

Stable isotopes of carbon and nitrogen in suspended matter and sediments from the Godavari estuary

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Abstract

Spatial distribution of carbon and nitrogen content and their isotopic enrichments in suspended matter and sediments were measured in the Godavari estuary to identify sources and transformation mechanism of organic matter. Significant variability in isotopic distribution was found over the entire length of the Godavari estuary suggesting multiple sources of organic matter. The mean isotopic ratios ($\delta^{13}\text{C}_{\text{sed}}$: -25.1 ± 0.9 ; $\delta^{13}\text{C}_{\text{sus}}$: -24.9 ± 1 ; $\delta^{15}\text{N}_{\text{sed}}$: 8.0 ± 2 and $\delta^{15}\text{N}_{\text{sus}}$: 6.5 ± 0.9 ‰) and elemental concentrations (C_{sed} : $0.45\% \pm 0.2\%$; C_{sus} : $0.9 \pm 0.7\%$; N_{sed} : $0.07 \pm 0.05\%$ and N_{sus} : $0.16 \pm 0.1\%$) support a predominantly terrigenous source. Significant enrichment in isotopic ratios of $\delta^{13}\text{C}$ from upper to lower estuary in both suspended (-27.5 and -24.3 ‰ respectively) and sedimentary (-26.2 and -24.9 ‰ respectively) phases indicates decrease in influence of terrigenous material towards mouth of the estuary. A significant positive relationship exists between $\delta^{13}\text{C}$ of suspended and sediment which indicates that these two organic carbon pools are likely coupled in the form of a significant exchange between the two phases. A positive relationship exists between Chlorophyll *a* and suspended organic matter which may mean that a significant source to organic carbon is the *in situ* produced phytoplankton. But, applying a simple mixing model to our isotopes data yielded about 46% as the contribution of the terrestrial source to suspended matter that may support excessive heterotrophic activity in the Godavari estuary reported earlier.

Introduction

Rivers play an important role in both the long term geologic and shorter term surface carbon cycles and transport about 0.4 Gt ($Gt=10^{15}$ g) of organic carbon from the continents to the ocean, of which ~ 0.2 Gt is in the form of particulate organic carbon (POC) (Hedges and Keil, 1995; Ludwig et al., 1996; Hedges et al., 1997). About 90% of organic carbon brought by rivers is buried within the river-dominated continental margins (Bernier, 1982, 1989; Bernier and Raiswell, 1983; Hedges and Keil, 1995). POC in the estuary is derived from both allochthonous (eg. Soil organic matter, higher plant debris) and autochthonous sources (eg. phytoplankton, benthic algae) (Onstad et al., 2000; Kendall et al., 2001; Wetzel, 2001) whereas riverine organic matter (OM) is mainly contributed by allochthonous terrestrial origin, including modern and ancient OM (eg. Longworth et al., 2007; Wu et al., 2007). Extensive modification of organic matter occurs in the tidal estuaries due to long residence time of both water and particles (Heip et al., 1995; Frankignoulle et al., 1998; Middelburg and Herman, 2007). However, it is difficult to delineate the pathways of particulate organic matter (POM) in the estuaries due to intensive physical mixing and biological processes. Stable carbon isotope ($\delta^{13}C$) has been used frequently to characterize riverine POM for the temporal and spatial variations in its biological origin and biogeochemical processes (Owens, 1985; Hamilton and Lewis, 1992; Bird et al., 1998; Hellings et al., 1999; Dehairs et al., 2000; Kendall et al., 2001; Bouillon et al., 2002; Bellanger et al., 2004; Middelburg and Herman, 2007; Chen and Jia, 2009). Besides, stable nitrogen isotopes ($\delta^{15}N$) have also been found to be a potentially useful tracer for aquatic biogeochemical studies (Kendall et al., 2001; Delong and Thorp, 2006). Hence dual isotopes (both $\delta^{13}C$ and $\delta^{15}N$) along with the content of carbon and nitrogen will be helpful in identifying sources of organic matter to the estuary (Middelburg and Herman, 2007). However, systematic investigations using combined $\delta^{13}C$ and $\delta^{15}N$ techniques on spatial and seasonal variations of POM are still rare.

Stable carbon and nitrogen isotopes and C/N elemental ratios have been used elsewhere to evaluate the sources and fate of organic matter in estuarine and marine sediments (eg. Thornton and McManus, 1994; Lee, 1994; Bird and Grocke, 1997; Andrews et al., 1998; Middelburg and Herman, 2007). Other studies have demonstrated that the assumption that estuarine organic material is simply a mixture of natural inputs may be incorrect in many instances (Lucotte, 1989; Matson and Brinson, 1989; Andrews et al., 1998). Middelburg and Herman (2007) observed that tidal estuaries are characterized by high suspended particulate matter (SPM) and uniform organic carbon (OC) content even as $\delta^{13}C$ values ranged between -24 and -26 ‰. Organic matter (OM) in the tidal estuaries has been inferred as extensively modified by heterotrophic activities from the increase in $\delta^{15}N$ values up to 20 ‰. Gupta et al. (1997) observed that Godavari river transports 2.8×10^6 tons of POC and 0.29×10^6 tons of particulate nitrogen (PN) to the Bay of Bengal. Dehairs et al. (2000) and Bouillon et al. (2002) studied carbon and nitrogen stable isotopic ratios in the benthic invertebrates and suspended matter in the mangrove ecosystem of the Gautami-Godavari delta. Dehairs et al. (2000) found that $\delta^{13}C$ of

suspended matter in the mangrove channels is relatively depleted (-24.5 ‰), which is heavier than mangrove leaf litter (-28 ‰) and lighter than the (Kakinada) Bay (-22.7 ‰). Bouillon et al. (2002) noticed that phytoplankton is the main source of organic matter to the suspended matter and sediment organic matter is rather small in the mangrove ecosystem. They further observed marked selectivity of benthic invertebrate community for pelagic and benthic microalgal food sources and indicate that mangrove-derived and other terrestrial carbon is not a significant food source for benthic invertebrates community in the ecosystem. The $\delta^{13}\text{C}$ values indicate terrestrial organic matter is not a major contributor to the sediment organic matter pool in the ecosystem. Similarly Bouillon et al (2000) found that zooplankton showed a much wider range of $\delta^{13}\text{C}$ (-30.1 to -16.4‰) than in the suspended matter (-30.9 to -19.2‰) with more spatial differences in former than latter. This indicate that zooplankton feed on a component of suspended matter pool, which has more pronounced seasonal variation than total suspended matter in the mangrove estuary of Godavari estuary. All these studies were carried out in the mangrove region close to the Godavari estuary. On the other hand, recently Sarma et al. (2009) observed that in situ primary production is much less than the heterotrophic respiration in the middle and upper estuary and 40-80% of the heterotrophic carbon demand is met by the terrestrial organic matter. The purpose of this study is to investigate the sources and fate of organic matter in the Godavari estuary using coupled isotopic and elemental ratios of carbon and nitrogen ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) in the suspended matter and sediment.

Study area

Godavari river is located between 16-18° N and originates at an altitude of about 1600 m near Nasik city in the Western Ghats. It flows eastwards across the peninsular India for about 1480 km and drains into the Bay of Bengal at Bhairawapalem on the central east coast of India ([Fig. 1](#)). Godavari river ranks 34th and 32nd in terms of catchment area and water discharge respectively, amongst the 60 largest rivers of the world (Ludwig et al., 1996; Gaillardet et al., 1999). Godavari is the largest monsoonal river in India and created an extensive delta on the east coast of India. The basin climate is generally dry with an average rainfall of 1512 mm y⁻¹. The catchment receives about 82% of annual rainfall during summer and the remaining in winter monsoon (CPCB, 1995). The discharge in to the Godavari estuary is high during June to December with a peak in August and almost dries up in the upstream between January and May. The Godavari catchment is spread out in an area of 3.1 x 10⁵ km², with an annual discharge of 105 km³ and 25 tributaries that join the river in the entire stretch (Rao, 1975). Balakrishna and Probst (2005) suggested that large-scale erosion and deforestation in the catchment led to higher organic carbon in the Godavari compared to other major world rivers. Sarin et al. (2002) found that dissolved inorganic carbon dominates carbon transport (75%), with the remaining distributed between POC(21%) and DOC (4%). They further found that DOC fluxes exceed that of POC in the upper river basin, and in contrast, POC export to the lower river is lessened by 35%, attributed to entrainment of sediments in river channels and dam sites. The fluvial system downstream of Rajahmundry is regulated

by a century old “Low Dam” at Dowalaiswaram (Fig. 1). After the dam, the river bifurcates into two major distributaries. The eastward flowing major tributary is Gautami-Godavari, while the other flowing southwards is Vasistha-Godavari. The latter distributary is relatively smaller compared to the former, and hence the sampling was conducted in the Gautami-Godavari.

Material and methods

Sampling of surface water, suspended matter and sediment samples were collected at 11 stations in the Godavari estuary during the dry period (6-8th June 2010) by mechanized boat. Temperature and salinity of the water was measured using Conductivity, Temperature and Depth (CTD) sensors (*19 plus*, Sea Bird Electronics, USA). About 500 ml of sample was filtered through GF/F filter at gentle vacuum and Chl-a on the filter was extracted to dimethyl formamide (DMF) and fluorescence of the extract was measured using Varian Eclipse fluorescence photometer (Varian Electronics., UK) following Suzuki and Ishimaru (1990). Nutrients were measured following spectrophotometric method (Grashoff et al., 1983). Sediment texture analysis was carried out following Folk (1974). Suspended Particulate matter (SPM) were measured as weight difference of material retained on 0.2 µm polycarbonate filter (Millipore) after passing 500-1000 ml of water. About 1 litre of water samples was filtered through pre-combusted GF/F filter, 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 the desiccators to remove inorganic carbon and organic carbon on the filter was measured using Elemental analyzer. Surface sediment samples were collected using Van-Veen grab and aliquot of the sample was dried at 60° C, and ground to a fine powder. Subsamples of ~5-10 mg were taken in to silver cup and few drops of dilute HCl were added to remove carbonates and were dried. Subsamples for δ¹⁵N analysis did not receive this treatment as this has been reported to affect δ¹⁵N values (Goering et al., 1990; Bunn et al., 1995; Pinnegar and Polunin, 1999). Benthic macro fauna were identified and picked using stereo zoom microscope, cleaned, dried at 60°C and fine powered. In order to remove inorganic carbon, powdered samples were taken to the silver micro cups and were acidified with 10% hydrochloric acid, dried at 60°C and were washed with distilled water to remove excess acid. The dried cups were introduced to the elemental analyzer attached to the Isotope ratio mass spectrometer.

Measurement of stable isotope and elemental ratios

The content and isotopic ratios of carbon and nitrogen in the sediment and suspended matter were measured on elemental analyser coupled with Isotope Ratio Mass Spectrometer (EA-IRMS-Delva V, Finnigan, Germany) and results are expressed relative to conventional standards i.e., PDB for carbon (Coplen, 1996) and atmospheric N₂ for nitrogen (Mariotti, 1983) as δ values, defined as:

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

Where $R = {}^{13}\text{C}$ or ${}^{15}\text{N}$, and $X = {}^{13}\text{C}/{}^{12}\text{C}$ or ${}^{15}\text{N}/{}^{14}\text{N}$. The high-purity tank CO_2 and N_2 were used as working standard for carbon and nitrogen. These gases were calibrated with internal reference materials of Glutamic acid, Alanine and marine sediment. Standard deviation on twenty aliquots of the same samples was lower than 0.2 ‰ for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

The estuary is divided into upper and lower estuary depending on the tidal oscillations. Our monthly time-series data suggest that tidal influence can be observed up to 40 kms from the mouth of the estuary and it is considered to be lower estuary and the stations beyond this towards upstream considered to be upper estuary where always freshwater is observed.

Results

Longitudinal variability in hydrographic and sediment characteristics

Salinity at the mouth of the estuary was ~ 30.0 psu and it decreased gradually to near zero at 50 km from the mouth (Fig. 2a). Ammonia concentrations varied between 1.0 and 3.9 μM and it decreased from lower to upper estuary (Fig. 2a). SPM varied from 9.1 to 23.7 mg l^{-1} with higher concentrations at the mouth of the estuary and in the middle of the estuary between 30-40 kms from the mouth of the estuary (Fig. 2b). The latter maximum is called turbidity maximum zone. Chl-a ranged from 1.6 to 21 mg m^{-3} and sharp increase in Chl-a from ~ 10 to 21 mg m^{-3} was observed at turbidity maximum zone at 38 km from the mouth where almost freshwater was found (~ 0.5 psu; Fig. 2a). Large contribution of sand (>70%) to the total sediment was noticed at 8.7, 24.5, 37.1 and 50.5 km from the mouth including at the turbidity maximum zone.

Spatial variability in content and isotopic ratios of carbon and nitrogen in suspended matter and sediment

Organic carbon and nitrogen in the suspended matter ranged from 0.2 to 2.4% and 0.04 to 0.35% respectively and the higher concentrations were observed at the turbidity maximum zone (Fig. 2c). Organic carbon and nitrogen in the sediment varied from 0.1 to 0.9% and 0.01 to 0.18% respectively. Both carbon and nitrogen content in the sediment were higher at the mouth of the estuary and close to turbidity maximum zone (Fig. 2d). The maximum in organic carbon and nitrogen in the suspended matter was not exactly associated with maximum in sediments. The isotopic ratios of $\delta^{13}\text{C}$ ranged from -23.0 to -28.0 and -23.1 to -26.2 ‰ in the suspended matter and sediment respectively (Fig. 3). The carbon isotope and C/N ratios show a clear difference between the upper and lower estuary whereas nitrogen isotope did not show significant difference. Slightly higher carbon (1.11 ± 0.08 %) and C/N ratio (6.9 ± 0.1) were found in the suspended matter in the upper estuary compared to the lower estuary ($0.91 \pm 0.8\%$ and 5.4 ± 0.7) whereas the $\delta^{13}\text{C}$ of suspended matter became heavier from -27.5 ± 0.7 ‰ at the fresh-water end member (upper estuary) to -24.3 ± 1.1 ‰ in the lower estuary. Sediments with low

organic carbon content ($0.3 \pm 0.2\%$), however, were located in the upper estuary for which higher C/N ratios (14.0 ± 6) were found. The $\delta^{13}\text{C}$ of sedimentary organic matter shows a small gradient from -26.2 ± 0.2 in the upper estuary to -24.9 ± 0.9 in the lower estuary (Table 1). The $\delta^{15}\text{N}$ of sediments varied from $11.2 \pm 5\%$ in the upper estuary to $7.3 \pm 1.7\%$ in the lower estuary whereas the $\delta^{15}\text{N}$ of suspended matter ranged from 5.4 ± 0.4 to $6.7 \pm 0.7\%$, with a clear maximum of about $7.3-7.8\%$ in the middle of the estuary (Fig. 3b) associated with turbidity maximum. C/N ratios were relatively higher in the sediment (3.5 to 18.5) than suspended matter (4.6 to 7.0) and relatively higher ratios in both sediments and suspended matter were observed in the upper than the lower estuary.

Discussion

Factors influencing content and isotopic ratios of carbon and nitrogen

The content of organic carbon and nitrogen in the sediment displayed significant correlation coefficients, negative with sand ($r^2=0.83$ for carbon and 0.70 for nitrogen; $p<0.001$) and positive with silt ($r^2=0.8$ for carbon and 0.62 for nitrogen; $p<0.001$) and clay ($r^2=0.54$ for carbon and 0.54 ; $p<0.001$) in the sediments of Godavari estuary. Therefore the overall distribution of organic carbon and nitrogen contents was likely controlled by sediment composition than the source of material alone.

The mean isotopic ratios ($\delta^{13}\text{C}_{\text{sed}}$: -25.1 ± 0.9 ; $\delta^{13}\text{C}_{\text{sus}}$: -24.9 ± 1.7 ; $\delta^{15}\text{N}_{\text{sed}}$: 8.0 ± 2.7 and $\delta^{15}\text{N}_{\text{sus}}$: $6.5 \pm 0.9\%$) and elemental concentrations (C_{sed} : $0.45\% \pm 0.2\%$; C_{sus} : $0.9 \pm 0.7\%$; N_{sed} : $0.07\% \pm 0.05\%$ and N_{sus} : $0.16 \pm 0.1\%$; Table 1) suggest that organic matter of suspended matter and sediment is mixture of both terrigenous and marine derived materials as the isotopic ratios varied between these two end members (Tables 1 and 2). Significant enrichment in isotopic ratios of $\delta^{13}\text{C}$ from upper to lower estuary in suspended matter (-27.5 ± 0.7 and $-24.3 \pm 1\%$ respectively), approaching marine phytoplankton ratio of 23.1% (Table 1 and 2; Fig. 3a) suggests a corresponding decrease in the influence of terrigenous matter towards mouth of the estuary. Significant tidal influence can be noticed, in terms of salinity, up to $\sim 30-40$ km from the mouth of the estuary (Fig. 2a) and clear transition of $\delta^{13}\text{C}$ from heavier to lighter can be noticed at this location (Fig 3a). The significant positive relationship between $\delta^{13}\text{C}_{\text{sus}}$ and $\delta^{13}\text{C}_{\text{sed}}$ ($r^2=0.45$; $p<0.001$) indicates these two organic pools were likely coupled and a significant exchange is possible between the two pools. The sediment $\delta^{13}\text{C}_{\text{sed}}$ was relatively lighter than suspended matter in the lower estuary by 0.7 to 2.1% could possibly be due to contribution of benthic invertebrates. We have measured isotopic ratios of 7 species of macrobenthic organisms in the Godavari estuary and their $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were ranged from -23.9 to -20.3% and 5.9 to 9.9% respectively (Table 4). Among them *Spionidae* spp. was the dominant and contributed about $60-70\%$ with reference to biomass which has relatively lower isotopic ratio (-23.9%) than others. These values are slightly lower than those observed, ca, $23.6 \pm 0.6\%$ in the mangrove creeks adjacent to the Godavari estuary, $-21.5 \pm 0.9\%$ in the mangrove outlets, $-18.8 \pm 0.8\%$ in the Kakinada Bay adjacent to the mangroves and much higher

isotopic value ($-16.7 \pm 1.4\text{‰}$) in the central and northern part of the Bay that opens to the Bay of Bengal (Bouillon et al., 2002). Lighter isotopic ratios in the benthic organisms were the result of a preferential consumption of lighter isotopic carbon during their feeding. The differences in the isotopic values are also dependent on the substratum of the food the organisms feed on. The lighter isotopic ratios of benthic organisms in the Godavari suggest that microalgal carbon may be major source of food for them (Bouillon et al., 2004).

Spatial distribution of sedimentary and suspended matter characteristics

Longitudinal variations in $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N characteristics of estuarine particulate material have been used to study the mixing of continental (riverine and terrestrial) and marine particulates (eg. Salomons and Mook, 1981; Thornton and McManus, 1994); Middelburg and Herman, 2007). These studies are based on the assumption that local (*in situ*) inputs can be neglected. The residence time of water during the study period was ~ 30 days based on tidal prism method (Sridevi et al., 2011). The water column Chl-a displayed positive relation with organic carbon in the suspended matter ($r^2=0.82$; $p<0.001$) whereas suspended nitrogen showed negative correlation with ammonia ($r^2=0.64$; $p<0.001$) suggesting biological processes (photosynthesis and bacterial degradation) control content of carbon and nitrogen in the suspended matter. The POC/Chl-a ratio ranged between 12 and 100 and increased towards lower estuary indicating that larger contribution of phytoplankton biomass to the POC in the upper than lower estuary is taking place. Bouillon et al. (2004) observed a higher POC/Chl-a ratio (>100) during postmonsoon 2001 in the mangrove region attached to Godavari estuary. They found higher POC values, by 5-10 times than that of our values, with relatively high POC/PN ratio (7.5 ± 0.8) indicating that initiation of discharge during the period of their observation led to contribution of terrigenous organic matter. Our results conform to previous studies in the tidal estuaries with long residence times (eg. Mariotti et al., 1984; Cifuentes et al., 1988) that autochthonous organic matter contributes significantly to the total suspended matter during dry period. In the lower estuary, the $\delta^{15}\text{N}$ values of bottom sediments ($\delta^{15}\text{N} = 7.3 \pm 1 \text{‰}$) were close to that in the suspended particulate matter ($\delta^{15}\text{N} = 6.7 \pm 0.7 \text{‰}$), but in the upper estuary sedimentary $\delta^{15}\text{N}$ was enriched by 5.8 ‰ relative to suspended matter (Table 1). The $\delta^{13}\text{C}$ values of sedimentary and suspended matter were significantly different, with suspended matter being depleted in the upper estuary (by 1.3‰) and enriched by 0.6 ‰ in the lower estuary than sediment. Sedimentary C/N ratios (14 ± 6 and 6.7 ± 3 in the upper and lower estuary respectively) were higher than those of suspended matter (6.9 ± 0.1 and 5.4 ± 0.7 in the upper and lower estuary respectively). High C/N ratios in the sediment suggest that sedimentary organic matter has the largest contribution by terrestrial organic matter, partly due to preferential decomposition of the more labile riverine, estuarine and marine organic matter in the water column and sediments and consequent sedimentary accumulation of refractory terrestrial organic matter, and also partly due to seasonal effect. The samples were collected during dry period; therefore, they contain a relatively large fraction of newly produced organic matter, whereas sedimentary organic

matter contains information on the annual integrated organic matter source. The linear relationship of $\delta^{13}\text{C}$ of suspended with sedimentary organic matter ($r^2=0.45$, $p<0.001$) indicates these two organic pools were rather coupled and a significant fraction of re-suspended sediment in the particulate fraction. The turbidity maximum was occurred at ~ 5 psu salinity, which was nearly 38 kms from the estuarine mouth (Fig. 2c). The turbidity maximum was associated with high organic carbon in suspended matter, high water column Chl-a and low ammonia concentrations (Fig. 2). In contrast to this, the maximum in sedimentary organic carbon was not associated with suspended matter but was noticed at ~ 30 km from the mouth (Fig. 2d). The discrepancy in position of maximum organic matter in the suspended matter and sediment was caused by sediment texture as $\sim 74\%$ of the sediment was contributed by sand at the turbidity maximum zone that resulted in oxidation of organic matter in the sediment (Fig. 2b). On the other hand, the contribution of sand to the sediment was low ($\sim 20\%$) where organic carbon maximum in sediment was noticed close to the turbidity maximum zone. Therefore, the shift in sediment organic carbon maximum was rather controlled by sediment texture than the source of organic carbon from the water column.

Sources of Organic matter to the estuary

The composition of suspended and sedimentary organic matter contains information on the mixing of the various organic matter sources and their subsequent degradation history. If the degradation of organic matter is minimal or can be accounted, source of organic matter can be identified using elemental, isotopic and molecular biomarker parameters. In this study $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N ratios of suspended matter are used to characterize organic matter sources. Relationships among suspended $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ indicated contributions distinguished as due to three end member particulates: marine ($\delta^{13}\text{C} = -23.0 \pm 0.2 \text{‰}$, $\delta^{15}\text{N} = 6.1 \pm 0.2 \text{‰}$), terrestrial ($\delta^{13}\text{C} = -27.5 \pm 0.6$, $\delta^{15}\text{N} = 5.4 \pm 0.3$) and the intermediate estuarine ($\delta^{13}\text{C} = -24.6 \pm 0.9$, $\delta^{15}\text{N} = 6.9 \pm 0.7$) (Fig. 4). On the other hand, both $\delta^{13}\text{C}$ versus C/N and $\delta^{15}\text{N}$ versus C/N ratios diagrams do not allow distinction between terrestrial and estuarine material possibly due to significant modification of C/N ratios (Middelburg and Herman, 2007).

The terrestrial organic matter end-member (our extreme upstream samples at 50.5 and 55.7 km; Table 3) was enriched in nitrogen (C/N=6.9) and has characteristics $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (-27.5 and +5.4‰ respectively) similar to the $\delta^{13}\text{C}$ of terrestrial carbon which is in the range of -26 to -27 ‰ (Peters et al., 1978; Thornton and McManus, 1994; Wada et al., 1987; Middelburg and Nieuwenhuize, 1998; Hobbes et al., 2000), similar to that of C3 plants (Peterson and Fry, 1987). Riverine algae and their detritus are usually more depleted (-30 to -40 ‰) than terrestrial and sewage carbon (Hamilton and Lewis, 1992; Middelburg and Nieuwenhuize, 1998; Barth et al., 1998; Hellings et al., 1999; Boschker et al., 2005; Bontes et al., 2006). The riverine end member in the Godavari estuary (-27.5‰) is close to that of terrestrial signature rather than riverine algae. However, our terrestrial $\delta^{15}\text{N}$ ($5.4 \pm 0.4 \text{‰}$) and $\delta^{13}\text{C}$ ($-27.5 \pm 0.7 \text{‰}$) values are within the range observed in various estuaries in the world (table 2). Our

marine end member ($\delta^{13}\text{C} = -23.0 \pm 0.2\text{‰}$) was close to that reported by Dehairs et al. (2000; $-23.2 \pm 0.8\text{‰}$) in the Godavari estuary. The estuarine end-member ($\delta^{13}\text{C} = -24.6 \pm 0.9\text{‰}$ and $\delta^{15}\text{N} = 6.9 \pm 0.7\text{‰}$ and $\text{C/N} = 5.5 \pm 0.3$) is primarily distinguished through its heavy nitrogen isotope values, as observed before by Owens (1985), Mariotti et al., (1984) and Cifuentes et al. (1988). Owens (1985) reported $\delta^{15}\text{N}$ values for estuarine suspended matter up to 14.7‰ and attributed this $\delta^{15}\text{N}$ enrichment to intense biological processing of organic matter in the estuarine turbidity maximum. Recently Middelburg and Herman (2007) also reported $\delta^{15}\text{N}$ up to 23‰ in the Scheldt estuary (table 2). Mariotti et al. (1984) and Cifuentes et al. (1988) observed high $\delta^{15}\text{N}$ values for estuarine suspended matter in Shelde (maximum 24‰) and Delaware (maximum 18‰) estuaries respectively during spring, but $\delta^{15}\text{N}$ enrichment was lower during other seasons and absent during winter. These authors suggested that phytoplankton, which utilizes isotopically enriched, residual ammonium resulting from nitrification (Mariotti et al., 1984) or extensive algal uptake (Cifuentes et al., 1988), became a dominant pool of the suspended organic matter. Our data support their interpretation since the decrease in dissolved ammonia was accompanied by an increase in $\delta^{15}\text{N}$ values for suspended matter (Figure 2a and 3b). Moreover, enrichment in particulate $\delta^{15}\text{N}$ concurred with a maximum in gross primary production ($68 \text{ mmolO}_2 \text{ m}^{-3} \text{ d}^{-1}$) with net phytoplankton production was estimated to be negative ($-20.2 \text{ mmolO}_2 \text{ m}^{-3} \text{ d}^{-1}$) in this part of the estuary (Our unpublished data). Kromkamp and Peene (1995) also reported similar observations in Schelde estuary whereas high rates of chemoautotrophic production by nitrifiers seems to be major contributors for enriched $\delta^{15}\text{N}$ in Westerschelde estuary (Soetaert and Herman, 1995 a,b).

Transformation of organic carbon in the estuary

Godavari estuary develops a salt wedge structure during dry period /at the onset of monsoon and has longer water residence time (>30 days) during the study period. During such periods, suspended organic carbon is extensively mineralized due to heterotrophic activity. Sarma et al. (2009) noticed that water column respiration exceeds autotrophic production by an order of magnitude in the Godavari estuary with mean P:R ratio of 0.14. Similar situation was also found in some other estuaries too (Heip et al., 1995; Gattuso et al., 1998; Frankignoulle et al., 1998). The importance of tidal mixing on suspended organic carbon is evident. The suspended organic carbon in the estuary showed significant gradients with increase in contribution towards upper estuary. These gradients were caused by extensive mixing and dilution of seawater (Fig. 5a), which has lower POC content. Similarly, $\delta^{13}\text{C}$ of suspended matter was also linearly heavier towards lower estuary with clear end-member signatures (Fig. 5b). Similar features were observed in other tidal estuaries such as Rhine, Scheldt, Douro (Middelburg and Herman, 2007) and Apalachicola Bay, a river dominated estuary in Florida (Chanton and Lewis, 1999). Accordingly, extensive tidal mixing between marine and terrestrial end members and between organic matter inputs and the large standing stocks of suspended organic carbon is a

dominant feature in the Godavari estuary. However, the $\delta^{13}\text{C}$ values in the middle of the estuary were significantly enriched from that of simple mixing line suggesting that transformation of organic matter was possible in the estuary (Fig. 3a).

Nitrogen isotopes are useful tracers to identify estuarine organic matter and were applied successfully in several regions (Peters et al., 1978; Middelburg and Herman, 2007). The river end-member (Alamuru station) of $\delta^{15}\text{N}$ of suspended matter was lighter (5.6 ± 0.2 ‰) compared to the marine end member (station B.E, 6.1 ± 0.2 ‰). It was proposed that $\delta^{15}\text{N}$ values of estuarine particles provide an integrated measure of the N-loading (Middelburg and Nieuwenhuize, 200a; McClelland and Valiela, 1998). The relatively lighter $\delta^{15}\text{N}$ in the river end-member supports terrestrial organic matter of C3 plants (2 to 5 ‰; Kendall et al., 2001). On the other hand, $\delta^{15}\text{N}$ is potential tracer to identify internal organic matter cycling. It was observed that $\delta^{15}\text{N}$ in the middle of the estuary was heavier than both the end members in the Godavari estuary (Fig. 3b) suggesting that internal sources of organic matter with high $\delta^{15}\text{N}$ values. Such mid-estuarine maxima for $\delta^{15}\text{N}$ have been reported for the Tamar estuary (Owens, 1985), the Delaware estuary (Cifuentes et al., 1988) and the Scheldt estuary (Mariotti et al., 1984; Middelburg and Nieuwenhuize, 1998; De Brabandere et al., 2002). Ammonia loading was also higher in the upstream and decreased towards downstream (Fig. 2a). The increase in $\delta^{15}\text{N}$ might have been caused by consumption of river-derived ammonia by nitrifiers, as they preferentially uptake ^{14}N , leading to enrichment of $\delta^{15}\text{N}$ of remaining ammonia in solution in the downstream (Mariotti et al., 1984; Middelburg and Nieuwenhuize, 2001). Uptake of such heavy ammonia by phytoplankton, and bacteria in the middle estuary resulting in elevated $\delta^{15}\text{N}$.

The mean C/N ratio of suspended matter in the Godavari estuary (5.7 ± 0.9) was relatively lower than that found in major world rivers (8.1 to 12.9; Ittekkot and Zhang, 1989) suggesting that diagenetic transformations occurred in the suspended organic carbon that modified original signatures extensively. The strong positive correlation between POC and Chl-a ($r^2=0.8$; $p<0.001$) with mean POC:Chl-a ratio of 32.2 strongly suggests that estuarine phytoplankton contributed significantly to the suspended matter. Carbon to nitrogen ratios can also be used to identify organic matter sources as plankton and bacterial molar C/N ratios (6-7 and 4-5 respectively) are much lower than organic matter derived from higher plants (>20 ; Hedges et al., 1997). The C/N ratios of the suspended matter ranged between 4.6 and 7.0 with relatively higher ratios were found in the upper estuary (7.0 ± 0.1) than in the lower estuary (5.2 ± 0.4) suggesting that the organic matter is contributed by plankton and/or bacteria. This result is at variance with the $\delta^{13}\text{C}$ values which ranged between -23.0 and -28.0 ‰ that suggest a significant fraction of suspended matter being contributed by terrestrial organic matter in the Godavari estuary (Fig. 3). Further, a negative relation was observed between $\delta^{13}\text{C}$ of suspended matter and chlorophyll (Fig. 5d) suggests a significant fraction of terrestrial source exists for organic matter at the upper estuary. The C/N ratios of higher plant litter tend to decrease due to bacterial assimilation of

dissolved inorganic nitrogen (i.e., retention of nitrogen) whereas C/N ratios of algal detritus increase upon diagenesis (Hedges et al., 1997; Herman et al., 1999). The C/N ratios of particulate matter are surprisingly less variable (4.6 to 7.0) despite clear indication of different sources based on $\delta^{13}\text{C}$ values. The lack of power to resolve source of organic matter using C/N ratios was also noticed in other estuaries (Cifuentes et al., 1988; Thornton and McManus, 1994; Middelburg and Nieuwenhuize, 1998; Middelburg and Herman, 2007) due to its modification during diagenesis. Both isotopic and C/N ratios suggest that organic matter in the Godavari estuary was significantly modified.

Contribution of terrestrial carbon in the estuary

The estuarine suspended matter is contributed significantly by *in situ* production, marine production and particles of terrestrial origin. Salinity showed a significant relationship with $\delta^{13}\text{C}$ of suspended matter ($r^2=0.72$; $p<0.001$). The linear increase in $\delta^{13}\text{C}$ of suspended matter from fresh water to saline water signifies mixing of isotopically lighter terrestrial with heavier marine organic matter. The isotopic ratios of $\delta^{13}\text{C}$ of suspended matter in the estuary were significantly heavier than simple mixing line (Fig. 5b). This enrichment is mainly controlled by the primary production and phytoplankton assemblages. The mean gross production was $42.5 \text{ mmol C m}^{-3} \text{ d}^{-1}$ in the Godavari estuary during study period and heterotrophy was dominant as mean net community production was $-15.3 \text{ mmol C m}^{-3} \text{ d}^{-1}$ (Our unpublished data). The tight correlation between suspended organic carbon with Chl-a clearly indicates that *in situ* primary production contributed significantly to the organic carbon in the estuary. The mean $\delta^{13}\text{C}$ of suspended matter in the estuary was $-24.9\pm 1 \text{ ‰}$ which is slightly lighter than expected from phytoplankton production. Nagel et al (2009) observed linear increase of $\delta^{13}\text{C}$ of suspended matter with salinity in Kara Sea and noted that $\delta^{13}\text{C}$ of suspended matter was contributed by mixing of river and marine water masses. Since isotopic ratios of terrestrial, marine have distinct signatures, in order to separate them, simple mixing model was used.

$$\delta^{13}\text{C}_{\text{estuary}} = f_{\text{terrestrial}} \times \delta^{13}\text{C}_{\text{terrestrial}} + f_{\text{marine}} \times \delta^{13}\text{C}_{\text{marine}}$$

Where $f_{\text{terrestrial}}$ and f_{marine} are the fractions of the $\delta^{13}\text{C}$ originating from the terrestrial and marine regions respectively, and $\delta^{13}\text{C}_{\text{terrestrial}}$ and $\delta^{13}\text{C}_{\text{marine}}$ are the isotopic compositions of these two contributing sources. We used $\delta^{13}\text{C}$ values of -27.5‰ for terrestrial and -23.0‰ for marine in our calculations and were taken from the upper most data from the upper estuary (station Alamuru) and close to mouth of the estuary (station B.E). Applying this to our data set in the estuarine region yielded that $\sim 46\%$ of the suspended matter is contributed by the terrestrial origin. On the basis of Aluminum content of particulate matter, Regnier and Wollast (1993) have proposed a mixing model of suspended matter in the Schelde estuary and estimated that fluvial matter accounts for about 75% of the total suspended matter in the upper estuary and that the proportion of marine particles increases rapidly in the zone of turbidity maximum. Our estimated contribution of terrigenous organic to the estuarine

suspended matter is in good agreement with Sarma et al. (2009) who estimated that ~40-50% of the heterotrophic carbon demand is supported by the terrigenous carbon during nil discharge period based on plankton metabolic balance. Therefore, significant fraction of the terrigenous organic carbon supports the heterotrophic carbon demand and organic carbon significantly modifies in the Godavari estuary before it is transported to the coastal regions.

Summary and Conclusions

Spatial distribution of carbon and nitrogen content and their isotopic values of suspended matter and sediments were measured at 11 stations in the Godavari estuary to identify sources and transformation of organic matter in the estuary. The mean isotopic and elemental ratios indicate that organic carbon in the suspended matter and sediment was contributed by terrigenous, marine and *in situ* production. Significant enrichment in isotopic ratios of $\delta^{13}\text{C}$ from upper to lower estuary in both suspended matter and sediment indicates decrease in influence of terrigenous material towards mouth of the estuary. Strong positive relation between suspended organic carbon with Chl-a suggests that *in situ* production contributed significantly to the bulk particulate organic carbon. The relationship between $\delta^{13}\text{C}$ of suspended and sediment further indicates these two organic pools are rather coupled and a significant fraction of exchange is possible. C/N ratios and $\delta^{15}\text{N}$ of suspended matter suggests that significant modification occurred in the water column. Based on two end member mixing model, ~46% of the suspended matter is contributed by the terrestrial organic matter and supported heterotrophic carbon demand in the Godavari estuary.

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References

- Andrews, J.E., A.M. Greenway, and P.F. Dennis (1998): Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary. Hunts Bay, Kingston Harbour, Jamaica. *Estuarine, Coastal and Shelf Sci.*, **46**, 743-456.
- Balakrishna, K., and J.L. Probst (2005): Organic carbon transport and C/N ratio variations in a large tropical river: Godavari as a case study, India. *Biogeochem.* **73**, 457-473.
- Barth, J.A.C., J. Veizer, B. Mayer (1998): Origin of particulate organic carbon in the upper St. Lawrence: Isotopic constraints. *Earth Planet. Sci. Lett.* **162**, 111-121.

Bellanger, B., S. Huon, P. Steinmann, F. Chabaux, F. Velasquez, V. Valles, K. Arn, N. Clauer, A. Mariotti (2004): Oxidic-anoxic conditions in the water column of a tropical freshwater reservoir (Pena-Larga dam, NW Venezuela). *Applied Geochem.* **19**, 1295-1314.

Berner, R.A. (1982): Burial of organic-carbon and pyrite sulfur in the modern ocean – its geochemical and environmental significance. *American J Sci.*, **282**, 451-473.

Berner, R.A. (1989): Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. *Global and Planetary Change*, **75**, 97-122.

Berner, R.A., and R. Raiswell (1983): Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. *Geochem. Cosmochim. Acta* **47**, 855-862.

Bird, M.I., P. Giresse, and S. Ngos (1998): A seasonal cycle in the carbon-isotope composition of organic carbon in the Sanaga river catchment, Cameroon. *Limnol. Oceanogr.* **43**, 111-114.

Bird, M.I., and D.R. Grocke (1997): Determination of the abundance and carbon isotope composition of elemental carbon in sediments. *Geochim. Cosmochim. Acta*, **61**, 3413-3423.

Bontes, B., R. Pel, B.W. Ibelings, H.T.S. Boschker, J.J. Middelburg, E. van Donk (2006): The effects of biomanipulation on the biogeochemistry, carbon isotopic composition and pelagic food web relations of a shallow lake. *Biogeosciences* **3**, 69-83.

Boschker, H.T.S., J.J. Middelburg, J. Kromkamp (2005): Biomarker and carbon isotopic constraints on bacterial and algal community structure and functioning in a turbid, tidal estuary. *Limnol. Oceanogr.* **50**, 70-80.

Bouillon, S., A.V. Raman, P. Dauby, and F. Dehairs (2002): Carbon and Nitrogen stable isotope ratios of subtidal benthic invertebrates in an estuarine mangrove ecosystem (Andhra Pradesh, India), *Estuarine, Coastal Shelf Sci.*, **54**, 901-913.

Bouillon, S., M. Frankignoulle, F. Dehairs, B. Velimirov, A. Eiler, G. Abril, H. Etcheber, and A.V. Borges (2003). Inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra Pradesh, India) during pre-monsoon: The local impact of extensive mangrove forests. *Global Biogeochem. Cycles*, **17**, doi:10.1029/2002GB002026.

Bouillon, S., N. Koedam, W. Baeyens, B. Satyanarayana, and F. Dehairs (2004). Selectivity of subtidal benthic invertebrate community for local microalgal production in an estuarine mangrove ecosystem during the post-monsoon period. *J. Sea Res.*, **51**, 133-144.

Bunn, S.E., N.R. Longergan, and M.A. Kempster (1995): Effects of acid washing samples on stable isotope ratios of C and N in penaeid shrimps and seagrass: implications for food web studies using stable isotopes. *Limnol. Oceanogr.*, **40**, 622-625.

Chen, F., and Jia, G., 2009. Spatial and seasonal variation in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of particulate organic matter in a dam-controlled subtropical river. *River Res. And Appl.*, **25**, 1169-1176.

Cifuentes, A.A., Sharp, J.H., Fogel, M.L., 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnol. Oceanogr.*, **33**, 1102-1115.

Central Pollution Control Board (CPCB), 1995, Basin sub-basin inventory of Water Pollution Godavari Basin. CPCB, Delhi.

Coplen, T.B., 1996. New guidelines for reporting stable hydrogen, carbon and oxygen isotope-ratio data. *Geochimica et Cosmochimica Acta*, **60**, 3359-3360.

Chanton, J.P., Lewis, F.G., 1999. Plankton and dissolved inorganic carbon isotopic composition in a river-dominated estuary: Apalachicola Bay, Florida. *Estuaries* **22**, 575-583.

Darnaude, A.M., C. Salen-Picard, M.L. Harmelin-Vivien (2004): Depth variation in terrestrial particulate organic matter exploitation by marine coastal benthic communities off the Rhone River delta (NW Mediterranean). *Mar. Ecol. Prog. Ser.*, **275**, 47-57.

Dehairs, F., R.G. Rao, P. Chandra Mohan, A.V. Raman, S. Marguillier, and L. Hellings (2000): Tracing mangrove carbon in suspended matter and aquatic fauna of the Gautami-Godavari Delta, Bay of Bengal (India). *Hydrobiologia*, **431**, 225-241.

De Brabandere, L., F. Dehairs, S. van Damme, N. Brion, P. Meire, and N. Daro (2002): $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ dynamics of suspended organic matter in fresh water and brackish waters of the Scheldt estuary. *J. Sea Res.* **48**, 1-15.

DeLong, M.D., and Thorp, J.H. 2006. Significance of instream autotrophs in trophic dynamics of the Upper Mississippi River. *Oecologia*, **147**, 76-85.

Folk, R.L. (1974): Petrology of sedimentary rocks, Hemphill, Austin, pp 182.

Frankignoulle, M., G. Abril, A. V. Borges, I. Bourge, C. Canon, B. Delille, E. Libert, and J.M. Theate (1998): Carbon dioxide emission from European estuaries. *Science* **282**, 434-436.

Gaillardet, J., B. Dupre, P. Louvat, P., and C.J. Allegre (1999): Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* **159**, 3-30.

Galvan, K., J.W. Fleeger, and B. Fry (2008). Stable isotope addition reveals dietary importance of phytoplankton and microphytobenthos to salt marsh infauna. *Mar. Ecol. Prog. Ser.*, **359**, 27-49.

Gattuso, J.P., M. Frankignoulle, and R. Wollast (1998): Carbon and carbonate metabolism in coastal aquatic ecosystems. *Anne. Rev. Ecol. Syst.* **29**, 405-434.

Goering, J., V. Alexander, and N. Haubenstock (1990): Seasonal variability of stable carbon and nitrogen isotope ratios of organisms in a North Pacific Bay. *Estuarine, Coastal and Shelf Sci.*, **30**, 239-260.

Grasshoff, K., M. Ehrhardt, and K. Kremling (Eds.). (1983): *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, pp. 89-224.

Gupta, L.P., V. Subrahmanian, V. Ittekkot (1997). Biogeochemistry of particulate organic matter transported by the Godavari river, India. *Biogeochem.*, **38**, 103-128.

Haake, B.G., N. Lahajnar, K.Ch. Emeis, D. Unger, T. Rixen, A. Suthhof, V. Ramaswamy, H. Schulz, A.L. Paropkari, M.V.S. Guptha, and V. Ittekkot (2005): Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean. *Mar. Chem.*, **96**, 243-255.

Hamilton, S.K., and W.M. Lewis (1992): Stable carbon and nitrogen isotopes in algae and detritus from the Orinoco River flood plain. Venezuela. *Geochim. Cosmochim. Acta*. **56**, 4237-4246.

Hedges, J.I., and R.G. Keil (1995): Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.*, **49**, 81-115.

Hedges, J.I., R.G. Keil and R. Benner (1997). What happens to terrestrial organic matter in the ocean? *Org.Geochem.* **27**,195-212.

Heip, C.H.R., N.K. Goosen, P.M.J. Herman, J. Kromkamp, J.J. Middleburg, and K. Soetaert (1995): Production and consumption of biological particles in temperate tidal estuaries. *Oceanogr. Mar. Biol. Annu. Rev.***33**,1-150.

Hellings, L., F. Dehairs, M. Tackx, E. Keppens, and W. Baeyens (1999): Origin and fate of organic carbon in the freshwater part of the Scheldt estuary as traced by stable carbon isotope composition. *Biogeochem.* **47**, 167-186.

Herman, P.M.J., and C.H.R. Heip (1999): Biogeochemistry of the maximum turbidity zone of estuaries (MATURE): some conclusions. *J. Mar. Syst.* **22**, 89-104.

Hobbies, J.M., H.P. Fitznar, G. Kattner (2000): Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean. *Geochim. Cosmochim. Acta* **64**, 2973-2983.

Ittekkot, V, and S. Zhang (1989): Patterns of particulate nitrogen transport in world rivers. *Global Biogeochem. Cycles* **3**, 383-391.

Kao, S.J., and K.K. Liu (2000): Stable carbon and nitrogen isotope systematic in a human disturbed watershed (Lanyang-His) in Taiwan and the estimation of biogenic particulate organic carbon and nitrogen fluxes. *Global Biogeochem. Cycles* **14**, 189-198.

Kendall, C., S.R. Silva, and V.J. Kelly (2001): Carbon and nitrogen isotopic compositions of particulate organic matter in four large-river systems across the United States. *Hydrological Processes* **15**, 1301-1346.

Kromkamp, J., and J. Peene (1995): Possibility of net phytoplankton primary production in the turbid Schelde Estuary (SW Netherlands). *Mar. Ecol. Prog. Ser.* **121**: 249-259.

Lee, C. (1994): Controls on carbon preservation – new perspectives. *Chem. Geol.* **114**, 285-288.

Longworth, B.E., S.T. Petsch, P.A. Raymond, and J.E. Bauer (2007): Linking lithology and land use to sources of dissolved and particulate organic matter in headwaters of a temperate, passive-margin river system. *Geochim. Cosmochim. Acta* **71**, 4233-4250.

Lucotte, M. (1989): Organic carbon isotope ratios and implications for the maximum turbidity zone of the St. Lawrence upper estuary. *Estuarine, Coastal and Shelf Sci.*, **29**, 297-304.

Ludwig, W., J.L. Probst, and S. Kemp (1996): Predicting the oceanic input of organic carbon by continental erosion. *Global Biogeochem. Cycles* **10**, 23-41.

Matson, E.A., and M.M. Brinson (1989): Stable carbon isotopes and the C:N ratio in the estuaries of the Pamlico and Neuse rivers, North Carolina. *Limnol. Oceanogr.*, **35**, 1290-1300.

Mariotti, A. (1983): Atmospheric nitrogen is a reliable standard for natural ¹⁵N abundance measurements. *Nature*, **303**, 685-687.

Mariotti, A., C. Lancelot, and G. Billen (1984): Natural isotopic composition of nitrogen as a tracer of origin for suspended matter in the Scheldt estuary. *Geochim. Cosmochim. Acta*, **48**, 549-555.

McClelland, J.W.M. and I. Valeila (1998): Linking nitrogen in estuarine producers to land-derived sources. *Limnol. Oceanogr.* **43**, 577-585.

Middelburg, J.J. and J. Nieuweuwenhuize (1998): Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. *Mar. Chem.*, **60**, 217-225.

Middelburg, J.J. and P.M.J. Herman (2007): Organic matter processing in tidal estuaries. *Mar. Chem.* **106**, 127-147.

Nagel, B., B. Gaye, L.A. Kodina and N. Lahajnar (2009): Stable carbon and nitrogen isotopes as indicators for organic matter sources in the Kara Sea. *Mar Geol.*, **266**, 42-51.

Onstad, G.D., D.E. Canfield, P.D. Quay, and J.I. Hedges (2000): Sources of particulate organic matter in rivers from the continental USA: Lignin phenol and stable carbon isotope compositions. *Geochim. Cosmochim. Acta* **64**, 3539-3546.

- Owens, N.J.P. (1985): Variations in the natural abundance of ^{15}N in estuarine suspended particulate matter: a specific indicator of biological processing. *Estuarine Coast. Shelf Sci.*, **20**, 505-510.
- Peters, K.E., R.E. Sweeney, and I.R. Kaplan (1978): Correlation of carbon and nitrogen stable isotopes in sedimentary organic matter. *Limnol. Oceanogr.*, **23**, 598-604.
- Peterson, B.J., and B. Fry (1987): Stable isotopes in ecosystem studies. *Ann. Rev. Ecol. Syst.* **18**, 293-320.
- Pinnegar, J.K. and N.V.C. Polunin (1999): Differential fractionation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ among fish tissues: implications for the study of trophic interactions. *Functional Ecology*, **13**, 225-231.
- Rao., K.L. (1975): India's water wealth, its assessment, uses and projections. Orient Longman, New Delhi, 255 p.
- Regnier, P., and R. Wollast (1993): Distribution of trace metals in suspended matter of the Scheldt estuary. *Mar. Chem.*, **43**, 3-19.
- Riera, P., and P. Richard (1996): Isotopic determination of food sources of *Crassostrea gigas* along a trophic gradient in the estuarine bay of Marennes Oleron. *Estuarine Coastal and Shelf Sci.*, **42**, 347-360.
- Salmons, W., and W. Mook (1981): Field observations of the isotopic composition of particulate organic carbon in the southern North Sea and adjacent estuaries. *Mar. Geol.* **41**, 125-130.
- Sarin, M.M., A.K. Sudheer, K. Balakrishna (2002). Significance of riverine carbon transport: A case study of a large tropical river, Godavari (India). *Science in China Series C-Life Science*, **45** (suppl.), 97-108.
- Soetaert, K., and P.M.J. Herman (1995a): Nitrogen dynamics in the Westerschelde estuary (W.W. Netherlands) estimated by means of the ecosystem model MOSES. *Hydrobiologia*, **311**, 225-246.
- Soetaert, K., and P.M.J. Herman (1995b). Carbon flows in the Westerschelde estuary (the Netherlands) evaluated by means of a global ecosystem model (MOSES). *Hydrobiologia* **311**, 247-266.
- Sarma, V.V.S.S., S.N.M. Gupta, P.V.R. Babu, T. Acharya, N. Harikrishnachari, K. Vishnuvardhan, N.S. Rao, N.P.C. Reddy, V.V. Sarma, Y. Sadharam, T.V.R. Murty, and M.D. Kumar (2009): Influence of river discharge on plankton metabolic rates in the tropical monsoon driven Godavari estuary, India, *Estuarine Coastal Shelf Sci.* **85**, 515-524.
- Sridevi, B., V.V.S.S. Sarma, N.P.C. Reddy, T.V.R. Murty, and Y. Sadharam (2011): Variability in stratification and flushing rates of the Gautami-Godavari estuary, India, *Estuarine, Coastal and Shelf Sci.*, in review.
- Suzuki, R., and T. Ishimaru (1990): An improved method for the determination of phytoplankton chlorophyll using *N,N*-dimethylformamide. *J. Oceanogr.* **46**, 190-194.

Thornton, S.F., and J. McManus (1994): Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. *Estuarine Coastal Shelf Sci.* **38**, 219-233.

Wada, E., M. Minagawa, H. Mizutani, T. Tsuji, R. Imizumi, and K. Karasawa (1987): Biogeochemical studies on the transport of organic matter along the Otsuchi River watershed, Japan. *Estuarine Coastal Shelf Sci.*, **25**, 321-336.

Wetzel, R.G., (2001): *Limnology: Lake and River Ecosystems*. Academic Press: New York.

Wu, Y., J. Zhang, S.M. Liu, Z.F. Zhang, Q.Z. Yao, G.H. Hong, and L. Cooper (2007): Sources and distribution of carbon within the Yangtze River system. *Estuarine, Coastal and Shelf Sci.*, **71**, 13-25.

Zetsche, E., B. Thornton, A.J. Midwood and U. Witte (2011). Utilisation of different carbon sources in a shallow estuary identified through stable isotope techniques. *Continental Shelf Res.*, **31**, 832-840.

Table 1: Comparison of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N between upper and lower and between sediment and suspended matter

Component	Upper estuary	Lower estuary
Sedimentary		
C/N	14.0±6	6.7±3
$\delta^{13}\text{C}$	-26.2±0.2	-24.9±0.9
$\delta^{15}\text{N}$	11.2±5.0	7.3±1.7
Suspended		
C/N	6.9±0.1	5.4±0.7
$\delta^{13}\text{C}$	-27.5±0.7	-24.3±1
$\delta^{15}\text{N}$	5.4±0.4	6.7±0.7
$\Delta\delta^{13}\text{C}_{\text{sed-sus}}$	1.3±0.8	-0.6±1.0
$\Delta\delta^{15}\text{N}_{\text{sed-sus}}$	5.8±5.2	0.6±1.8

Table 2: C/N, $\delta^{13}\text{C}$ org and $\delta^{15}\text{N}$ values for different estuarine systems

	C/N	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\delta^{15}\text{N}$ (‰)	Reference
Terrigenous sediment	12.17 19.50	to -25.4 to -28.0	+0.2 to +4.0	Thornton and McManus, 1994
		-26.0		Middelburg and Nieuweuwenhuize 1998, Middelburg and Herman, 2007
		-27.1 to -28.3		Andrews et al., 1998; Zetsche et al., 2011
Marine plankton	11.27	-23.2	5.9	Thornton and McManus, 1994, Galvan et al., 2008
		-21.3	2.54 to 4.26	Riera and Richard (1996), Haake et al., 2005
Estuarine plankton		-23.5 to -23.1		Riera and Richard (1996), Andrew et al., 1998, Bouillon et al., (2003), Riera and Richard (1996)
Benthic microalgae		-17.6 to -14.9		
Surface sediments		-25.4 to -24.25		Darnaude et al., 2004
Terrestrial plants (C3)	22.7 to 50.9	-29.5 to -24.4	-7.2 to -3.5	kao and Liu, 1999
Terrestrial plants (C4)	36.2 to 37.1	-14.4 to -12.9	-4.1 to -2.6	kao and Liu, 1999
Aquatic plants	10.4 to 14.6	-33.2 to -27.5	-4.4 to -3.6	kao and Liu, 1999
Soil	6.3 to 19.9	-26.9 to -24.0	-1.2 to 2.6	kao and Liu, 1999
Mangrove		-28.8	+4.5	Bouillon et al., 2002.
Suspended matter in EMS estuary		-24.2 to -22.1	6.1 to 10	Middelburg and Herman, 2007
Suspended matter in Elbe estuary		-29.1 to -20.3	2.2 to 14.3	Middelburg and Herman, 2007
Suspended matter in Thames estuary		-27.5 to -21.5	4.9 to 10.2	Middelburg and Herman, 2007
Suspended matter in Rhine estuary		-31.5 to -20.2	3.1 to 11.2	Middelburg and Herman, 2007
Suspended matter in Scheldt estuary		-27.5 to -19.3	0.3 to 23.1	Middelburg and Herman, 2007
Suspended matter in Loire estuary		-26.8 to -23.6	6.4 to 8.3	Middelburg and Herman, 2007
Suspended matter in Gironde estuary		-27.2 to -23.1	2.5 to 10.4	Middelburg and Herman, 2007
Suspended matter in Douro estuary		-29.5 to -22.5	3.2 to 9.1	Middelburg and Herman, 2007
Suspended matter in Sado estuary		-25.6 to -22.8	0.5 to 6.5	Middelburg and Herman, 2007
Suspended matter in Godavari estuary	4.6 to 7.0	-28.0 to -23.0	5.1 to 7.8	This study

Table 3: Elemental concentrations and isotopic ratios of organic carbon (OC) and nitrogen (N) in the sediment (sed) and suspended matter (sus) in the Godavari estuary. The bolded data represents upper estuary and other lower estuary. Distance was calculated from the mouth of the estuary.

Stations	Distance (km)	Salinity (psu)	OC _{sed} (%)	TN _{sed} (%)	C/N _{sed}	$\delta^{13}\text{C}_{\text{sed}}$ (‰)	$\delta^{15}\text{N}_{\text{sed}}$ (‰)	POC (%)	PN (%)	CN _{SUS}	$\delta^{13}\text{C}_{\text{SUS}}$ (‰)	$\delta^{15}\text{N}_{\text{SUS}}$ (‰)
Alamuru	55.7	0	0.51	0.05	9.6	-26.2	7.6	1.05	0.15	7.0	-27.0	5.6
Kapileswaram	50.5	0	0.12	0.01	18.5	NA	14.7	1.16	0.17	6.9	-28.0	5.1
Kotipalli	37.1	4	0.28	0.03	8.4	-24.6	7.0	2.45	0.35	7.0	-26.6	7.0
Near Kotipalli	31.9	6	0.91	0.14	6.7	-25.3	5.3	1.83	0.31	5.9	-24.5	7.8
Dangeru	27.8	9	0.72	0.13	5.4	-26.0	6.1	1.40	0.27	5.2	-24.7	7.3
Bramhapuri	24.5	10	0.19	0.01	14.8	NA	11.0	0.62	0.11	5.5	-24.0	6.1
Injarum	21.5	13	0.43	0.06	7.1	-24.8	8.1	0.61	0.12	5.2	-23.9	5.9
Yanam	17.8	20	0.59	0.10	5.9	-24.9	7.5	0.57	0.12	4.9	-23.7	7.6
V.E.	8.7	22	0.18	0.05	3.5	-25.8	8.1	0.25	0.05	4.6	-25.1	6.6
V3	2.5	25	0.77	0.18	4.4	-23.1	6.1	0.20	0.04	5.5	-23.1	6.2
B.E.	0	30	0.21	0.05	3.9	-25.1	6.3	0.28	0.06	4.7	-23.0	6.1

NA: not available

Table 4: The isotopic ratios of carbon and nitrogen in different species of macro benthic fauna.

Benthic fauna	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
<i>Penae</i> sp.	-20.5	7.9
<i>Penae</i> sp-1	-20.3	8.2
<i>Onuphis</i> sp.	-22.6	8.1
<i>Glycera</i> sp.	-21.8	8.8
<i>Prionospio</i> sp.	-23.2	7.7
<i>Spionidae</i> sp.	-23.9	5.9
<i>Gastropoda</i> sp.	-21.8	9.9

Figure: 1: Station locations in the Gautami-Godavari estuary.

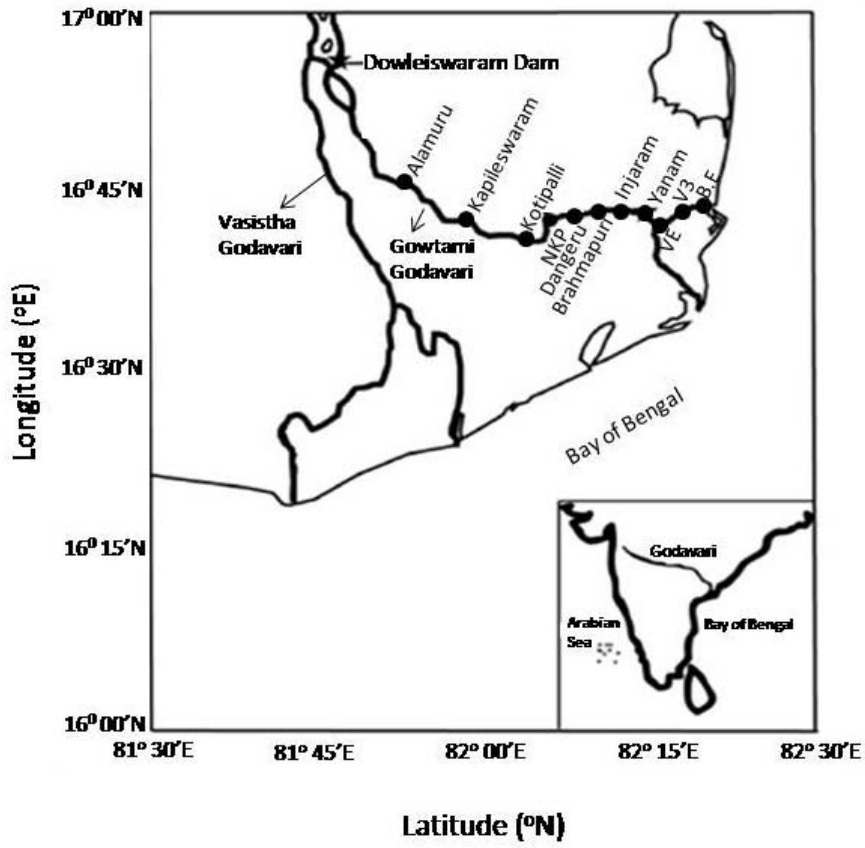


Figure 2: Longitudinal distribution of a) salinity (open circles), Chl-a (closed circles) and ammonia (plus), b) sediment texture, sand (black), silt (stripped), clay (white) and suspended particulate matter (SPM; mg l^{-1}) (line) c) carbon (C_{sus} ; open circles) and nitrogen content (N_{sus} ; closed circles) in suspended matter, and d) carbon (C_{sed} ; open circles) and nitrogen content (N_{sed} ; closed circles) in sediment.

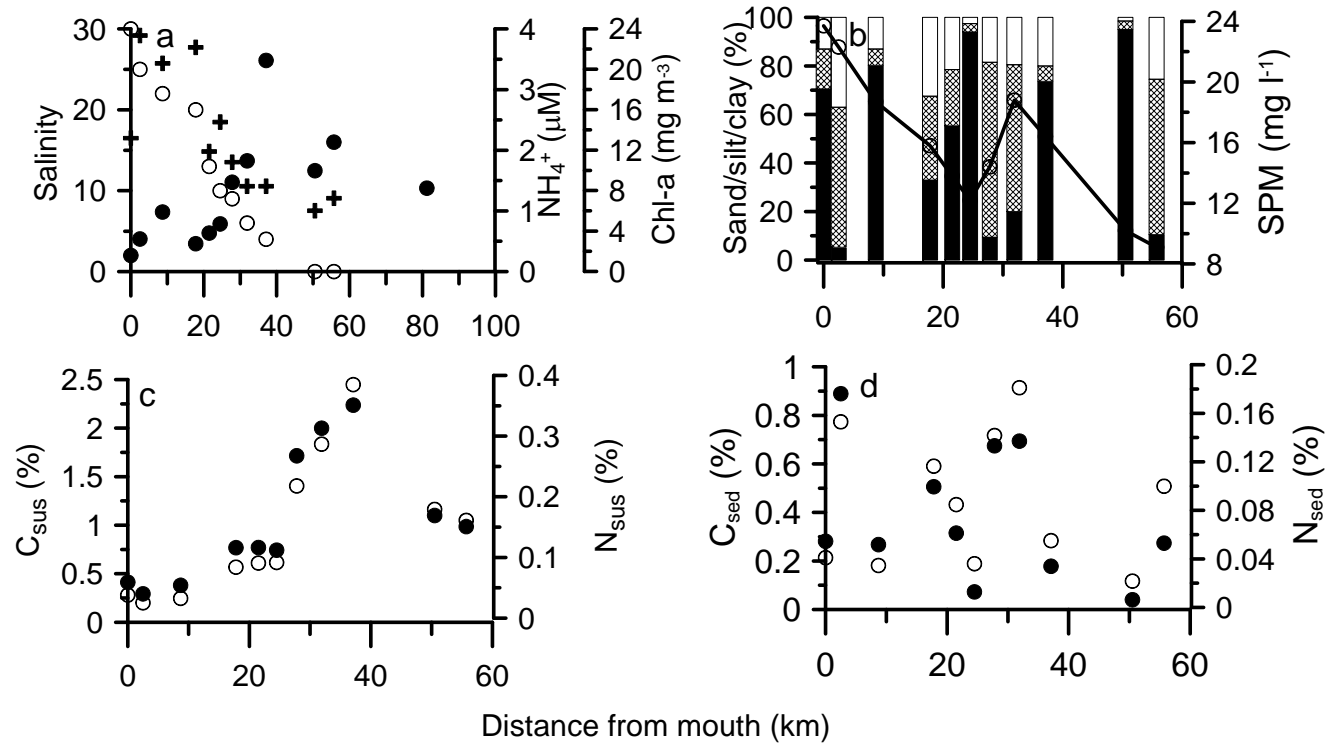


Figure 3. Longitudinal variations in a) $\delta^{13}\text{C}$, b) $\delta^{15}\text{N}$ and c) C/N ratios in suspended matter (open circles) and sediments (closed circles). X-axis denotes distance from mouth. The mixing line between riverine and estuarine end members were shown in (a) for $\delta^{13}\text{C}$ of suspended matter.

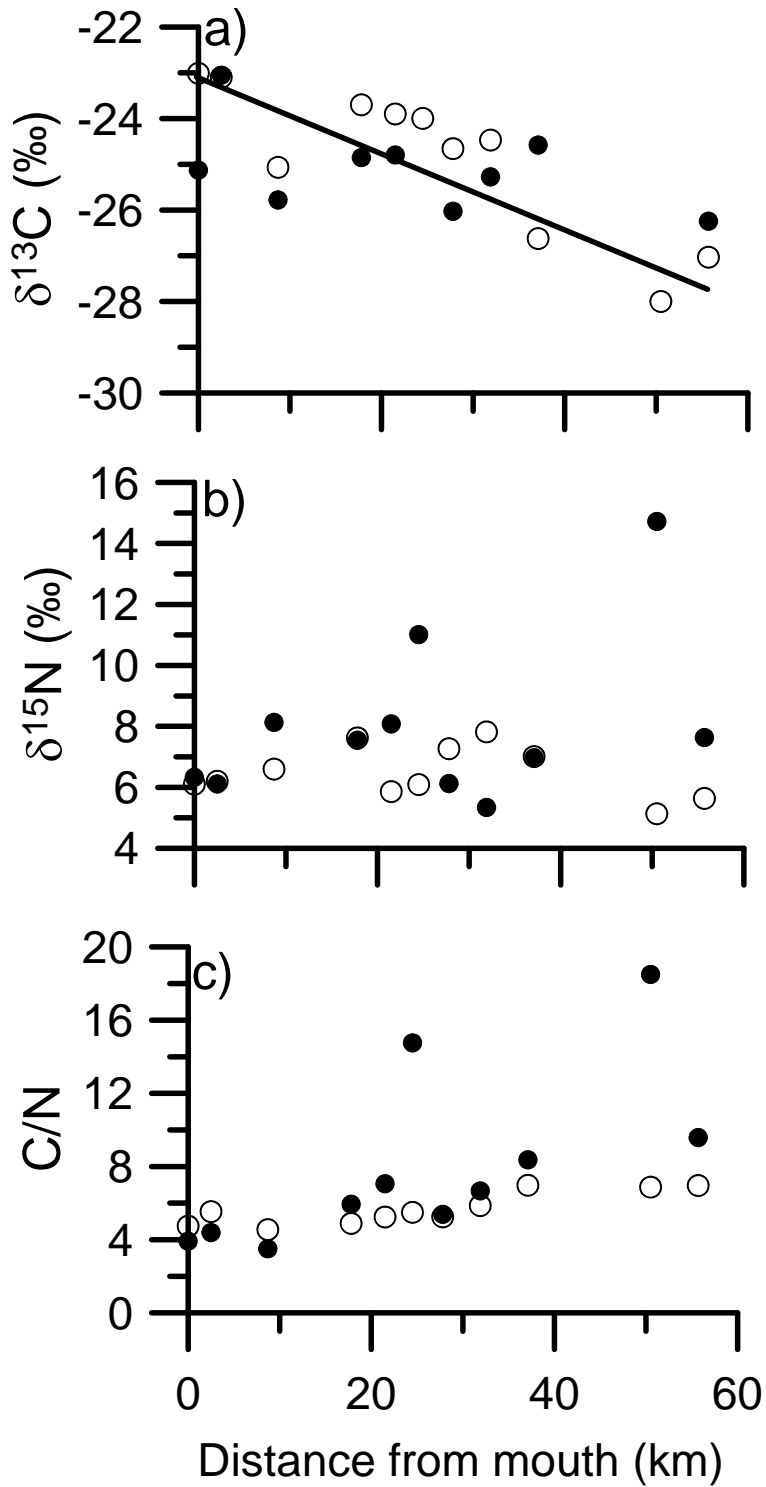


Figure 4. Relationship of a) $\delta^{13}\text{C}$ with $\delta^{15}\text{N}$, b) $\delta^{13}\text{C}$ with C/N and c) $\delta^{15}\text{N}$ with C/N ratio in suspended matter (open circles) and sediment (closed circles). T, E and M represent terrestrial, estuarine and marine end members respectively.

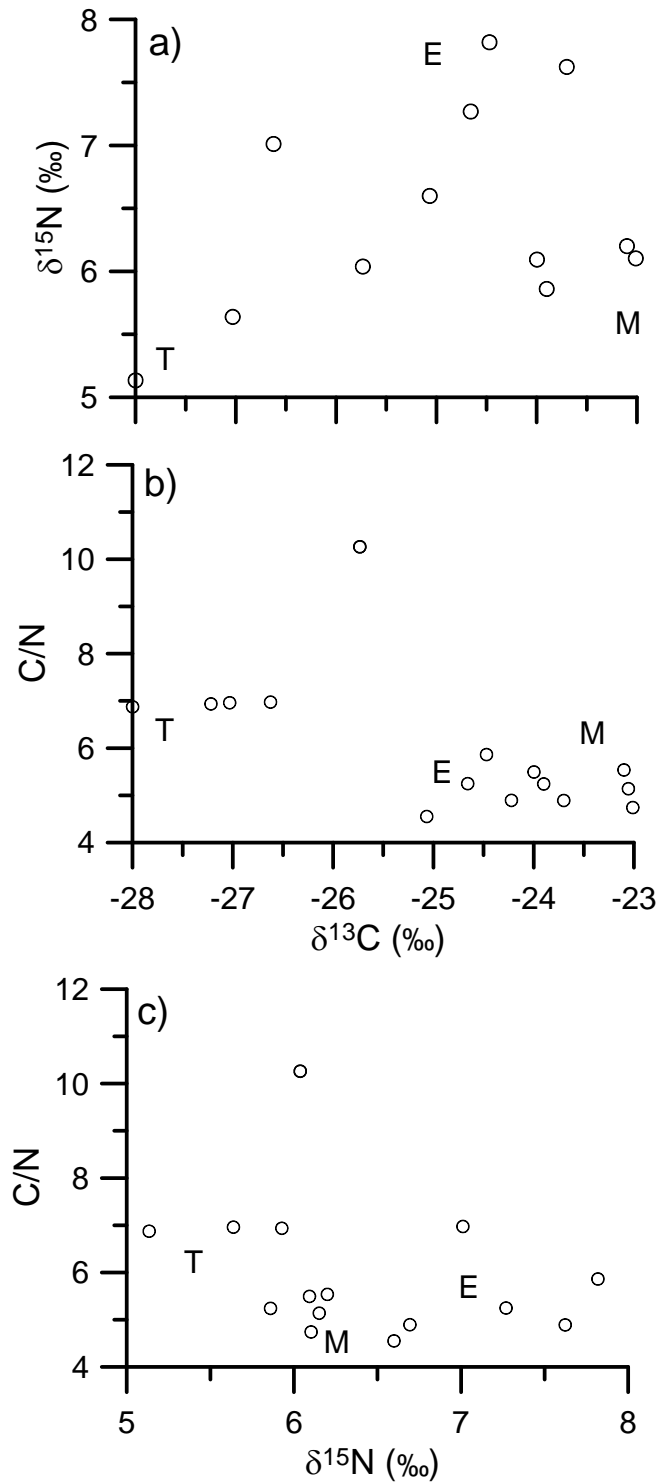


Figure 5: Relationship of salinity with a) suspended particulate carbon (C_{SUS}), b) with $\delta^{13}C$ of suspended particulate carbon ($\delta^{13}C_{SUS}$), c) suspended particulate carbon (C_{SUS}) and nitrogen (N_{SUS}) and d) $\delta^{13}C$ of suspended particulate carbon ($\delta^{13}C_{SUS}$) with chlorophyll-a.

