

Distribution and sources of particulate organic matter in the Indian monsoonal estuaries during monsoon

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Abstract

The distribution and sources of particulate organic carbon (POC) and nitrogen (PN) in 27 Indian estuaries were examined during the monsoon using the content and isotopic composition of carbon and nitrogen. Higher phytoplankton biomass was noticed in estuaries with deeper photic zone than other estuaries receiving higher suspended matter. The $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ data suggests that relatively higher $\delta^{13}\text{C}_{\text{POC}}$ (-27.9 to -22.6‰) and lower $\delta^{15}\text{N}_{\text{PN}}$ (0.7 to 5.8‰) were noticed in the estuaries located in the northern India, north of 16°N, and lower $\delta^{13}\text{C}_{\text{POC}}$ (-31.4 to -28.2‰) and higher $\delta^{15}\text{N}_{\text{PN}}$ (5 to 10.3‰) in the estuaries located in the southern India. This is associated with higher Chl-a in the northern than southern estuaries suggesting that *in situ* production contributed significantly to the POC pool in the former whereas terrestrial sources are important in the latter estuaries. The spatial distribution pattern of $\delta^{15}\text{N}_{\text{PN}}$ is consistent with fertilizer consumption in the Indian subcontinent, which is twice as much in the northern India as in the south whereas $\delta^{13}\text{C}_{\text{POC}}$ suggests that *in situ* production is a dominant source in the southern and terrestrial sources are important in the northern estuaries. Based on the SIAR (Stable Isotope Analysis in R) model, 40-90% (70-90%) of organic matter is contributed by C₃ plants (freshwater algae) in the estuaries located in the northern (southern) India.

Key words: particulate organic matter, river discharge, stable isotopes of carbon and nitrogen isotopes, Indian estuaries.

Introduction

Estuaries are links between land and ocean and contribute to a high amount of sediments [Milliman, 1991] and, particulate organic matter (POM) to the ocean [Meybeck, 1993]. Oceans receive about 0.4×10^{15} g of carbon annually from land, out of which about 35% is in particulate form [Ludwig *et al.*, 1996; Hedges *et al.*, 1997]. It was estimated that about 35% of the POM is contributed in the labile form that is easily degradable by the microbes [Ittekkot and Laane, 1991]. The POM contributes to organic carbon burial in marine sediments [Duarte *et al.*, 2005; Hedges *et al.*, 1997]; however, extensive degradation, bioturbation and resuspension prevent their accumulation in the estuaries [Aller *et al.*, 1996]. Besides organic matter brought from the watershed, the active biological pump in the estuaries produces a substantial amount of organic matter *in situ* [Wollast and Mackenzie, 1989; Smith and Hollibaugh, 1993; Wollast, 1998]. Though river-borne organic matter is expected to be refractory and is mostly unavailable for metabolic breakdown [Meybeck, 1982; Ittekkot and Laane, 1991], several investigators have reported that dominant heterotrophy in the estuaries is supported by terrestrial organic matter [Heip *et al.*, 1995; Ram *et al.*, 2003; Caffrey, 2004; Gazeau *et al.*, 2004, 2005; Gupta *et al.*, 2008; Sarma *et al.*, 2009]. Abril *et al.* [2002] studied organic matter (both dissolved and particulate) in nine European estuaries during different periods and noticed that human activity, through waste water loads, significantly contributes to the organic carbon in European rivers and estuaries. They further noticed that sewage driven organic matter is more reactive than soil derived during estuarine mineralization and attributed that the increased carbon load due to land use change would undergo a limited mineralization in estuaries.

Indian estuaries are significantly different from other estuaries with reference to the discharge pattern. Indian estuaries are characterized by seasonal discharge during monsoon period (3 to 4 months) when significant monsoonal precipitation occurs. The magnitude of discharge in various rivers on Indian subcontinent depends on the monsoonal precipitation pattern. Indian subcontinent receives annual monsoon rainfall in the order of 3000 km^3 [Soman and Kumar, 1990] and it depends on the south-west and north-east monsoons, shallow cyclonic depressions, disturbances and local storms. The influence of south-west monsoon between June and September is more significant for monsoon precipitation, which shows strong spatial variations. For instance, southwestern India receives the maximum rainfall (~3000 mm) followed by northeastern India (1000-2500 mm) and the least over the southeast (300-500 mm) and

northwestern India (200-500 mm) [Soman and Kumar, 1990]. Hence, the spatial variations in river discharge by various rivers are governed by the rainfall received over their watershed.

Due to heavy discharge during monsoon period, the estuaries turn into lakes of freshwater with no vertical salinity gradient [Vijith *et al.*, 2009; Sridevi, 2013]. Such a pattern is in contrast to many American and European estuaries where stratification occurs associated with fresh water discharge [Christopher *et al.*, 2002]. During other period, monsoonal estuaries are dominated by seawater due to the dry climate. The river discharge also brings a substantial amount of organic matter to the estuary, besides nutrients and suspended particulate matter (SPM) [Gupta *et al.*, 1997]. Recently Sarma *et al.* [2012] reported higher levels of partial CO₂ pressures (pCO₂) in the Indian estuaries during discharge than dry period and attributed it to intensive organic matter modification within the estuary during the former period.

The river-borne nutrients may have a significant impact on the phytoplankton biomass in the monsoonal estuaries. Although high nutrient concentrations are observed during peak discharge period, lower phytoplankton biomass is noticed in several Indian estuaries [Cochin estuary - Gupta *et al.*, 2009; Godavari estuary - Sarma *et al.*, 2009; Mandovi-Zuari estuary- Pednekar *et al.*, 2011] than during dry period due to high turbidity that inhibits light penetration. The concentrations of SPM and photic depth are crucial parameters controlling phytoplankton biomass in estuaries [Cloern *et al.*, 1985; 2012; Sin *et al.*, 2013]. On the other hand, enhanced phytoplankton biomass was noticed during the dry period associated with lower SPM and nutrient concentrations than peak discharge period [Sarma *et al.*, 2009; Pednekar *et al.*, 2011] suggesting that the clarity of water is more important than nutrients in the Indian estuaries.

Due to variable discharge rates associated with precipitation pattern over Indian subcontinent, diverse sources of organic matter, such as *in situ*, land-derived (C₃ and C₄ plants), soil organic matter and anthropogenic, enter estuary and the contribution from each of these sources is expected to vary from estuary to estuary depending on size, tidal amplitude, discharge characteristics, SPM concentrations and variable residence time of water. The objective of this study is to understand the distribution and sources of organic matter in the Indian estuaries using content and isotopic composition of carbon and nitrogen. The aim of this work is to test the hypothesis that though it is the monsoonal precipitation, which influences the Indian estuaries, the impact of this precipitation, due to spatial variations in monsoon

intensity over Indian sub-continent, may not be uniform on production of organic matter in different estuaries.

2. Material and methods

Sampling of hydrographic properties

Sampling was carried out in 27 major and minor estuaries along the Indian coast during discharge period (Figure 1). River discharge data were collected from *Kumar et al.* [2005] and also from the dam authorities wherever available (Table 1). Though discharge takes place only during 3 to 6 months in a year, the mean discharge during this period is represented as annual mean. Due to high discharge and low flushing rates, uniform concentrations can be expected in the estuary [*Sarma et al.*, 2009; *Sarma et al.*, 2012]. In order to get representative mean, 3 to 5 samples were collected at ~5 kms distance apart between mouth and upper estuary. All samples were collected within 3 weeks (28th July to 18th August 2011) from the 27 estuaries to examine the variability in concentration and isotopic composition of POM during peak discharge period. Temperature, salinity and depth were measured using a CTD system (Sea Bird Electronics, SBE 19 plus, USA). Nutrients were measured using colorimetric method following *Grashoff et al.* [1992] using autoanalyzer. Dissolved Oxygen (DO) was measured using Winkler's titration method of *Carritt and Carpenter* [1966]. The analytical precision, expressed as standard deviation, was 0.07% for DO. About 500 ml of sample was filtered through Glass Fiber (GF/F; 0.7 μm pore size; 47mm diameter; Whatman) filter at gentle vacuum and Chlorophyll-a (Chl-a) retained on the filter was extracted to dimethyl formamide (DMF) and fluorescence of the extract was measured using Varian Eclipse fluorescence photometer (Varian Electronics., USA) following *Suzuki and Ishimaru* [1990]. Suspended Particulate Matter (SPM) was measured as weight difference of material retained on 0.2 μm polycarbonate filter (Millipore) after passing 200-500 ml of water. About 1 liter of water samples was filtered through pre-combusted GF/F filter (0.7 μm pore size; 47mm diameter; Whatman) at 300° C for 6 h, at low vacuum and dried at 60° C for at least 24 h. Filters were acid fumigated for 12 h in desiccator to remove inorganic carbon and organic carbon on the filter was measured using elemental analyzer. Subsamples for $\delta^{15}\text{N}$ analysis did not receive acid treatment as this has been reported to affect $\delta^{15}\text{N}$ values [*Goering et al.*, 1990; *Bunn et al.*, 1995; *Pinnegar and Polunin*, 1999].

Measurement of stable isotope and elemental ratios

The content and isotopic composition of carbon and nitrogen in the SPM were measured on elemental analyzer coupled with Isotope Ratio Mass Spectrometer (EA-IRMS-Delta V, Finnigan, Germany) and results are expressed relative to conventional standards, i.e., PDB for carbon [Coplén, 1996] and atmospheric N₂ for nitrogen [Mariotti, 1983], as δ values, defined as:

$$\delta R = [(X_{\text{sample}} - X_{\text{standard}}) / X_{\text{standard}}] \times 10^3 \quad \text{----- (1)}$$

Where R = ¹³C or ¹⁵N, and X = ¹³C/¹²C or ¹⁵N/¹⁴N. The high-purity tank CO₂ and N₂ were used as working standard for carbon and nitrogen. These gases were calibrated with internal reference materials of Glutamic Acid, Alanine, marine sediment and IAEA standards. The long term precision of the instrument is ca. ±0.2‰ for both C and N.

Multi Dimensional Scaling (MDS) plots were drawn for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of particulate matter to examine different sources, and similarities among Indian estuaries using PRIMER (Plymouth Routines in Multivariate Ecological Research) package (version 5.2.8) (Clarke and Gorley, 2001). STATISTICA package was used to derive regression equations and GRAPHER software to draw two dimensional plots.

Quantification of organic matter contributions from different source materials

Relative contribution of variable sources of organic matter to Indian estuaries were quantified using isotope mixing model ‘SIAR’ (Stable Isotope Analysis in R), which resolves mixing models within a Bayesian framework [Parnell *et al.* 2008; 2010] and it is an open source package (<http://cran.r-project.org/>). The advantage of this model is that it includes the residual error term in the form of standard deviation, unlike the model MixSIR [Jackson *et al.* 2009; Parnell *et al.*, 2010]. SIAR uses Markov Chain Monte Carlo (MCMC) method, which produces simulations of probable values of proportional source contributions, for fitting algorithms. Moreover, the model SIAR also includes the covariance structure, which gives information about functioning ability of the model to discriminate between sources, via diagnostic matrix plot of proportional source contributions. The matrix plot produces actual correlation coefficient of posterior distributions that represents the correlation between sources. For example, if the two sources are very close, then most feasible solutions could involve one

or other of sources but not both at the same time [Parnell *et al.*, 2010], hence, these two sources are expected to show negative correlation in their posterior distribution. Lower the correlation between sources better the performance of the model, i.e. the model is able to isolate contribution from each source. On the other hand, high correlation coefficient indicates that the model is struggling to differentiate between sources. Hence, matrix plot of the data is a good diagnostic tool for functioning of the model. The model 'SIAR' has already been used elsewhere for the source apportionment of organic matter in the coastal systems [Dubois *et al.* 2012; Carreon-Palau *et al.* 2013]. The model 'SIAR' uses both the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ along with uncertainties in estimation of the proportional contributions from possible sources and therefore yield reliable results than the models based on single isotope (either $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$). However, selection of end members is critical for the estimation of proportional contributions from different sources.

In order to obtain reliable estimates of proportional source contributions, we selected the end members of possible sources based on measurements of samples from representative locations. Dominant C_3 and C_4 plant material (leaf, stem and root) and soil samples were collected from drainage basin of the river Godavari for fixing the terrestrial end members. The freshwater phytoplankton was separated microscopically from water samples collected from the upstream Godavari, Mahanadi, Cochin, Mandovi and Tapti estuaries for fixing end members of *in-situ* sources. Mean $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios of C_3 ($-25.9\pm 1.2\text{‰}$ and $5.1\pm 2.1\text{‰}$, respectively) and C_4 ($-13.1\pm 1.2\text{‰}$ and $4.4\pm 2.1\text{‰}$) land plants, and soils ($-19.2\pm 2.4\text{‰}$ and $10.3\pm 2.7\text{‰}$), were taken as end members. Our measured end member values are very close to the values reported elsewhere for terrestrial C_3 [-30 to -23‰ ; Smith and Epstein, 1971] and C_4 [-17 to -9‰ ; Smith and Epstein, 1971; Sackett, 1989] plants. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of fresh water algae ranged from -32.2 to -30.3‰ and 4.8 to 6.5‰ respectively and these values are within the ranges of reported earlier [-31.5‰ ; Middelburg and Herman 2007]. In addition to this, $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) of the freshwater end member for all Indian estuaries varied between -4.8 and -7.3‰ (mean of $-6.7\pm 0.8\text{‰}$) (our unpublished data), except in Narmada and Mahisagar, suggesting that $\delta^{13}\text{C}$ of freshwater algae may not be significantly variable within the Indian estuaries. Hence we believe that the end member characteristics of freshwater algae measured in the 5 estuaries may represent all Indian estuaries. The content of carbon and nitrogen of C_3 ($12.1\pm 5\%$ and $0.92\pm 0.3\%$), C_4 ($13.0\pm 4\%$, and $0.81\pm 0.5\%$), soil organic matter ($1.6\pm 0.6\%$ and $0.05\pm 0.02\%$) and freshwater algae ($1.9\pm 0.3\%$ and $0.23\pm 0.1\%$) is also taken into consideration while computing contribution from different sources.

3. Results

3.1. Hydrographic features of the Indian estuaries

The annual mean river discharge ranges between 28 and 3505 m³ s⁻¹ in the Indian estuaries (Table 1). Except for 6 minor estuaries (Rushikulya, Vamsadhara, Nagavali, Vellar, Cauvery, and Vaigai), which displayed relatively higher salinity (~12 to 28.8), near freshwater (<10 salinity) was observed in other estuaries sampled in this study (Fig. 2a). The phytoplankton biomass, represented as Chlorophyll-a (Chl-a), varied from 0.8 to 10.7 mg m⁻³ and higher concentrations (>5 mg m⁻³) were observed in Krishna, Penna, Ponnayyar, and Cauvery estuaries. Chl-a increased with salinity from near freshwater region (2.8±2 mg m⁻³) to the intermediate salinity range of 10 to 15 (5.5±1 mg m⁻³) and decreased (1.4±0.4 mg m⁻³) at salinity >20 (Fig. 2b). Dissolved oxygen saturation ranged between 63 and 105% in the Indian estuaries and over-saturation (>100%) was noticed in the minor estuaries such as Rushikulya, Nagavali, Penna, Ambalyaar and Vaigai (Fig. 2c).

3.2. Suspended particulate matter (SPM)

The concentrations of SPM ranged from 6.5 to 905 mg l⁻¹ in the Indian estuaries (Fig. 2d). Relatively higher concentrations of SPM were observed in Narmada and Godavari estuaries with high river discharge. Overall major rivers received relatively higher concentrations of SPM and displayed linear relation with river discharge (r²=0.85; p<0.001; Table 2). Higher phytoplankton biomass was noticed in the estuaries that contained low SPM (<100 mg l⁻¹) and vice versa suggesting that turbidity is the major controlling factor for growth of phytoplankton than nutrients. The concentrations of SPM in the Indian estuaries were similar to those found in the European estuaries [Middelburg and Herman, 2007].

3.3. Particulate organic carbon (POC) and nitrogen (PN)

The distribution of particulate organic carbon (POC) and nitrogen (PN) varied from 51 to 750 µM and 5.3 to 60.3 µM respectively in the Indian estuaries (Fig. 3). The distribution of POC and PN is governed primarily by the dynamics of suspended particles. Concentrations of POC and PN were higher (>200 µM and >40 µM) in turbid estuaries such as Godavari, and Narmada and lower in the less turbid estuaries such as Vaigai, and Penna (<200 µM and <8 µM; Figure. 2 and 3). Higher load of SPM is reflected by the higher concentrations of POC and PN and vice versa suggesting that SPM is a strong

source of organic matter to the Indian estuaries. Since our prime interest is to study the processing of organic matter in the Indian estuaries, POC and PN are represented as the percentage of organic carbon (OC) and nitrogen (ON) in the SPM (wt %) respectively. The concentrations of OC and ON varied from ~1.0 to 18.3% and 0.1 to 2.1% (Fig. 3a,b) respectively and the highest OC (>10%) and ON (>1.5%) were noticed in Rushikulya, Mahanadi and Bharatakulza estuaries. The C/N ratios in the SPM varied between 5.1 and 14.1 (mean 8.7 ± 2) with weak spatial variations in the Indian estuaries (Fig. 3c).

3.4. *Isotopic composition of particulate organic carbon and nitrogen*

The isotopic composition of POC varied from -31.4 to -22.6‰ in the Indian estuaries and relatively lower values were observed in the minor estuaries (-31.4 to -26.8‰) such as Kali, Sharavati, Ponnayyar, Netravati etc than major estuaries (-25.5 to -22.6‰) such as Narmada, Tapti, Godavari etc. (Table 2). The POC was relatively heavier $\delta^{13}\text{C}_{\text{POC}}$ values in the estuaries received high turbidity ($\text{SPM} > 150 \text{ mg l}^{-1}$), moderately depleted values with SPM range of 50 to 150 mg l^{-1} and highly depleted values at lower turbidity levels ($\text{SPM} < 50 \text{ mg l}^{-1}$). The lowest stable isotopic composition of POC was found in estuaries with high concentrations of Chl-a (Krishna, Penna, Ponnaiyyar, Kali and Sharavati) (Figure 2 and 4).

The stable isotopic composition of PN varied from 0.7 to 16.7‰ (Fig. 4b) and did not display significant variations with reference to turbidity levels. However, exceptionally higher values were observed in Penna (13.5‰), Vellar (14.2‰), and Cauvery (16.7‰) estuaries and were associated with high phytoplankton biomass (Fig. 2b). Relatively higher $\delta^{15}\text{N}_{\text{PN}}$ were associated with lower $\delta^{13}\text{C}_{\text{POC}}$ values. The range of $\delta^{15}\text{N}_{\text{PN}}$ values were associated with the same found in the European estuaries [*Middelburg and Herman, 2007*].

4. Discussion

4.1. *Hydrographic setting of monsoonal estuaries during discharge period*

Indian subcontinent experiences seasonal precipitation with the average rainfall is more during summer (June–August) than in winter [November–February; *Soman and Kumar, 2005*]. The discharge of each river, in terms of quantity and timing, is tuned to this precipitation pattern. Hence, the estuaries in India are called “Monsoonal estuaries” and exhibit non-steady state behavior [*Vijith et al., 2009*]. During the times of peak discharge, the runoff far exceeds the total volume of the estuary when the entire estuary

turns like freshwater lake with no vertical gradient in salinity [Sarma *et al.*, 2009, 2010, and 2011]. Discharges of variable magnitudes occur for a period of 3 to 6 months and the upstream rivers almost dry up during the other periods allowing the dominance of seawater in the estuary. Hence, the biogeochemical processes in monsoonal estuaries during discharge period could be completely different from those in dry period.

The hydrological conditions of the Indian estuaries are widely variable from low freshwater flow and longer residence time to high freshwater flow and short residence time. The rate of mean annual discharge from the Indian estuaries varied from ~ 28 to $3505 \text{ m}^3 \text{ s}^{-1}$ (Table 1) and the spatial variations in discharge were controlled by precipitation pattern over peninsular India and also the origin of the river. For instance, some rivers, such as Godavari, Mahanadi, and Krishna, originated in the western India and flow towards east covering >1500 kms. Although the highest precipitation is received in the western India [Soman and Kumar, 1990], the length of the rivers also originating in the western India, such as Mandovi, Zuari, Kali, is short (~ 100 kms) leading to low discharge. The rivers located in the southern India (south of 16° N) originated in the central India, such as Penna, Cauvery, Ponnayyar, Kochi etc, are relatively small rivers due to much less precipitation that is received in this part of Indian subcontinent. Therefore, size of the river, location and precipitation pattern controls the magnitude of discharge into the coastal ocean.

Salinity of the estuary depends on the magnitude of discharge and varied from near freshwater (0.05) to brackish (24.7) in the Indian estuaries during the study period. Higher salinity (>10) was noticed in Rushikulya, Vamsadhara, Nagavali, Vellar, Cauvery and Vaigai estuaries, which received less discharge from the upstream river (Table 1). The water column stability and stratification depends on the magnitude of discharge. In the case of Godavari, the entire estuary fills with freshwater when discharge exceeds $1000 \text{ m}^3 \text{ s}^{-1}$ [Sarma *et al.*, 2010]. The water column structure depends on the length and width of the estuary as well. For instance, near freshwater was noticed in some minor estuaries, such as Mandovi, Sabarmati, Ambalayar, which received discharge $\leq 100 \text{ m}^3 \text{ s}^{-1}$ (Table 1).

The concentration of SPM displayed large spatial variability ($6.5\text{-}905 \text{ mg l}^{-1}$) and positive relation to discharge ($r^2=0.85$; $p<0.001$; Table 2), except in the case of Mahanadi and Krishna estuaries. The concentrations of SPM was higher by an order of magnitude ($223\pm 83 \text{ mg l}^{-1}$) in the estuaries that receive high discharge ($>200 \text{ m}^3 \text{ s}^{-1}$) than others ($29.7\pm 12 \text{ mg l}^{-1}$). Discharge also brings substantial amount of

nutrients to the estuary and followed discharge pattern. Relatively higher concentration of dissolved inorganic nitrogen (DIN), dissolved inorganic phosphate (DIP) and dissolved inorganic silicate (DSi) were observed in the estuaries received $>200 \text{ m}^3 \text{ s}^{-1}$ (DIN= $16.4 \pm 9 \text{ } \mu\text{M}$; DIP= $7.0 \pm 4 \text{ } \mu\text{M}$ and DSi= $36.5 \pm 9 \text{ } \mu\text{M}$) than others (DIN= $8.7 \pm 4 \text{ } \mu\text{M}$; DIP= $4.0 \pm 2 \text{ } \mu\text{M}$ and DSi= $28.8 \pm 9 \text{ } \mu\text{M}$). The distribution of phytoplankton biomass (in terms of Chl-a) also followed the SPM than nutrients and their concentrations were higher ($3.5 \pm 1 \text{ mg m}^{-3}$) in the estuaries that received low discharge ($<200 \text{ m}^3 \text{ s}^{-1}$) than other estuaries ($1.8 \pm 0.9 \text{ mg m}^{-3}$). The relation between SPM and Chl-a (Fig. 5a) suggests that higher Chl-a was noticed at SPM $<200 \text{ mg l}^{-1}$ and uniformly low concentrations were observed at higher SPM suggesting that turbidity has significant impact on phytoplankton biomass in the Indian estuaries due to decrease in light penetration depth. Furthermore, higher discharge also introduced instability of water column that further decreases phytoplankton biomass as such conditions do not favour phytoplankton growth [Cloern *et al.*, 1985]. Occurrence of phytoplankton blooms were observed in Indian estuaries in association with lean discharge when water column contains low SPM and stratified water column [Gupta *et al.*, 2008; Pednekar *et al.*, 2011; Acharyya *et al.*, 2012].

Except in five minor estuaries, under-saturation of dissolved oxygen was observed ($89 \pm 5\%$) in the Indian estuaries (Fig. 2c) suggesting that intense bacterial decomposition of organic matter leading to formation of CO_2 and efflux to atmosphere [Sarma *et al.*, 2012]. The significant positive correlation of POC with pCO_2 [$r^2=0.43$; $p<0.001$; Sarma *et al.*, 2012] and inverse relation with dissolved oxygen ($r^2=0.32$; $p<0.001$; Table 2) indicating that microbial decomposition enhanced with increase in POC content and significant modification occurred in the Indian estuaries. In addition to this, linear correlation was reported between pCO_2 and river discharge suggesting that increased inputs of substratum (POM) leading to enhanced bacterial decomposition [Sarma *et al.*, 2012]. Therefore significant modification of POM occurs in the Indian estuaries to support heterotrophic carbon demand. In addition to this, part of the over saturation of CO_2 may also be contributed through mineralization in the intertidal areas, seepage of ground water and soil water CO_2 . However quantification of contribution from different sources requires further studies.

4.2. Particulate organic carbon (POC) and nitrogen (PN) in the Indian monsoonal estuaries

The composition of organic matter in the SPM is governed by sources, their degradation, transformation in the water column and sediments and the interaction between these two pools. The potential sources of

organic matter to estuary during discharge period are terrestrial, sewage, *in situ* biological processes and their detritus [Middelburg and Herman, 2007]. The spatial distribution pattern of POC and PN followed discharge rate in the Indian estuaries. The concentrations of POC and PN were more than double in the estuaries that receive high discharge ($>200 \text{ m}^3 \text{ s}^{-1}$) (368 ± 85 and $33.8 \text{ } \mu\text{M}$) than others (153 ± 62 and $21.7 \pm 17 \text{ } \mu\text{M}$). The contribution of POC and PN to the SPM (OC and ON respectively) varied from 1.0 to 18.3% and 0.1 to 2.1% respectively with relatively higher contribution in the high discharge estuaries (7.6 ± 4 and $0.9 \pm 0.4\%$) than low discharge estuaries (4.7 ± 3 and $0.6 \pm 0.5\%$) indicating that discharge is a significant source of organic matter to the Indian estuaries. The POC/Chl-a ratio is an indicator to understand the contribution of *in situ* phytoplankton biomass to the POC pool. This ratio normally varied between 40 and 50, if the entire POC is contributed by phytoplankton. This ratio ranged from 126 to 5614 (1308 ± 785) in the Indian estuaries with relatively higher ratios in the high discharge estuaries (1980 ± 875) than low discharge estuaries (486 ± 110) indicating that the contribution from *in situ* phytoplankton was more significant in the latter than former estuaries. The organic carbon (OC) and organic nitrogen (ON) of SPM are both correlated with Chl-a ($r^2=0.60$; $p<0.001$ and $r^2=0.53$; $p<0.001$ respectively) at OC and ON levels $<8\%$ and $<1\%$ with the slope of 0.64 and 0.093 respectively (Fig. 5b,c). The slopes of the relation were higher at high concentrations ($r^2=0.43$; $p<0.001$ for OC and 0.30; $p<0.01$ for ON with the slope of 0.76 and 0.2 respectively) suggesting different plankton communities might be contributing to the organic matter pool. Such high OC and ON levels were found mainly in low discharge estuaries located in the southern India such as Ambalyaar, Bharatapuzha, Sharavati, Mandovi, Chalakudi and Kali (Fig. 5b,c). These rivers contained relatively lower N:P ratios (2.3 ± 0.5) and lower fucoxanthin:Chl-a ratio (0.02; marker pigment for diatoms) and Zeaxanthin:Chl-a ratio (0.03; marker pigment for cyanobacteria) than other rivers (N:P= 5.4 ± 1 ; 0.05 and 0.13 for fucoxanthin:Chl-a and Zeaxanthin:Chl-a ratios respectively; Our unpublished data) strongly indicating that cyanobacteria was dominant in the high discharge estuaries. This could be caused by variations in nutrients concentrations in the Indian estuaries that result in variable contribution by the differing phytoplankton composition and slope of relation of Chl-a with OC and ON (Fig. 5b,c). Acharyya *et al.* [2012] noticed that formation of phytoplankton bloom during the onset and termination phase of the discharge due to enhanced nutrient inputs, strong stratification and relatively low SPM load. Microscopic analysis in the Godavari estuary suggested that these blooms were mainly contributed by freshwater phytoplankton [Bharati, 2014]. Similar phenomenon was also observed in Mandovi-Zuari estuarine system [Pednekar

et al., 2011] and Cochin back waters [N. Madhu, personal communication, 2014] on the west coast of India. Hence, the positive relation of OC with Chl-a suggests that discharge driven phytoplankton blooms might have contributed significantly to the OC and ON in the Indian estuaries during the study period.

4.3. Sources of particulate organic matter to the Indian monsoonal estuaries

The elemental ratios and isotopic composition of carbon and nitrogen can be used to identify source of organic matter in the estuarine system. However, these signals are modified by high SPM concentrations and longer residence time of water as large stock of estuarine particles mask the source characteristics and substantial modification of organic matter respectively. Hence, an attempt has been made here to study the dual isotopes (carbon and nitrogen) and elemental ratios to identify sources of organic matter and possible modifications in the Indian estuaries during the study period.

4.3.1. Elemental ratios in the Indian estuaries

Variable ratios of carbon to nitrogen (C:N) for plankton (6-7), bacteria (4-5) and organic matter from higher plants (>20) can be used as a tracer to identify sources of organic matter [Hedges *et al.*, 1997]. However, several diagenetic processes modify C:N ratios. For instance, C:N ratio of higher plant litter decreases due to bacterial assimilation and retention of dissolved inorganic nitrogen while increases in algal detritus upon diagenesis due to preferential removal of nitrogen [Hedges *et al.*, 1997; Herman and Heip, 1999]. Though these modifications will not allow identifying exact source of organic matter, it is possible to understand at least the occurrence of modification [Middelburg and Herman, 2007]. The C:N ratios of POM in the Indian estuaries ranged between 5.1 and 14.1 and such low variations indicate possible alternation of organic matter. This lack of power to resolve organic matter sources has been observed in other estuaries also [Cifuentes *et al.*, 1988; Thornton and McManus, 1994; Middelburg and Nieuwenhuize, 1998; Middelburg and Herman, 2007]. The overall molar C:N ratio of our data set (8.7 ± 2) is similar to that reported for particles in the major world rivers [8.1 to 12.9; Ittekkot and Zhang, 1989]. This similarity among riverine and estuarine particles suggests that POM was extensively modified in the Indian estuaries.

4.3.3. Isotopic composition of particulate organic matter in the Indian estuaries

The $\delta^{13}\text{C}$ of POC ($\delta^{13}\text{C}_{\text{POC}}$) and $\delta^{15}\text{N}$ of PN ($\delta^{15}\text{N}_{\text{PN}}$) can be used as a potential tool to identify source of organic matter to the Indian estuaries. The isotopic values of $\delta^{13}\text{C}_{\text{POC}}$ display wide range among different sources of organic matter, for instance, -18 to -23.5‰ for marine organic matter [Thornton and McManus, 1994; Middelburg and Nieuwenhuize, 1998; Bouillon et al., 2003], -28 to -26‰ for C_3 , -14 to -12.9‰ for C_4 plants derived organic matter [Thornton and McManus, 1994; Middelburg and Nieuwenhuize, 1998; Hobbes et al., 2000; Kao and Liu, 2000], -28 to -14‰ for sewage [Andrews et al., 1998] and -30 to -40‰ for freshwater algae and their detritus [Hamilton and Lewis, 1992; Middelburg and Nieuwenhuize, 1998; Barth et al., 1998; Chanton and Lewis, 1999; Hellings et al., 1999; Boschker et al., 2005; Bontes et al., 2006]. On the other hand, though nitrogen isotopes of organic matter ($\delta^{15}\text{N}_{\text{PN}}$) are also promising tracer to identify sources of estuarine organic matter [eg: Peters et al., 1978; Middelburg and Herman, 2007], the modification through food web dynamics and diagenesis hampers to some extent but it is an excellent tool to identify source of nutrients to the system [eg: Caraco et al., 1998; Mayer et al., 1998; De Brabandere et al., 2002]. Therefore, the combination of these two tracers is used here to evaluate the source of organic matter to the Indian estuaries.

The stable isotope composition of POC ($\delta^{13}\text{C}_{\text{POC}}$) and PN ($\delta^{15}\text{N}_{\text{PN}}$) displayed wide range (-31.4 to -23.5‰ and 0.7 to 10.3‰ respectively) in the Indian estuaries suggesting that variable source of organic matter is possible (Fig. 4; Table 1). The POC was significantly depleted in $\delta^{13}\text{C}_{\text{POC}}$ (-31.4 to -28.0‰) than even C_3 plant detritus of -28 to -26‰ [Thornton and McManus, 1994; Hobbes et al., 2000] but enriched than freshwater algae (-30 to -40‰) [Hamilton and Lewis, 1992; Middelburg and Nieuwenhuize, 1998] in the estuaries such as Krishna, Sharavati, Kali, Kochi back waters etc. which are mostly located south of 16°N (Fig. 1) indicating that mixture of these two pools might have contributed to POM. These estuaries received relatively less discharge and SPM (Table 1; Fig 2) from the upstream river resulting in increased depth of photic zone and stable water column favoured phytoplankton growth [Cloern et al., 1985; 2012; Sin et al., 2013; Acharyya et al., 2012]. This is consistent with phytoplankton biomass, which was higher in the estuaries that have lower $\delta^{13}\text{C}_{\text{POC}}$ ($4.3 \pm 1 \text{ mg m}^{-3}$) than other estuaries ($2.1 \pm 1 \text{ mg m}^{-3}$). Relatively low POC/Chl-a ratio (618 ± 128) was observed in the estuaries that have low $\delta^{13}\text{C}_{\text{POC}}$ than others (2675 ± 1846) indicating that higher contribution of *in situ* phytoplankton to POM in the former estuaries. Since spatial variations of phytoplankton biomass were

governed by concentrations of SPM, the variability in $\delta^{13}\text{C}_{\text{POC}}$ was also dependent on the amount of SPM in the water column. The SPM to $\delta^{13}\text{C}_{\text{POC}}$ relation suggests that the large variations in isotopic values were found at SPM $<200 \text{ mg l}^{-1}$ (-31.4 to -23.5‰) whereas nearly uniform ratios (-24.3 \pm 0.6‰) were noticed in estuaries containing high SPM ($>200 \text{ mg l}^{-1}$) (Fig. 5d). This could possibly be due to the existence of favourable conditions for diversified phytoplankton to grow at low SPM concentrations resulting in large variations in $\delta^{13}\text{C}_{\text{POC}}$. The strong inverse correlation between $\delta^{13}\text{C}_{\text{POC}}$ and Chl-a ($r^2=0.53$; $p<0.001$; Fig. 6a) suggests that phytoplankton biomass has significant impact on isotopic composition of POC. Strong inverse relation was also observed between $\delta^{13}\text{C}_{\text{POC}}$ and dissolved oxygen saturation ($r^2=0.57$; $p<0.001$; Fig. 6b) suggesting that biological processes have significant impact on the isotopic composition of POC as lower isotopic value resulted from high biological production and heterotrophic modification is responsible in the case of higher isotopic values.

Similar to the $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$ also displayed significant spatial variations in the Indian estuaries. Exceptionally higher $\delta^{15}\text{N}_{\text{PN}}$ values were noticed in Penna (13.5 \pm 2‰), Vellar (14.2 \pm 3‰) and Cauvery (16.7 \pm 0.5‰) estuaries, which are heavily polluted due to local industrial and domestic sewage [Rao and Sarma, 2013]. Unlike $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$ did not show any relation with SPM. The $\delta^{15}\text{N}_{\text{PN}}$ linearly related with Chl-a ($r^2=0.45$; $p<0.001$) and dissolved oxygen saturation ($r^2=0.54$; $p<0.001$) suggesting strong impact of biological processes (Fig. 6c,d). Higher $\delta^{15}\text{N}_{\text{PN}}$ values were associated with high biological production and vice versa suggesting that variable sources of nutrients are possible in the Indian estuaries. The range of $\delta^{15}\text{N}_{\text{PN}}$ values observed in the Indian estuaries is consistent with other estuaries in the world [Middelburg and Herman, 2007]. The MDS plot of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ displays three pools (Fig. 7) with 1) relatively higher $\delta^{13}\text{C}_{\text{POC}}$ (-27.9 to -22.6‰) and lower $\delta^{15}\text{N}_{\text{PN}}$ (0.7 to 5.8‰) from estuaries located in the northern India (north of 16°N), 2) lower $\delta^{13}\text{C}_{\text{POC}}$ (-31.4 to -28.2‰) and higher $\delta^{15}\text{N}_{\text{PN}}$ (5 to 10.3‰) from estuaries located in the southern India (south of 16°N) and 3) exceptionally higher $\delta^{15}\text{N}_{\text{PN}}$ (13.5 to 16.7‰) and moderate $\delta^{13}\text{C}_{\text{POC}}$ (-28.1 to -29‰) values from heavily polluted estuaries [Penna, Vellar and Cauvery; Rao and Sarma, 2013]. Such large spatial variations in $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ in the Indian estuaries most likely reflect the spatial variations in nitrogen loading, variable sources of organic matter and conditions favouring biological production in the estuaries.

The lower $\delta^{15}\text{N}_{\text{PN}}$ of PN values in estuaries located in the northern India could be attributed to possible sources of both terrestrial and artificial nutrients, such as fertilizers, as these sources are relatively lower [0.2 to 4 and $\sim 0\%$ respectively; *Thornton and McManus*, 1994]. Interestingly the spatial variations in $\delta^{15}\text{N}_{\text{PN}}$ were consistent with the variations in fertilizer consumption over the Indian subcontinent. The fertilizers, such as urea, di-ammonium phosphate and potash (nitrogen-phosphorus-potassium), consumption in the agricultural fields is almost double ($171.6 \text{ kg km}^{-2} \text{ y}^{-1}$) in the northern India than southern India ($88 \text{ kg km}^{-2} \text{ y}^{-1}$; Ministry of Agriculture, Government of India, http://eands.dacnet.nic.in/latest_2006.htm). Paddy and wheat, which are the major crops in India, are cultivated during summer monsoon period, when this region receives plentiful rainfall. Excess fertilizer applied in the field during this time is washed by the rainfall and ultimately makes its entry in different water bodies including estuaries. Fresh water discharge into the monsoonal estuaries also peaks during the same time period making them dually prone for cultural and natural eutrophication [*Cloern*, 1991; *Howarth et al.*, 2000; *Acharyya et al.*, 2012]. Since stable isotopic composition of fertilizer nitrogen is lower, as it is formed from the atmospheric nitrogen, and its incorporation into the biological processes leads to lower nitrogen isotopic value of SPM in the estuaries located in the northern India. Therefore the lower $\delta^{15}\text{N}_{\text{PN}}$ in the northern estuaries were the result of both terrestrial organic matter and artificial nitrogen inputs into these estuaries. *McClelland and Valiela* [1998] proposed that $\delta^{15}\text{N}_{\text{PN}}$ values of estuarine particles and organisms provide an integrated measure of N-loading. The discharge to $\delta^{15}\text{N}_{\text{PN}}$ relationship displays narrow variations in $\delta^{15}\text{N}_{\text{PN}}$ in the northern estuaries where a large variations in discharge (61 to $3505 \text{ m}^3 \text{ s}^{-1}$) was observed; in contrast, the $\delta^{15}\text{N}_{\text{PN}}$ displayed wide range of variability (5.0 to 16.7%) despite narrow range of river discharge (28 to $677 \text{ m}^3 \text{ s}^{-1}$) noticed in the southern estuaries (Fig. 8a). This suggests that irrespective of the rate of river discharge, significant fraction of terrestrial organic matter contributed to the northern compared to southern estuaries. On the other hand, despite wide variations in dissolved inorganic nitrogen (DIN) concentrations (4.9 to $23.9 \text{ }\mu\text{M}$), the variations in $\delta^{15}\text{N}_{\text{PN}}$ were quite narrow in the northern estuaries and vice versa in the southern estuaries (Fig. 8b). In addition to this, inverse relation was observed between DIN and $\delta^{15}\text{N}_{\text{PN}}$ ($r^2=0.52$; $p<0.001$) in the southern estuaries and no such relationship was observed in the northern estuaries suggesting that artificial nutrients might have supported *in situ* biological production in the northern estuaries and regenerated nutrients in the southern estuaries. Nevertheless, this could not be confirmed due to lack of data on $\delta^{15}\text{N}$ of DIN. However, the lower $\delta^{15}\text{N}_{\text{PN}}$ values were associated with higher $\delta^{13}\text{C}_{\text{POC}}$ (-27.9 to -22.6%) suggesting that

higher contribution of terrestrial sources to the northern estuaries as these values are within the range between C₃ and C₄ plants [-28 to -26‰ for C₃ and -14 to -12.9‰ for C₄ plants derived organic matter; *Thornton and McManus, 1994; Middelburg and Nieuwenhuize, 1998*]. In contrast, lower $\delta^{13}\text{C}_{\text{POC}}$ and higher $\delta^{15}\text{N}_{\text{PN}}$ values were noticed in the southern estuaries which could be due to a more dominant *in situ* production than in northern estuaries. The phytoplankton biomass in the southern estuaries was significantly higher ($4.3 \pm 1 \text{ mg m}^{-3}$) than in the northern estuaries ($2.1 \pm 1 \text{ mg m}^{-3}$) due to low SPM in the former group of estuaries ($33.5 \pm 18 \text{ mg l}^{-1}$) than latter ($255 \pm 90 \text{ mg l}^{-1}$) suggesting clear water promoted phytoplankton growth in them. The higher Chl-a and $\delta^{15}\text{N}_{\text{PN}}$ were found in the southern estuaries that received less DIN inputs from the upstream river due to low discharge rates. Such higher $\delta^{15}\text{N}_{\text{PN}}$ values in the southern Indian estuaries could possibly be caused by 1) utilization of isotopically enriched nitrogen, especially residual ammonium resulting from nitrification [*Mariotti et al., 1984*] and/or 2) extensive algal uptake of nitrogen leading to enrichment of leftover nitrogen, resulting in higher $\delta^{15}\text{N}_{\text{PN}}$ in the phytoplankton [*Cifuentes et al., 1988*]. However, it is also dependent on the isotopic composition of $\delta^{15}\text{N}$ of dissolved inorganic nitrogen utilized. *Owens* [1985] noticed higher $\delta^{15}\text{N}_{\text{PN}}$ values of 14.7‰ in the turbidity maximum zone and it was attributed to intense biological processing of organic matter. Seasonal PN enrichment in $\delta^{15}\text{N}_{\text{PN}}$ was also observed with a maximum of 24‰ in Schelde and 18‰ in Delaware estuaries during spring and was attributed to high nitrification and/or extensive algal uptake. The ammonium concentrations in the Indian estuaries were relatively higher in the estuaries located in the northern India ($0.6\text{-}15.3 \text{ }\mu\text{M}$; $4.8 \pm 3 \text{ }\mu\text{M}$) than in the southern India ($0.5 \text{ to } 2.6$; $1.2 \pm 0.5 \text{ }\mu\text{M}$) suggesting that higher rates of nitrification may be possible in the latter region. Though nitrification rates were not measured in this study, the occurrence of nitrification was reported during dry period in the Indian estuaries [$0.02\text{-}0.87 \text{ }\mu\text{mol N l}^{-1} \text{ d}^{-1}$; *Miranda et al., 2008; Rao and Sarma, 2013*]. Due to preferential uptake of ^{14}N during nitrification [*Mariotti et al., 1984; de Brabandere et al., 2002*], the leftover ammonium enriches with respect to ^{15}N . Incorporation of such isotopically enriched $\delta^{15}\text{N}$ in ammonium by algae [*Mariotti et al., 1984; Cifuentes et al., 1988; 1989*], and heterotrophic bacteria [*Caraco et al., 1998; Middelburg and Nieuwenhuize, 2000a,b*] lead to higher $\delta^{15}\text{N}_{\text{PN}}$ values. It was observed that nitrification is a major process in estuaries that contribute to significant decrease in DO in the estuaries [*Vanderborgh et al., 2002; Hofmann et al., 2008*]. In contrast, dissolved oxygen saturation displayed linear relationship with $\delta^{15}\text{N}_{\text{PN}}$ in the Indian estuaries ($r^2=0.54$; $p<0.001$) suggesting that nitrification may not be significant process responsible for higher $\delta^{15}\text{N}_{\text{PN}}$.

Heterotrophic bacterial processes extensively modify particles during transit through the estuary, however, this would not alter the $\delta^{13}\text{C}_{\text{POC}}$ signature of particles significantly, homogenizes the C:N ratios and modifies $\delta^{15}\text{N}_{\text{PN}}$ values. The variations in isotopic composition $\delta^{15}\text{N}_{\text{PN}}$ depend on the balance between regeneration and consumption. If the latter is more than former, the isotopic composition $\delta^{15}\text{N}_{\text{PN}}$ increases and vice versa. Nitrate can be an important nitrogen substrate for heterotrophic bacteria [Middelburg and Nieuwenhuize, 2000] and partial assimilation of nitrate increases isotopic composition of left over pool [Caraco *et al.*, 1998]. The significant inverse correlation between DIN and $\delta^{15}\text{N}_{\text{PN}}$ ($r^2=0.52$; $p<0.001$) in the southern estuaries suggests that partial assimilation of nitrate may be responsible for enrichment of $\delta^{15}\text{N}_{\text{PN}}$. Though it is unclear as to whether it is nitrification of ammonium or uptake of nitrate by heterotrophs that increases $\delta^{15}\text{N}_{\text{PN}}$ in the Indian estuaries and detailed studies on nitrogen uptake by algae and bacteria is necessary. Both isotopic composition of $\delta^{15}\text{N}_{\text{PN}}$ and $\delta^{13}\text{C}_{\text{POC}}$ suggest that a significant fraction of the organic matter is contributed by fresh water algae in the southern estuaries whereas, artificial and terrestrial nutrients supported phytoplankton biomass in the in the northern estuaries and organic matter was significantly modified through microbial processes to support dominant heterotrophic activities in the Indian estuaries.

Such significant variations in $\delta^{13}\text{C}_{\text{POC}}$ values between northern and southern estuaries could be due to variations in vegetation in the drainage basin of rivers and their contribution to total POM in the estuary. The plants can follow different photosynthetic mechanism to fix the carbon, such as phosphoenolpyruvate (PEP) carboxylation mechanism by C_4 plants and RuBisCo carboxylation mechanism in C_3 plants. As a result the isotopic ratios of the organic matter from these sources are significantly different. Figure 1 describes the spatial distribution of vegetation over Indian subcontinent and suggests that the drainage basin of the rivers located in the west coast of India (Kochi back waters to Tapi) are dominated by C_3 plants (Rice, Forest and Scrub), and watershed regions of rivers Sabarmati and Mahisagar are dominated by C_4 plants (Bajra, Jute and Wheat). On the other hand, most of the rivers opened to the east coast of India (Godavari, Krishna, Mahanadi) flow from west to eastern India and covers wide variety of vegetation of both C_3 and C_4 plants mainly Rice, Cotton, Sugarcane, Ragi, Bajra and Jowar. Therefore these rivers may carry organic matter derived from both these sources. On the other hand, rivers flowing in the northeastern India (Subernalekha, Baitarani) received organic matter from C_3 plants. Nevertheless, spatial distribution of vegetation map suggests that the rivers flowing east

receive organic matter from both C₃ and C₄ plants and mainly from C₃ plants for rivers opened in the western India whereas rivers opened to the northwestern region dominated by C₄ plant. *Goni et al.* [1997] found heavy isotopic values (-21.7 and -19.7‰) in the surface sediment from the shelf and slope regions of the Gulf of Mexico and attributed to significant contribution from erosion from extensive C₄ grassland soils [-17 to -9‰; *Smith and Epstein*, 1971; *Gearing*, 1988; *Sackett*, 1989]. However, the spatial variations in vegetation did not reflect in the isotopic composition of $\delta^{13}\text{C}_{\text{POC}}$ suggesting that mixture of various sources such as *in situ* phytoplankton derived, C₃, C₄ plants detritus and soil organic matter may be possible.

4.3.3. Quantification of sources organic matter to Indian Estuaries

The relative contribution of organic matter from different sources, such as terrestrial derived organic matter from soil organic matter, C₃, C₄ type plants, and *in situ* produced freshwater algae, in the Indian estuaries was derived using SIAR model. Significant spatial variations in contribution of different sources were noticed in the Indian estuaries with higher contribution from C₃ plants (35-90%) in the estuaries fallen in the group 1 which are mainly located in the northern India whereas fresh water algae contributed significantly (85 to 90%) in the estuaries fallen in group 2 from the southern India (Fig. 9). Since substantial amount of sewage is received in the estuaries fallen in group 3, with exceptionally higher $\delta^{15}\text{N}_{\text{PN}}$ values than all possible sources (end members), the contribution of different sources of organic matter to the estuaries could not be derived. These estimations may have additional errors as we have not measured freshwater algae in all Indian estuaries and assumed that $\delta^{15}\text{N}$ of DIN is uniform in all Indian estuaries due to lack of data. Therefore, the errors on the estimated fractions from various sources may be more than represented. More precise estimation are required to be made in the future measuring endmember characteristics from all Indian estuaries. Nevertheless, this study suggests that estuaries located in the southern estuaries received relatively less discharge and also SPM that promoted *in situ* phytoplankton to grow that contributed significantly to the POM pool. On the other hand, high SPM prevented *in situ* phytoplankton to grow and POM was mainly contributed by terrestrial sources in the estuaries located in the northern India. Such spatial variations were caused by precipitation pattern, fertilizer utilization and vegetation pattern over Indian subcontinent.

Summary and Conclusions

The content and isotopic composition of carbon and nitrogen were studied in 27 Indian monsoonal estuaries during monsoon (discharge) period to examine distribution and sources of organic matter. Discharge displayed significant spatial variability in the Indian estuaries and it is associated with precipitation pattern over Indian subcontinent. The estuaries located in the southern India received relatively lower discharge and SPM that created conducive environment for phytoplankton growth and vice versa was observed in the estuaries located in the northern India. The strong relation of organic carbon (OC) and nitrogen (PN) with Chl-a suggested that discharge driven phytoplankton blooms contributed significantly to OC in the Indian estuaries during the study period. The variability in isotopic composition of $\delta^{13}\text{C}_{\text{POC}}$ depends on the amount of SPM as large variations were found at $\text{SPM} < 50 \text{ mg l}^{-1}$ (-31 to 24‰) whereas nearly uniform ratios ($-24.6 \pm 0.8\text{‰}$) were observed at high SPM ($> 200 \text{ mg l}^{-1}$) due to the existence of conducive conditions for growth of diversified phytoplankton at low SPM. Relatively lower $\delta^{15}\text{N}_{\text{PN}}$ found in the estuaries located in the northern India than south indicating larger contribution of terrestrial and artificial nitrogen inputs in the former region. This pattern is also consistent with the spatial distribution in fertilizer usage in India, which is double in the northern than southern India. Both $\delta^{15}\text{N}_{\text{PN}}$ and C:N ratios suggest that significant fraction of the organic matter was modified through microbial activities to support dominant heterotrophic activities in the Indian estuaries. The relative contribution of organic matter from various sources, such soil organic matter, freshwater algae, C_3 and C_4 plants detritus, was estimated using signatures of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ that suggested that 40-80% was contributed by C_3 and 70-90% by freshwater algae in the northern and southern estuaries respectively. Our study proved the hypothesis that influence of monsoonal precipitation is not uniform; however, the relative composition of organic matter from different sources was controlled by precipitation pattern over Indian subcontinent, thus, magnitude of discharge, and suspended matter concentration in the Indian estuaries.

Acknowledgements

We would like to thank Director, NIO and Scientist-in-charge, regional centre for their encouragement and support. We would like to acknowledge Council of Scientific and Industrial Research for financial support. We would like to thank two anonymous reviewers for their valuable suggestions for

improvement of early version of manuscript. We acknowledge Drs. P. Parameswaran, and R. Rengarajan for their local support during samples at SW and NW Indian estuaries. This is NIO contribution number.....

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Legends to figure

Figure 1: Map showing estuaries sampled in this study. Map also shows major agricultural crops on the Indian subcontinent (Source: <http://www.mapsofindia.com/indiaagriculture/>).

Figure 2: Variations in a) salinity, b) Chl-a (mg m^{-3}), c) O_2 saturation (%), and d) SPM (mg l^{-1}) in the Indian estuaries. The light and dark shaded estuaries drain to Bay of Bengal and Arabian Sea respectively.

Figure 3: Variations in particulate organic carbon, nitrogen and their ratios (C:N) in the Indian estuaries. The light and dark shaded estuaries drain to Bay of Bengal and Arabian Sea respectively.

Figure 4: Variations in isotopic composition of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ of particulate organic matter in the Indian estuaries. The light and dark shaded estuaries drain to Bay of Bengal and Arabian Sea respectively.

Figure 5: The relationship of a) Chl-a with SPM, b) Chl-a with percent of POC contribution to SPM (OC), c) Chl-a with percent of PN contribution to SPM (ON) and d) SPM with $\delta^{13}\text{C}_{\text{POC}}$ in the Indian estuaries. The letters in the b) and c) represents names of the rivers (A-Ambalyaar, B-Bharathakulza, C-Chattuva, K-Kali, M- Mahanadi, N-Mandovi, R-Rushikulya, and S-Subarnarekha)

Figure 6: Relationship of $\delta^{13}\text{C}_{\text{POC}}$ with a) Chl-a, b) dissolved oxygen saturation and $\delta^{15}\text{N}_{\text{PN}}$ with c) Chl-a and d) dissolved oxygen saturation. V-represents data from Vaigai estuary.

Figure 7: MDS plot of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ in the Indian estuaries. The short-cut names of the estuaries are given in Table 1.

Figure 8: Relationship of $\delta^{15}\text{N}_{\text{PN}}$ with a) discharge and b) dissolved inorganic nitrogen (DIN). The estuaries located in southern and northern India are given in open and closed circles respectively.

Figure 9: The contribution of soil organic matter, C3, C4 Plants and freshwater algae (FP) in the estuaries fallen as a) group 1, and b) group 2, as shown in the Figure 7.

Legends to Table

Table 1: Area, annual mean discharge, tidal amplitude, salinity, $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ in the Indian estuaries are given during discharge period.

Table 2: Rank correlation matrix (Spearman's rs) of many physical and chemical parameters measured in the Indian estuaries

Table 1:

Estuary	Area (km ²)	Annual mean discharge (m ³ s ⁻¹)	Tidal [§] amplitude (m)	Salinity	$\delta^{13}\text{C}_{\text{POC}}$	$\delta^{15}\text{N}_{\text{PN}}$
					‰	‰
Rivers reaching to Bay of Bengal						
Haldia (HLD)	18.15	1600	7.01	0.71±0.12	-25.0±0.8	2.5±3.5
Subarnarekha (SUB)	23.15	392 [#]	*	3.97±0.83	-24.1±1.3	4.2±0.4
Baitarani (BAI)	22.69	903 [#]	*	0.09±0.02	-27.9±0.3	1.9±1.4
Rushikulya (RUS)	12.57	61	*	20.7±5.82	-24.4±0.9	0.7±1.7
Mahanadi (MAH)	13.56	2121 [#]	2.82	0.07±0.01	-26.8±1.6	3.5±1.8
Vamsadhara (VAM)	15.05	111	*	13.26±3.31	-26.8±0.7	3.7±1.4
Nagavali (NAG)	13.94	63	2.17	28.78±5.56	-25.5±1.4	1.8±0.6
Godavari (GOD)	241.1	3505	2.1	0.16±0.08	-24.0±1.5	5.0±3.6
Krishna (KRI)	36.49	577	1.98	5.27±0.82	-29.7±0.8	9.7±2.2
Penna (PEN)	27.97	200	*	9.27±2.61	-28.1±3.4	13.5±6.3
Vellar (VEL)	20.63	29	1.51	11.57±2.65	-29.1±1.7	14.2±3.6
Ponnayaar (PON)	9.89	51	*	0.29±0.12	-30.4±0.5	9.1±0.6
Cauvery (CAU)	20.63	677	*	12.04±3.88	-29.0±0.9	16.7±7.2
Ambalayaar (AMB)	4.57	28	*	4.23±0.66	-24.0±1.7	5.8±1.5
Vaigai (VAI)	0.22	36	*	27.89±4.33	-23.5±0.5	3.9±0.5
Rivers reaching to Arabian Sea						
Kochi back waters (KBC)	231.1	391	1.34	3.50±1.11	-29.9±0.5	8.4±2.8
Chalakuudi (CHA)	9.69	61	*	0.05±0.06	-28.8±1.4	6.5±0.2
Bharatapuzha (BHA)	19.12	161	*	0.18±0.15	-28.4±0.2	5.8±0.3
Netravathi (NET)	18.54	351	*	0.06±0.08	-29.9±1.8	5.0±0.2
Sharavathi (SHA)	16.44	144	*	0.14±0.11	-30.8±1.0	10.2±1.6
Kali (KAL)	17.59	152	*	5.86±1.35	-31.4±0.7	9.1±2.4
Zuari (ZUA)	14.62	103	2.7	7.32±1.11	-29.4±1.5	9.7±1.3
Mandoviv(MAN)	27.68	105	2.7	0.42±0.32	-28.2±1.5	10.3±0.9
Narmada(NAR)	115.5	1447 [#]	10.9	0.14±0.11	-22.6±1.7	4.2±0.3
Tapti(TAP)	41.04	472 [#]	*	0.16±0.10	-23.6±0.2	1.6±0.6
Sabarmathi (SAB)	66.29	120 [#]	*	0.04±0.05	-24.1±0.8	3.0±0.5
Mahisagarv(MAH)	14.28	349	7.63	0.11±0.13	-25.1±1.0	4.9±0.4

*Data not available

represents data taken from *Kumar et al.*, 2005 and others taken from Dam authorities of respective river.

[§] Dr. S.R. Shetye Personal communication.

Table 2:

	SPM	DO	Chl-a	DIN	POC	PN	OC	ON	$\delta^{13}\text{C}_{\text{POC}}$	$\delta^{15}\text{N}_{\text{PN}}$
Discharge	0.85***	0.15	--	0.53***	0.37***	0.31***	-0.23**	-0.25**	0.12	0.04
SPM		0.04	0.36**	0.46***	0.65***	0.60***	-0.62***	-0.65***	0.33**	0.05
DOsat			0.23**	0.60***	0.32**	0.29**	--	--	0.57***	0.54***
Chl-a				0.24**	-0.38***	-0.32***	0.60***	0.53***	0.53***	0.45***
DIN					0.32***	0.12	0.10	0.11	--	0.52***
POC						0.82***	-0.28**	-0.24**	0.42***	-0.22
PN							-0.12	--	0.52***	-0.32***
OC								0.90***	--	--
ON									--	--
$\delta^{13}\text{C}_{\text{POC}}$										0.45***

*** p<0.001

** p<0.01

Figure 1:

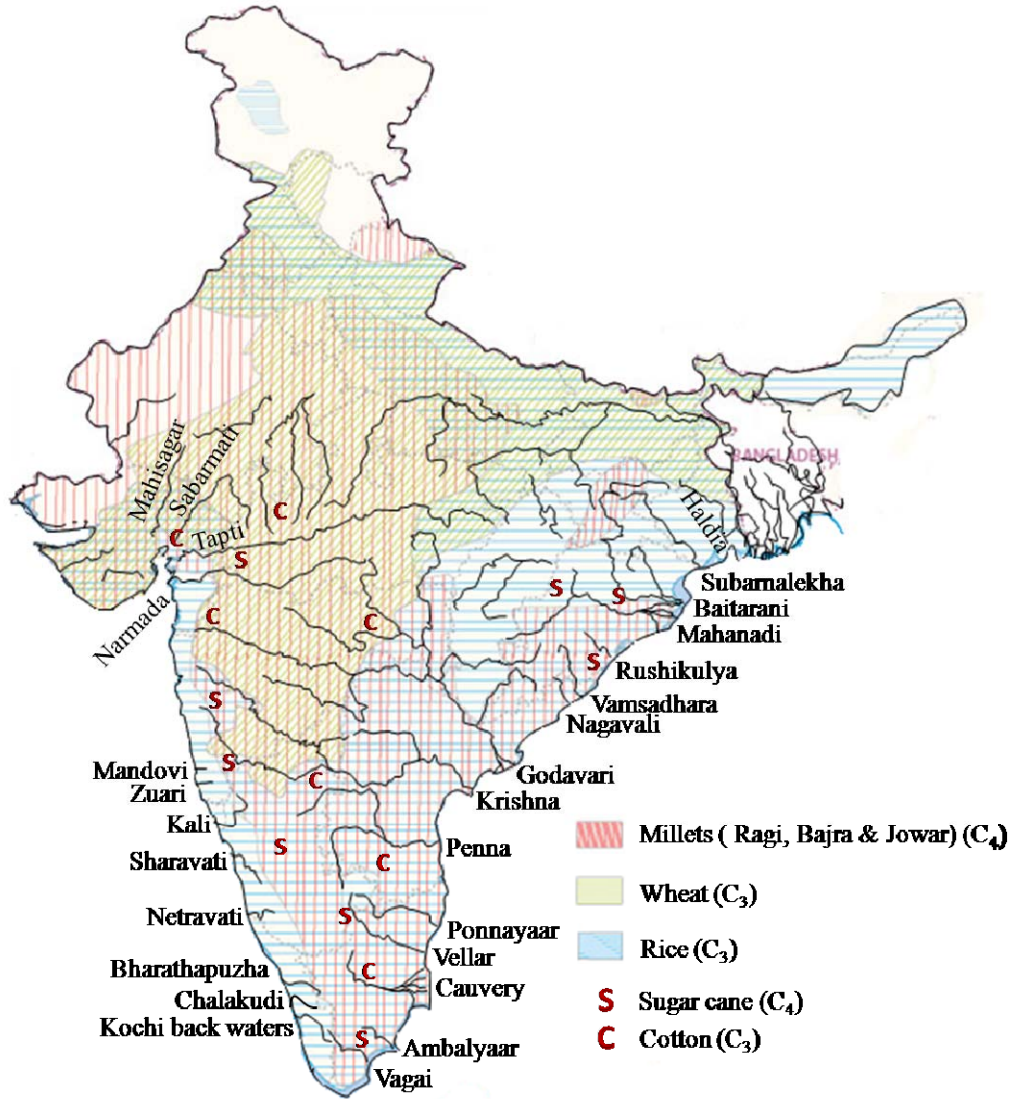


Figure 2

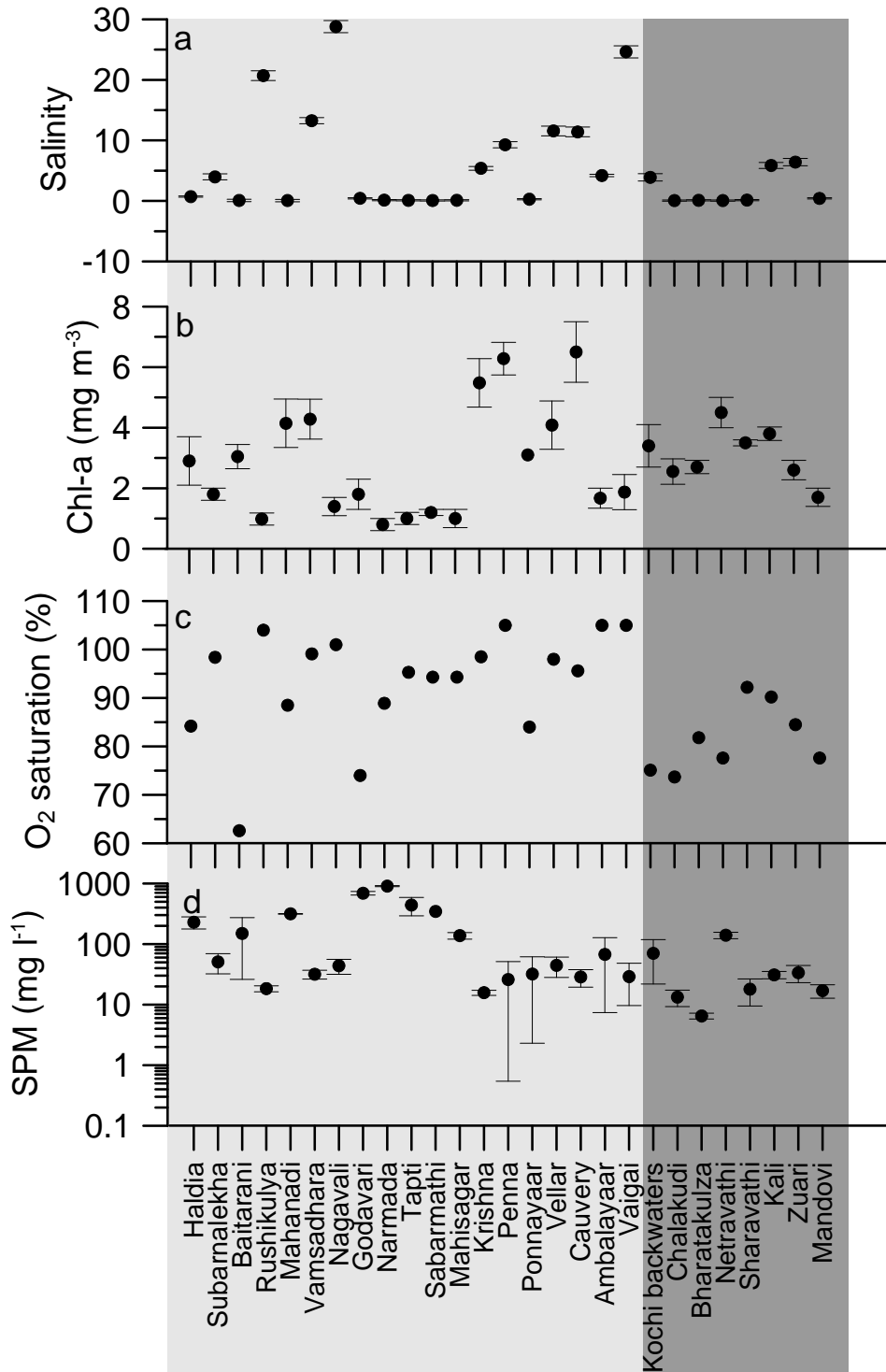


Figure 3:

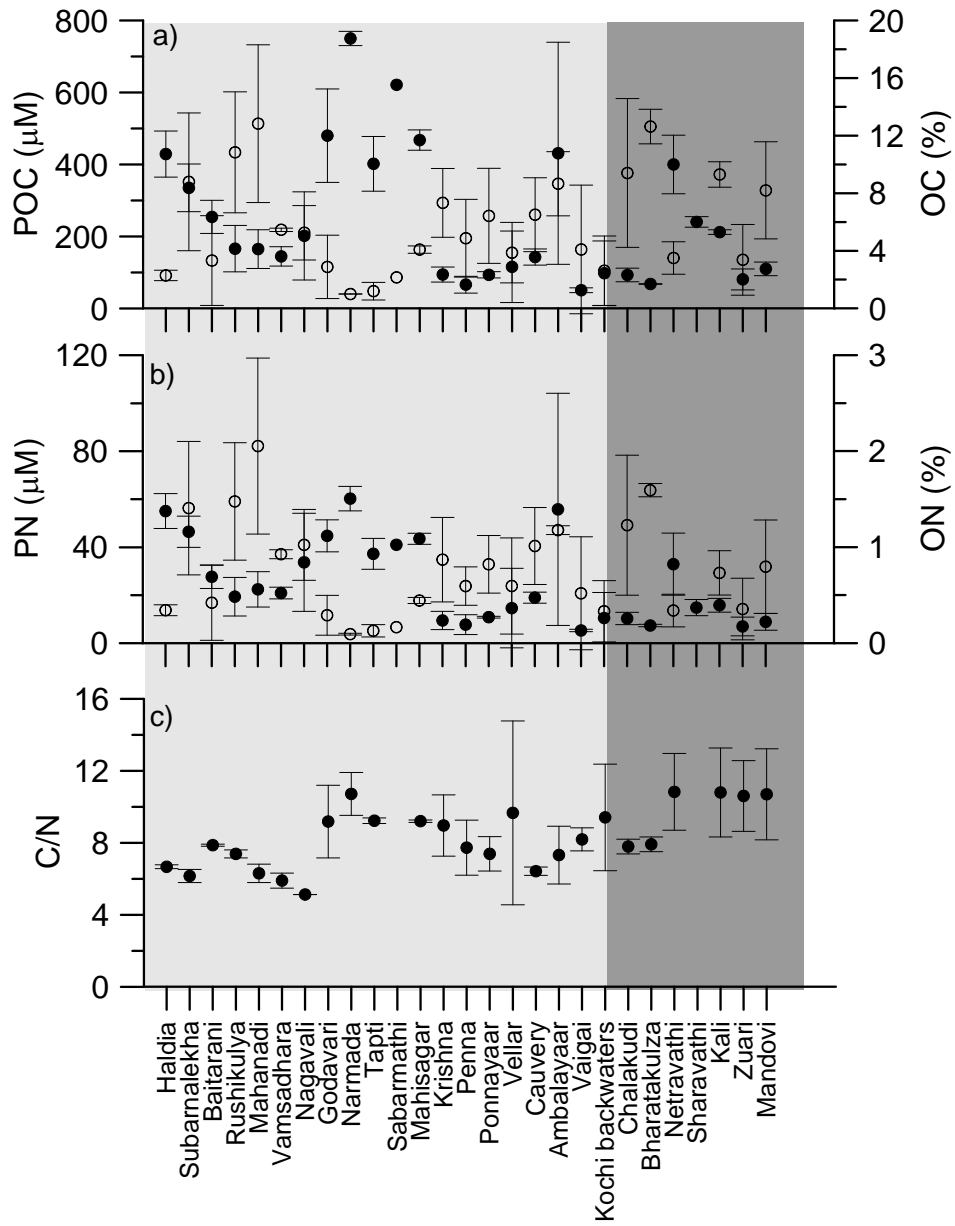


Figure 4:

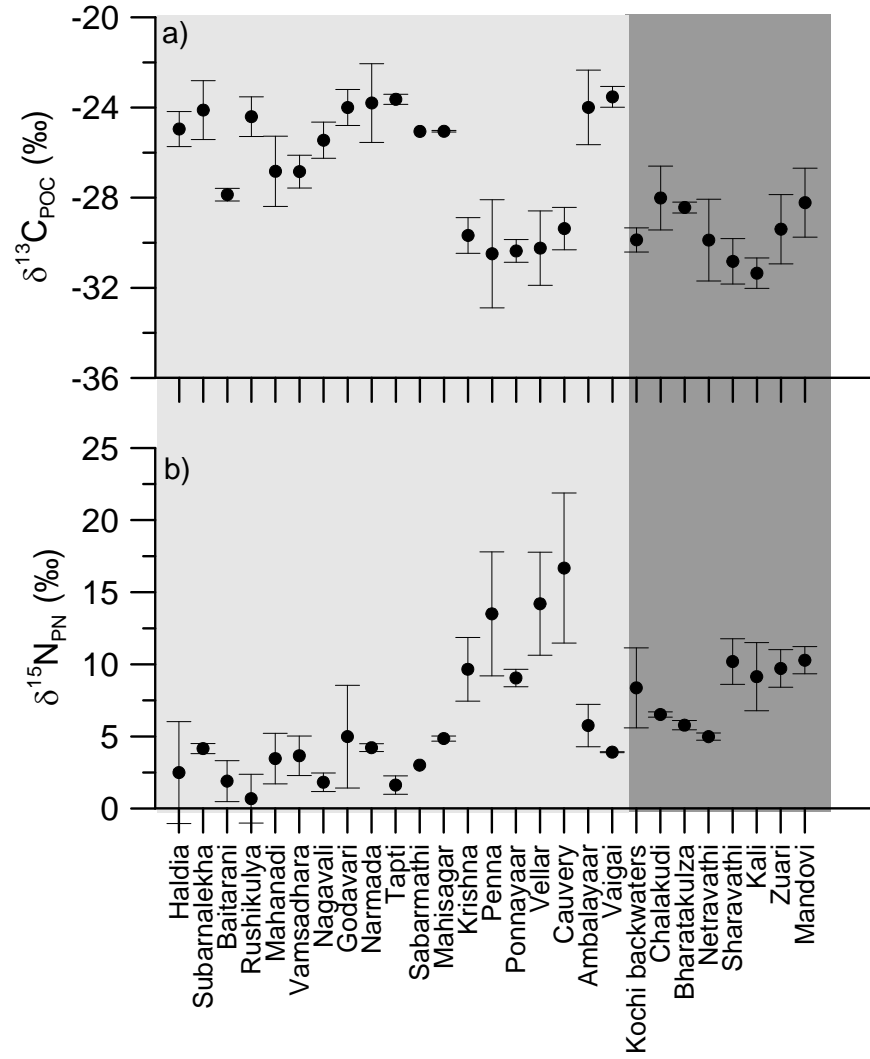


Figure 5:

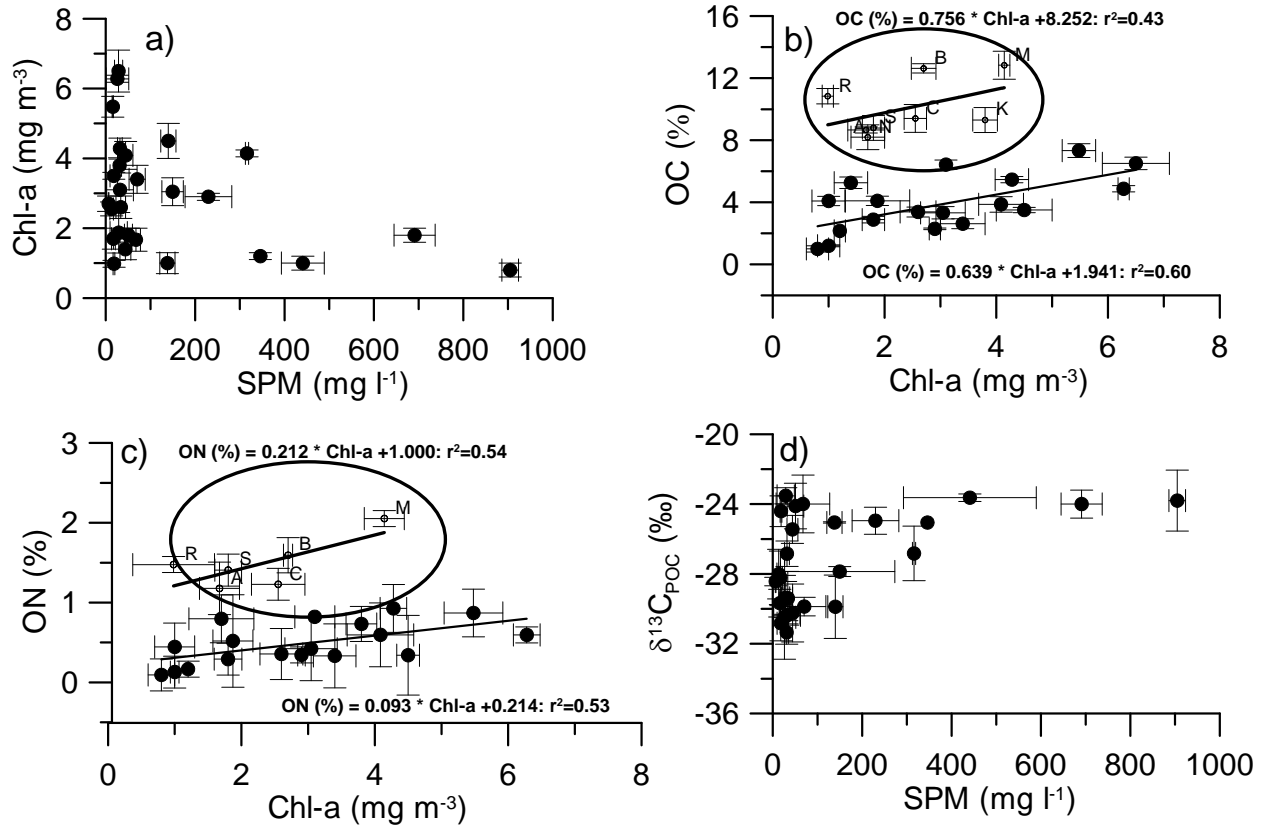


Figure 6:

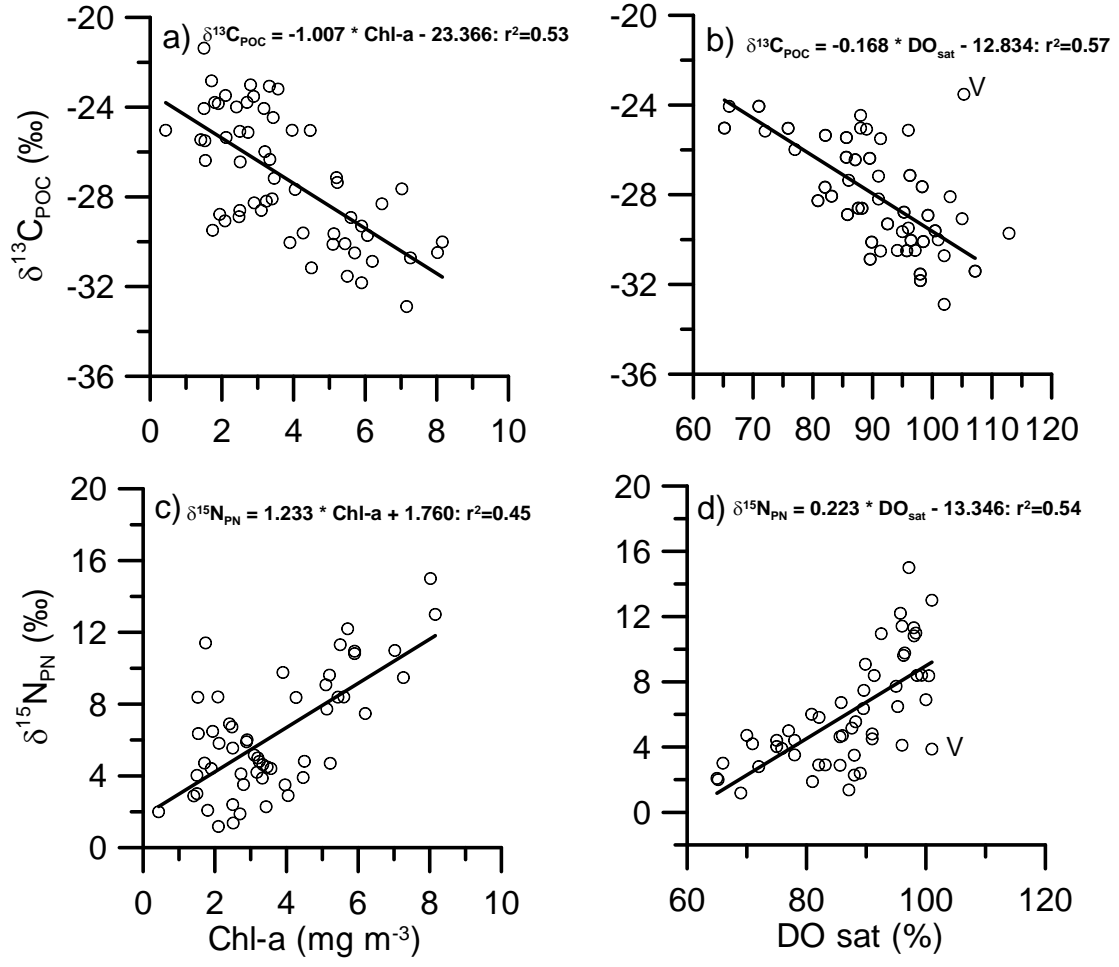


Figure 7:

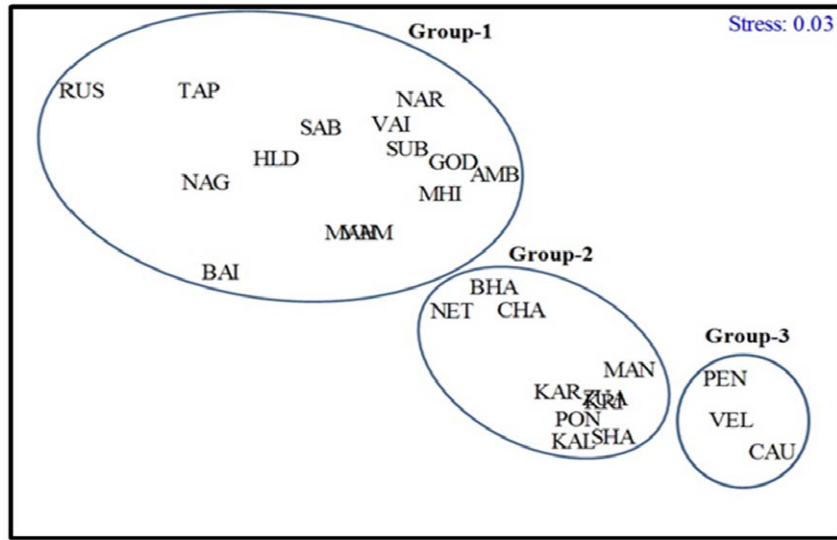


Figure 8:

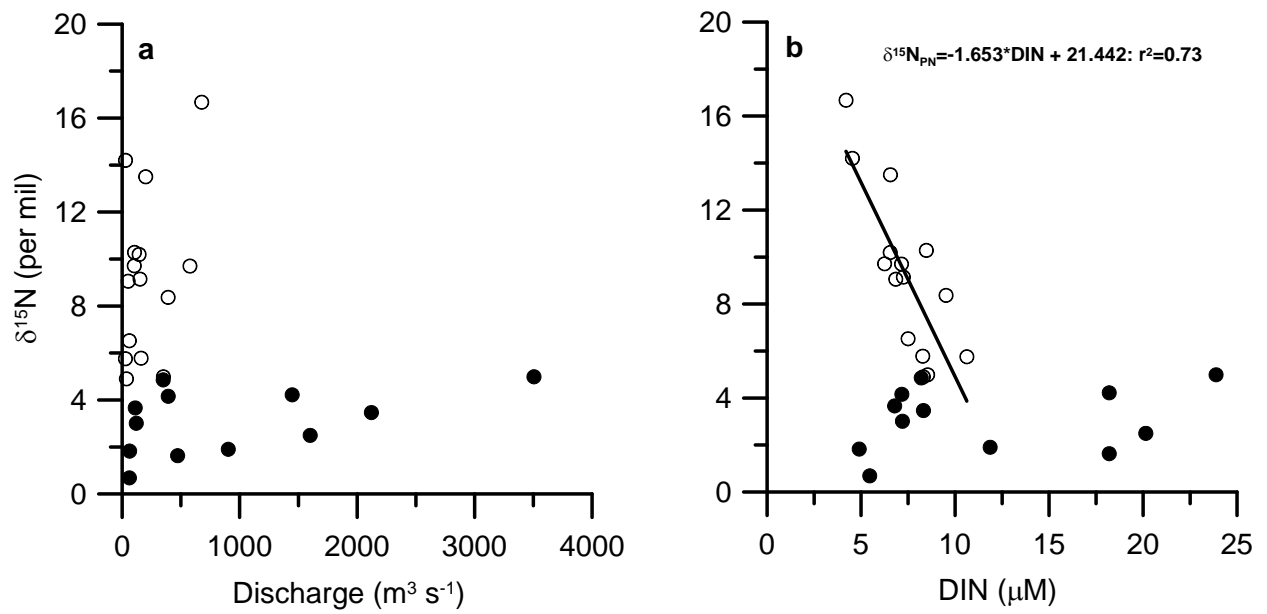


Figure 9

