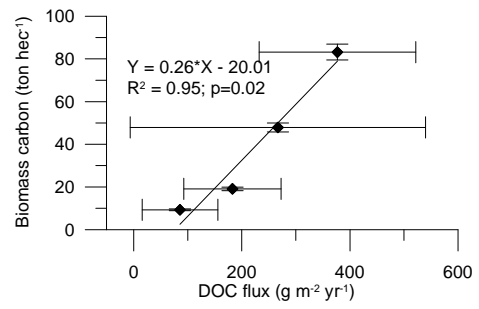


Fig. 5c

Name of the estuary	Catchment area (million km ²)	Annual discharge(km ³)	DOC ($\mu\text{mol l}^{-1}$)	DON ($\mu\text{mol l}^{-1}$)	DOC load ($\times 10^9 \text{g yr}^{-1}$)	DON load ($\times 10^9 \text{g yr}^{-1}$)	DOC flux ($\text{g m}^{-2} \text{yr}^{-1}$)	DON flux ($\text{g m}^{-2} \text{yr}^{-1}$)	DOC:DON ratio
Haldia	0.010	50.46	321	40.5	194	28.6	1903	280.4	7.9
Subernarekha	0.019	12.36	339	37.6	50	6.5	261	33.7	9.0
Baitarani	0.014	28.48	357	51.9	122	20.7	859	145.7	6.9
Mahanadi	0.142	66.89	528	78.2	423	73.2	299	51.7	6.7
Rushikulya	0.009	1.93	421	32.2	10	0.9	108	9.7	13.1
Vamsadhara	0.011	3.50	301	32.5	13	1.6	115	14.5	9.2
Nagavali	0.009	1.99	314	28.3	8	0.8	80	8.4	11.1
Godavari	0.313	110.53	341	54.9	453	84.9	145	27.1	6.2
Narmada	0.099	45.63	353	86.6	193	55.3	195	55.9	4.1
Tapti	0.065	14.88	716	142.2	128	29.6	197	45.6	5.0
Sabarmati	0.022	3.78	288	51.0	13	2.7	60	12.4	5.6
Mahisagar	0.026	11.02	537	60.8	71	9.4	278	36.8	8.8
Krishna	0.259	69.79	368	54.4	309	53.1	119	20.5	6.8
Penna	0.055	6.31	344	56.3	26	5.0	47	9.0	6.1
Ponnyaar	0.016	1.60	450	32.3	9	0.7	54	4.5	13.9
Vellar	0.009	0.90	276	56.5	3	0.7	35	8.3	4.9
Cauvery	0.088	21.35	745	67.2	191	20.1	217	22.8	11.1
Ambalyaar	-	0.88	1079	166.9	11	2.1	-	-	6.5
Vaigai	0.007	1.14	239	43.9	3	0.7	46	10.0	5.4
Kochi back waters	-	12.33	274	48.0	40	8.3	-	-	5.7
Chalakudi	0.002	1.92	419	23.2	10	0.6	567	36.7	18.0
Bharathappuzha	0.006	5.08	429	25.6	26	1.8	422	29.3	16.8
Netravati	0.003	11.06	37	7.5	5	1.2	152	36.4	4.9
Sharavati	0.004	4.55	200	2.9	11	0.2	303	5.2	68.6
Khali	0.004	4.79	248	45.4	14	3.0	339	72.5	5.5
Zuari	0.001	3.25	370	3.9	14	0.2	1443	17.9	94.1
Mandovi	0.004	3.31	434	39.2	17	1.8	479	50.4	11.1

Table 1: Name of the monsoonal estuary along with its catchment area (million km²) and mean annual volume of discharge (km³) sampled in this study. Concentrations of dissolved organic carbon (DOC) ($\mu\text{M l}^{-1}$) and dissolved organic nitrogen (DON) ($\mu\text{M l}^{-1}$) during study period and annual load of DOC ($\times 10^9 \text{g yr}^{-1}$) and DON ($\times 10^9 \text{g yr}^{-1}$) to the northern Indian Ocean with a catchment area normalized fluxes of DOC ($\text{g m}^{-2} \text{yr}^{-1}$) and DON ($\text{g m}^{-2} \text{yr}^{-1}$) were provided. Elemental DOC:DON ratios were also shown.

Name of the River	Concentration	Reference
DOC ($\mu\text{mol l}^{-1}$)		
Amazon	372	<i>Richey et al., 1991</i>
Nile	246	<i>Abu el Ella, 1993</i>
Ganges/Brahmaputra	323	<i>Safiullah et al., 1987</i>
Niger	309	<i>Martins and Probst, 1991</i>
Columbia	177	<i>Dahm et al., 1981</i>
Rhone	139	<i>Kempe et al., 1991</i>
Rioni	88	<i>Romankevitch and Artemyev, 1985</i>
Gambia	199	<i>Lesack et al., 1984</i>
Mississippi	489	<i>Bianchi et al., 2004</i>
Congo	604	<i>Probst and Suchet, 1992</i>
16 rivers entering into the Bohai Sea	722	<i>Bin and Longjun, 2011</i>
Indian estuaries	400±200	Present study
DON ($\mu\text{mol l}^{-1}$)		
Arctic rivers	7.9 – 65.0	<i>Holmes et al., 2012, Letscher et al., 2013</i>
Delaware and Hudson	12.9-46.4	<i>Seitzinger and Sanders, 1997</i>
Russian rivers draining into Arctic	27.1±5.0	<i>Gordeev et al., 1996; Wheeler et al., 1997</i>
rivers entering into the Baltic Sea	30.0±15.0	<i>Stepanauskas et al., 2002</i>
streams in Sweden	24.3±7.1	<i>Stepanauskas et al., 2000</i>
Indian estuaries	42.4±20.9	Present study
DOC load (Tg yr⁻¹)		
Amazon	26.33	<i>Richey et al. 1990</i>
Changjiang	10.34	<i>Gan Wei-bin et al. 1983</i>
Zaire	9.13	<i>N'Koukou and Probst, 1987</i>
Mississippi	4.28	<i>Leenheer, 1982</i>
Ob	3.67	<i>Romankevitch and Artemyev, 1985</i>
Mackenzie	1.35	<i>Telang et al., 1991</i>
Nile	0.17	<i>Abu el Ella, 1993</i>
Indian monsoonal rivers	2.37±0.47	Present study

Table2: Concentrations of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) ($\mu\text{mol l}^{-1}$) in the world major rivers. Annual transport load of DOC (Tg yr⁻¹) from the few major rivers in the world was also given.

Parameter	Catchment area (M km ²)	Volume of discharge (km ³)
DOC concentration (μmol l ⁻¹)	0.17 ^{§*}	0.00*
DON concentration (μmol l ⁻¹)	0.61 [§]	0.01*
DOC load (x10 ⁹ g yr ⁻¹)	0.77	0.92
DON load (x10 ⁹ g yr ⁻¹)	0.77	0.91
DOC flux (g m ⁻² yr ⁻¹)	0.05*	0.01*
DON flux (g m ⁻² yr ⁻¹)	0.01*	0.09*

*: statistically insignificant (p>0.05); §: logarithmic relation

Table 3: Correlation coefficients for linear relationship of concentrations (μmol l⁻¹), transport load (x10⁹g yr⁻¹) and catchment area normalized fluxes (g m⁻² yr⁻¹) of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) with that of the catchment area of the river (million km²) and volume of discharge (km³) of the Indian monsoonal rivers.