

Sources, distribution and preservation of organic matter in a tropical estuary (Godavari, India)

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Abstract

Major sources and distribution of organic matter (OM) was examined in a tropical monsoonal estuary, the Godavari using content and isotopic signatures in suspended particulate matter and surface sediments during no-discharge period. The lower (<10km from mouth) and upper (>10 km) estuaries have shown remarkably different features with reference to the sources, distribution and preservation of OM. The upper estuary is characterized by relatively high content of particulate organic carbon (OC) and chlorophyll-a (Chl-a), and low suspended matter and sediment OC. In contrast, the lower estuary is characterized by relatively low content of particulate OC and Chl-a, and high suspended matter and sediment OC. Our data and model results showed that suspended particulate OM is derived predominantly from freshwater phytoplankton in the upper (~85%) and lower (~60%) estuaries, with a minor contribution from estuarine phytoplankton (~25%) and terrestrial C₃ plants (~10%) in the lower estuary, during study period. On the other hand, sediment OM in the upper and lower estuaries derived from both autochthonous and allochthonous sources with nearly equal contributions. Although, relatively high in-situ production was observed in the upper than the lower estuary, relatively low sediment OC was found in the former than the latter region suggesting that strong influence of preservation conditions rather than surface biological production on OC accumulation in sediments. This is attributed to intense transformation of OM by heterotrophs in the upper than the lower estuary because of prevailing conducive conditions for degradation of OM in the upper estuary during study period.

Keywords: Godavari estuary, carbon and nitrogen, stable isotopes, organic matter, sediment, particulate matter

Introduction

Estuaries receive organic matter (OM) from multiple sources, including terrestrial C₃ and C₄ plants, soil, freshwater, estuarine and marine phytoplankton, and domestic and industrial sewage (Andrews et al. 1998; Middelburg and Nieuwenhuize 1998). Contribution of OM from the diverse sources makes the OM cycling in estuaries more complex. Biogeochemical cycling of OM in aquatic systems is of global concern as it strongly influences the global carbon cycle by acting as sink or source for the atmospheric carbon dioxide (CO₂). Being highly productive zones (Countway et al. 2007) estuaries can act as sink, or due to extensive processing of OM (Martin et al. 1971; Schubel and Kennedy 1984; Minor et al. 2001) they can be source of atmospheric CO₂. For example, the Indian estuaries, Godavari (pCO₂: 221-34016µatm; Sarma et al. 2011), Hooghly (220-1200µatm; Mukhopadhyay et al. 2003), Mandovi (110-2300µatm; Sarma et al. 2001) and Cochin (up to 6000µatm; Gupta et al. 2009) were reported as seasonal source of CO₂ to the atmosphere. High CO₂ emissions were reported in the monsoonal Godavari estuary (Sarma et al. 2011) during peak discharge period and attributed to decomposition by heterotrophic activity of the terrestrial OM. Processing of OM in estuaries is, therefore, a key component in the global carbon cycle. However, the quality and composition of OM, resident heterotrophic activity, residence time of particles and water in the estuary strongly influence the processing of OM. In tidal estuaries, processing of OM is more intensive (Heip et al. 1995; Frankignoulle et al. 1998) because of long residence times of water and particles.

Composition of OM in the Indian estuaries, which are under influence of the monsoon climate, follows the seasonal pattern with a predominance of terrestrial OM (allochthonous) during southwest monsoon (discharge period) and in-situ phytoplankton produced OM (autochthonous) during non-monsoon (no-discharge period) season. Quantification of relative contribution from allochthonous and autochthonous pools of OM is important for better understanding the biogeochemical cycling of OM as they have different affinity towards the heterotrophic activity. Though several investigations have been carried out to understand possible sources and biogeochemical cycling of OM in estuaries of the major rivers in the world (e.g. Mantoura and Woodward 1983; Mariotti et al. 1984; Cifuentes et al. 1988; Cauwet and Mackenzie 1993; Peterson et al. 1994; Cai et al. 1998; Middelburg and Nieuwenhuize 1998; Dehairs et al. 2000; Canuel 2001; Hu et al. 2006; Zhang et al. 2007; Sarma et al. 2013 and references therein), the fate of OM is, still, not well understood due to complex interactions between various physical, chemical and biological processes that govern the

composition, distribution and processing of OM in estuaries (Deegan et al. 1985; Sharp et al. 1986; Hobbie 2000).

Sources and distribution of OM is poorly comprehended in the Indian monsoonal estuaries in general and the Godavari estuary in particular. In the mangrove region of the Gowtami-Godavari estuary, Dehairs et al. (2000) reported that the particulate OM is mainly of marine origin. From the same region, Bouillon et al. (2002) reported that terrestrial OM is not a main source for the benthic invertebrate community during pre-monsoon (no-discharge) season. Though some studies were reported from this region (e.g. Bouillon et al. 2000; 2003), they were confined to mangrove region of the estuary. Very recently, Sarma et al. (2013) reported that terrestrial OM is predominant in the estuary. A few studies reported bulk sediment organic carbon (e.g. Krupadam et al. 2007), but no comprehensive studies were carried out so far on the basin scale to understand major sources, relative composition and preservation of OM in the Godavari estuary. The objectives of our study are (i) to investigate the major sources of OM and to quantify the proportional contribution from each source, and (ii) to identify the controlling mechanism for distribution and preservation of OM in sediments of the Godavari estuary. We hypothesize that there are several physical and biological processes controlling the preservation and decomposition of OM such as residence time of water and grain size of sediment in upper and lower parts of the Godavari estuary. We used content, elemental ratios and stable isotopes of carbon (C) and nitrogen (N) ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively) as potential tracers because these are well established and widely used tracers to distinguish the terrestrial versus in-situ sources of OM and their transformation pathways in several estuaries, for example, the Huanghe (Yellow; Cauwet and Mackenzie 1993), the Delaware (Cifuentes et al. 1988), the Schelde (Middelburg and Nieuwenhuize 1998), the Godavari (Dehairs et al. 2000; Bouillon et al. 2002, Sarma et al. 2013), the Pearl (Hu et al. 2006), the Changjiang (Cauwet and Mackenzie 1993; Zhang et al. 2007), and the York river (VA estuary; Countway et al. 2007).

Dual isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) provide better and reliable information than the single isotope studies because some sources have similar $\delta^{13}\text{C}$ but distinct $\delta^{15}\text{N}$ ratios or *vice versa*. For example, estuarine and marine phytoplankton reported to have similar range of $\delta^{13}\text{C}$ (-23.5 to -23.1‰; Thornton and McManus, 1994; Riera and Richard 1996; Andrews et al. 1998; Bouillon et al. 2003) but their $\delta^{15}\text{N}$ ratios are reported to be relatively enriched up to 23‰ (Mariotti et al. 1984; Owens 1985; Cifuentes et al. 1988; Middelburg and Herman 2007) due to assimilation by estuarine phytoplankton of isotopically enriched residual ammonium resulted from nitrification or extensive algal uptake in estuaries. Similarly freshwater and marine phytoplankton have similar range of $\delta^{15}\text{N}$ ratios (Peters et

al. 1978) but distinctly different $\delta^{13}\text{C}$ (-31.5‰ and -23.2‰, respectively; Thornton and McManus, 1994; Dehairs et al. 2000; Middelburg and Herman 2007) due to assimilation by freshwater phytoplankton of isotopically depleted inorganic C (Middelburg and Nieuwenhuize 1998; Bontes et al. 2006).

Since the main aim of this study is the source apportionment of organic matter and to understand its preservation conditions, we measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in surface particulate OM and surface sediments in the Godavari estuary and used dual isotope mixing model to estimate proportional contribution from major in-situ (freshwater, estuarine and marine phytoplankton) and terrestrial (C_3 and C_4 plants, and soil) sources. In addition to water column and sediment characteristics, source apportionment of organic matter provide better understanding on preservation of organic matter in sediments of the Godavari estuary.

Study area

The Godavari is the largest monsoonal river in India that originates in the Western Ghats at an altitude of ~1600 m and travels ~1480 km across the peninsular India before it drains into the Bay of Bengal. The river basin extends from 73°26' to 83°07'E and from 16°16' to 22°36' N with a catchment area of $3.1 \times 10^5 \text{ km}^2$, i.e. ~9.5% of the total geographical area of India (Gupta et al. 1997). It discharges annually about 1.1×10^{14} L of fresh water and ca. 170×10^6 tonnes of sediment, and occupies ninth rank in the sediment transport among the major rivers in the world (Biksham and Subramanian 1988). Major portion of the sediment load, i.e., 87×10^6 tonnes comes from the Deccan traps which constitutes 48% of the drainage basin followed by 27×10^6 tonnes from the Granite and hard rock (39%) and 13×10^6 tonnes from the sedimentary rocks (13%) (Biksham and Subramanian 1988; Vaithyanathan et al. 1988). Most of the fresh water (93-96%) and sediment (95%) discharge occurs during the southwest (SW) monsoon (June-September) season (Biksham and Subramanian 1980; 1988).

The climate variability over the basin changes between semi-arid and monsoonal with a mean annual rainfall of 1512 mm. The river basin receives major rainfall (>80%) during SW and the rest during northeast (NE) monsoon (CPCB 1995). Cultivable land in the upper portion of the drainage basin occupied mostly by agricultural crops of C_4 type (jowar and bajra), while the C_3 plants (cotton and rice) dominates the lower portion. River Godavari bifurcates into two channels after the dam at Dowleswaram, namely the Gowtami Godavari that flows eastward and drains into the Bay of Bengal at Bhiravapalem, and the Vasistha Godavari that flows southward and drains into the Bay of Bengal

at Antarvedi. The present study is confined to the Gowtami Godavari (hereafter Godavari), because it is the larger one from the points of view of the geographic area and the water discharge. In this study, the entire basin of the estuary was categorized into two parts based on distance from the mouth, viz, the lower and the upper estuaries with a distance of <10 km and >10 km from the mouth, respectively.

Material and Methods

The entire Godavari estuary (Fig. 1a) was sampled for water and surface sediments (top ca. 2cm) during no-discharge period (December, 2010). A total of 51 stations were covered in 25 transects (Fig. 1b) with a spacing of ~1 km between the adjacent transects. Van-Veen grab sampler was used for sediment collection and Niskin sampler for water. The material retained on GF/F filter (0.7 μm pore size; Whatman) after passing water (500 ml) under gentle vacuum was extracted to N,N-dimethyl formamide (DMF) and measured chlorophyll-a (Chl-a) using spectrofluorometer (Carry Eclipse, Varian) following Suzuki and Ishimaru (1990). The analytical precision for the method expressed as standard deviation was $\pm 4\%$. Total suspended matter (TSM) was determined by the weight difference of dried 0.22 μm polycarbonate filters before and after filtering of 500 ml water. Sediment grain size analysis (texture) was carried out using standard pipette analysis method (Folk 1974).

Particulate matter was obtained by filtering the water sample (~500 ml) through pre-combusted (400°C, 6h) GF/F filters (0.7 μm pore size; Whatman) under gentle vacuum. After drying (60°C), part of the filter was used for content and isotopes of total nitrogen (TN). For content and isotopic ratios of organic carbon (OC), the filters were acid fumigated in order to remove traces of the inorganic carbon. Bulk sediments were dried at 60°C for 24 hrs and ground to homogeneous fine powders. An aliquot of the sediment was used for content and stable isotopes of TN. For elemental OC and its stable isotope analyses, to the sediment (~10mg) was added ultrapure hydrochloric acid (HCl) in silver cup (Thermo, Germany) to remove the inorganic carbon content. The silver cup was dried (50°C) and repeated the process until complete removal of the inorganic carbon. The instrument used was Elemental Analyser (Flash EA; Thermo) coupled to an Isotopic Ratio Mass Spectrometer (IRMS, Delta V Plus, Thermo Electron, Germany) via ConFlo IV. The detection limit of this method for determination of OC and TN was <1 $\mu\text{g g}^{-1}$. The IAEA standards and laboratory standards such as glutamic acid, alanine, Organic Analytical Standard (OAS) were used as internal standards. Based on repeated analysis of standards, precision for the content of OC and TN were ± 0.05 and $\pm 0.005\%$ (relative standard deviation) respectively. The long term precision of the

instrument is $\pm 0.2\%$ for both C and N isotopes. Content of OC and TN were reported as mg l^{-1} in the particulate matter and wt. % in sediments. Stable isotopic ratios of OC and TN were reported in δ notation as given below.

$$\delta^{13}\text{C (or } \delta^{15}\text{N)} = \left[\frac{X_{\text{samp}} - X_{\text{std}}}{X_{\text{std}}} \right] \times 1000\text{‰}$$

Where, X_{samp} represents $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ of a sample, and X_{std} denotes $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ of standard, for carbon and nitrogen, respectively.

Quantification of OM contributions from different source materials

In the present study, we made an effort to quantify the relative contribution of OM from major sources using isotope mixing model ‘SIAR’ (Stable Isotope Analysis in R), which solves mixing models within a Bayesian framework (Parnell et al. 2008; 2010). It is an open source R package (<http://cran.r-project.org/>). The advantage of this model is 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 together, then most feasible solutions could involve one or other of sources but not both at the same time (Parnell 2010) and therefore, in their posterior distribution these two sources are expected to show negative correlation. Lower correlation coefficient between sources indicates that 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 OM 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 the end members is critical for estimation of proportional contributions from different sources.

In this study, 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 (Table 1). Dominant C₃ and C₄ plant material (leaf, stem and root) and soil samples were collected from drainage basin of the river Godavari for fixing the terrestrial end members. Similarly, the freshwater, estuarine and marine phytoplankton were separated microscopically from water samples collected from the upstream (at Kotipalli), estuary (at Yanam) and marine (at off Yanam) regions of the river Godavari for fixing end members of in-situ sources. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were measured in all these samples and are listed in Table 1. Mean $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios of C₃ (-25.9±1.2‰ and 5.1±2.1‰, respectively) and C₄ (-13.1±1.2‰ and 4.4±2.1‰) land plants, soils (-19.2±2.4‰ and 10.3±2.7‰), freshwater (-31.2±0.6‰ and 6.2±0.5‰), estuarine (-24.4±0.4‰ and 3.5±0.3‰) and marine (-23.6±0.3‰ and 9.2±0.8‰) phytoplankton were taken as end members of terrestrial C₃ and C₄ plants, soil, freshwater, estuarine and marine phytoplankton, respectively. Our measured end member values are very close to the values reported elsewhere for terrestrial C₃ (-30 to -23‰; Smith and Epstein, 1971) and C₄ (-17 to -9‰; Smith and Epstein, 1971; Sackett, 1989) plants, freshwater (-31.5‰; Middelburg and Herman 2007), estuarine (-25.3±0.6; Sarma et al, 2013) and marine (-23.2‰, Dehairs et al. 2000) phytoplankton.

Results

Water column characteristics

Sampling was conducted during dry period when virtually there was no discharge. During this time, surface salinity ranged from 16 at mouth to near zero (0.21) at Kotipalli station (Fig. 2a) which is about 36 km from mouth of the estuary. Surface temperature varied from 21.3 to 27.6 °C, with relatively warmer water in the upper compared to the lower estuary (Fig. 2b; t-test: p<0.001). Surface water Chl-a was higher in the upper (mean: 19.9±3.0 mg m⁻³) than in the lower estuary (3.5±2.6 mg m⁻³; Fig. 3a; t-test: p<0.001). Similarly, particulate OC (POC) was also higher in the upper (mean: 2.2 mg l⁻¹; range: 1.8-2.8 mg l⁻¹; Fig. 3b) than in the lower estuary (1.4 mg l⁻¹; 0.9-2.7 mg l⁻¹; t-test: p<0.001). The POC:Chl-a ratio that represents the contribution of Chl-a to the total particulate OM showed almost tenfold variation from 90.4 to 986.6, with relatively lower ratios in the upper than the lower estuary (Fig. 3c). Particulate N was also relatively higher in the upper (mean: 0.34 mg l⁻¹; range: 0.28-0.45 mg l⁻¹) than in the lower estuary (0.26 mg l⁻¹; 0.13-0.44 mg l⁻¹; Fig. 3d) (t-test: p<0.05). Relatively lower TSM was observed in the upper (2.9±0.9 mg l⁻¹) than in the lower (7.6±2.0) estuary (Fig. 3e; t-test: p<0.001). Carbon isotopes in particulate OM ($\delta^{13}\text{C}_{\text{POM}}$) ranged from -33.5 to -32.0‰ in the upper and from -31.9 to -25.7‰ in the lower estuary (Fig. 4a). Nitrogen

isotopes in particulate matter ($\delta^{15}\text{N}_{\text{sus}}$) varied widely between -2.6 to +7.5‰ in the lower estuary whereas it was only between +4.8 and +11.3‰ in the upper estuary (Fig. 4b). The negative $\delta^{15}\text{N}_{\text{sus}}$ values were observed only in the mangrove region. Excluding this region, $\delta^{15}\text{N}_{\text{sus}}$ varied between 0.5 and 7.5 ‰ with a mean value of 4.1 ± 1.8 ‰. These $\delta^{15}\text{N}_{\text{sus}}$ ratios are similar to those reported in the Changjiang river (1.8-7.3 ‰; Zhang et al. 2007), the Sado (0.5-6.5 ‰; Middelburg and Herman 2007), the Godavari (5.1-7.8 ‰; Sarma et al. 2013) and the Schelde (~1.5 ‰; Mariotti et al. 1984) estuaries. Elemental OC:N ratios in the suspended matter ranged from 4.2 to 10.6 with no significant difference between the upper and lower estuaries (mean: 7.0; Fig. 4c). Results of the SIAR model showed that particulate OM is largely contributed by freshwater phytoplankton (~85%) in the upper estuary (Fig. 5a), whereas, it is contributed by freshwater phytoplankton (~60%), estuarine phytoplankton (~25%) and terrestrial C_3 plants (~10%) in the lower estuary (Fig. 5b) during study period.

Surface sediments

Sedimentary OC (SOC) varied broadly between 0.02 and 1.61% (Fig. 6a), with relatively lower content in the upper (mean: 0.17 ± 0.30 %; range: 0.02 - 1.21%) than the lower estuary (0.82 ± 0.50 %; 0.03-1.61%) (t-test: $p < 0.001$). A similar range of SOC was also reported for the Godavari estuary (0.12-0.91%; Sarma et al. 2013) and the Pearl estuary (0.06-0.94%; Hu et al. 2006). TN in sediment (TN_{sed}) ranged from below detection limits to 0.13% (Fig. 6b), with relatively lower content in the upper (mean: 0.01 ± 0.02 %) than the lower estuary (0.05 ± 0.04 %), similar to the distribution of SOC. Carbon isotopes in surface sediments ($\delta^{13}\text{C}_{\text{sed}}$) are relatively depleted in the upper (mean: -25.4 ± 0.9 ‰; range: -28.6 to -24.4‰) than the lower estuary (-24.0 ± 1.0 ‰; -27.0 to -22.2‰; Fig. 6c). Nitrogen isotopes ($\delta^{15}\text{N}_{\text{sed}}$) varied widely between 1.0‰ and 16.6‰ (mean: 8.0 ± 4.8 ‰) in upper estuary, whereas it varied between 3.4 and 9.0‰ (mean: 6.0 ± 1.4 ‰) in the lower estuary (Fig. 6d). Elemental OC:N ratios in surface sediments ranged between 5.6 and 180 (Fig. 6e) except 565 at one station in the upper estuary. The sediment of the upper estuary is dominated by sand (mean: 78.5%; Fig. 7a) followed by silt (11.5%; Fig. 7b) and clay (10.0%; Fig. 7c), but the lower estuary is dominated by clay (41.5%) followed by silt (31.5%) and sand (27.0%) content. Based on $\delta^{13}\text{C}_{\text{sed}}$ and $\delta^{15}\text{N}_{\text{sed}}$ ratios, SIAR model revealed that in-situ sources such as freshwater, estuarine and marine phytoplankton together contribute up to (~60%), while remaining ~40% contributed by the terrestrial sources such as C_3 land plants and soils in the upper estuary (Fig. 8a). On the other hand, contribution from these two pools (in-situ and terrestrial) are almost equal, i.e., ~50% from each pool

in the lower estuary (Fig. 8b). Contribution from terrestrial C₄ plants to SOC is negligible in the upper estuary and minimal (~10%) in the lower estuary.

Discussion

During study (no-discharge period), the upper estuary is characterized by relatively warmer and low salinity surface water, whereas, the lower estuary is characterized by relatively cooler and high salinity water at surface indicating that intrusion of marine water and occurrence of tidally induced vertical mixing of bottom water with that of surface in the lower estuary.

Distribution of particulate organic matter

Relatively higher phytoplankton biomass (Chl-a: $19.9 \pm 3.0 \text{ mg m}^{-3}$), POC (2.2 mg l^{-1}) and TN (0.34 mg l^{-1}) were found in the upper than in the lower estuary ($3.5 \pm 2.6 \text{ mg m}^{-3}$, 1.4 mg l^{-1} , and 0.26 mg l^{-1} respectively) indicating that particulate organic matter is predominantly of in-situ origin in the former and terrestrial origin in the latter region. The POC:Chl-a ratio in particulate matter, an indicator for contribution of biomass to the total POC (Treguer et al. 1990) is relatively low in the upper (mean: 112 ± 19) than in the lower (480 ± 263) estuary suggesting that a predominance of freshly synthesized OM in the former and re-worked terrestrial OM in the latter region. A strong positive correlation between POC/Chl-a and salinity ($r^2=0.7$, $p<0.001$; Fig. 9a) also indicate that decreasing dominance of autochthonous OM towards mouth of the estuary. It could be due to tidally induced re-suspension of surface sediments as the vertical mixing is evidenced by relatively cooler and high salinity surface water in the lower estuary. Further, relatively higher TSM ($7.6 \pm 2.0 \text{ mg l}^{-1}$) in the lower than in the upper estuary ($2.9 \pm 0.9 \text{ mg l}^{-1}$) also indicates re-suspension of surface sediments in the lower estuary. Bathymetry of the estuary favours re-suspension of surface sediments as it is shallower at the mouth and deep in the mid of the estuary. Re-suspension of sedimentary particles makes the lower estuary more turbid and limit the light availability (Heip et al. 1995; Kromkamp and Peene 1995) for phytoplankton production resulting in low Chl-a in the lower estuary than in the upper estuary.

Sources of particulate OM

Estuaries receive OM from various sources, each of which has a distinct C and N isotope ratios because of differences in isotopic ratios of their source material (Thunell et al. 2004). Mean $\delta^{13}\text{C}$ of particulate OM ($\delta^{13}\text{C}_{\text{POM}}$) found in the upper estuary ($-32.7 \pm 0.4\text{‰}$) is in the range of $\delta^{13}\text{C}$ of freshwater algae (-33.2 to -27.5‰ ; Kao and Liu 1999), and also close to the $\delta^{13}\text{C}$ of riverine

phytoplankton reported from the Rhine estuary (-31.5‰; Middelburg and Herman 2007), Schelde estuary (-30.0‰; Middelburg and Nieuwenhuize 1998) and Changjiang river (-30.6‰; Cai and Han 1998), but depleted than typical terrestrial OM (-29.5 to -24.4‰; Kao and Liu 1999) and marine phytoplankton (-18 to -22‰; Thornton and McManus 1994; Middelburg and Nieuwenhuize, 1998). The mean $\delta^{15}\text{N}_{\text{SUS}}$ in the upper estuary (6.9 ± 2.0 ‰) is in the range of phytoplankton derived OM (~6-8) and is strongly enriched compared to the terrestrial OM (1.8 to 3.5‰; Peters et al. 1978; Wada et al. 1987; Thornton and McManus 1994), sewage OM (1.4 to 2.3‰; Owens and Law 1989; Sweeney and Kaplan 1980; Thornton and McManus 1994) and soil OM (3.6 to 4.4‰; Wada et al. 1987). Mean elemental OC:N ratio (7.2 ± 1.4) found in particulate matter of the upper estuary is close to the OC:N ratio of riverine phytoplankton in the Schelde estuary (7.5) and also in the range of phytoplankton produced OM (6.7; Redfield et al. 1963), but lower than terrestrial OM (>12; Hedges and Mann 1979; Meyers 1994; Hedges et al. 1997; Lamb et al. 2006). All these results strongly suggest that freshwater algae are the major source of particulate OM in the upper estuary. Middelburg and Herman (2007) also reported that the dominance of freshwater algae in the upper region of European estuaries, Schelde, Rhine, Elbe and Rouro. The dominance of riverine OM in the upper estuary is attributed to existence of favourable conditions, such as high nutrients discharged by the river, better light availability due to low TSM, and stable water column due to high flushing times, for production of freshwater phytoplankton during study period. Also, enrichment of $\delta^{13}\text{C}_{\text{POM}}$ with salinity indicates that decreasing influence of freshwater algae towards mouth of the river (Fig. 9b).

The range of $\delta^{13}\text{C}_{\text{POM}}$ found in the lower estuary (-31.9 to -25.7‰; -28.1 ± 1.5 ‰) suggests multiple sources of OM including the fresh water phytoplankton (-33.2 to -27.5‰; Kao and Liu 1999), estuarine phytoplankton (-25.3 ± 0.6 ; Sarma et al. 2013) and terrestrial OM (-29.5 to -24.4‰; Kao and Liu 1999) to the lower estuary during study period. Similarly, the range of $\delta^{15}\text{N}_{\text{SUS}}$ found in the lower estuary (0.5-7.5 ‰; mean: 4.1 ± 1.8 ‰) is also within the ranges of marine OM (6.9 ± 0.7 , Sarma et al. 2013), terrestrial OM (2‰, Peters et al. 1978; 1.8‰, Wada et al. 1987; 1.9‰, Thornton and Mcmanus 1994; 5.4 ± 0.3 , Sarma et al. 2013) and mixing of terrestrial and marine organic matter (1.5-4.5‰, Wu et al. 2003), indicating that possible contribution of OM from both in-situ and terrestrial sources. Elemental OC:N ratios (mean: 7.1 ± 1.3 ; range: 4.2-9.4) found in the lower estuary are also close to OC:N ratios for terrestrial (6.9 ± 0.1), estuarine (4.9 ± 0.3) and marine (5.1 ± 0.2) OM in the particulate matter of the Godavari estuary (Sarma et al. 2013), suggesting that possible contribution of OM from terrestrial and in-situ sources, as revealed by $\delta^{13}\text{C}_{\text{POM}}$ and $\delta^{15}\text{N}_{\text{SUS}}$ results .

Distribution and preservation of OM in surface sediments

Longitudinal distribution of SOC showed a clear demarcation between the upper and lower estuaries (t-test; $p < 0.001$), with relatively lower SOC in the former (mean: $0.17 \pm 0.30\%$) than in the latter ($0.82 \pm 0.50\%$) (Fig. 6a). Despite, relatively higher Chl-a ($19.9 \pm 3.0 \text{ mg m}^{-3}$) and POC (2.2 mg l^{-1}) was observed in the particulate matter of the upper estuary than the lower estuary ($3.5 \pm 2.6 \text{ mg m}^{-3}$ and 1.4 mg l^{-1} , respectively), relatively lower SOC in the upper than the lower estuary could be due to intensive transformation of OM in the upper estuary. Heterotrophic decomposition of OM to CO_2 is more dominant in freshwater than in saline water (Cole et al., 1988), and perennial dominance of heterotrophy was reported with a mean annual production to respiration ratio of 0.14 ± 0.02 in this estuary (Sarma et al. 2009; 2010). Further, particulate OM in the upper estuary is mostly derived from freshwater phytoplankton which is known to be labile and easily degradable by heterotrophic bacteria (Sohi et al. 2001; Lopez-Capel et al. 2006). Relatively long residence time of particles and water (Heip et al. 1995; Frankignoulle et al. 1998) due to low TSM and high flushing times respectively, increases oxygen exposure time of OM in the upper estuary. In addition, the upper estuary is characterized by sandy sediments (sand: $\sim 78\%$) which has more porosity and therefore, organic carbon is exposed to oxygen resulting in more degradation. A strong negative correlation of SOC with sand ($r^2 = 0.98$; $p < 0.001$; Fig. 9c) confirms that profound influence of sediment texture on OM preservation in the upper estuary.

In contrast, despite low Chl-a ($3.5 \pm 2.6 \text{ mg m}^{-3}$) and tidal induced cycles of re-suspension and re-deposition causes degradation of OM, higher SOC ($0.82 \pm 0.50\%$) was found in the lower estuary suggesting that better preservation of OM in the lower estuary. SOC is known to be controlled by grain size of the sediments (Calvert et al. 1995) as OC is generally associated with clay size particles because they provide large surface area and good binding sites for OM adsorption (Mayer 1994a,b; 1999; Keil et al. 1994a,b; Collins et al. 1995). Therefore, relatively higher clay (mean: $41.5 \pm 13.4\%$) and silt ($31.6 \pm 16.0\%$) contents found in the lower estuary may be responsible for better SOC accumulation. Relatively less porosity in the clayey and silty sediments than the sandy sediments restricts oxygen penetration, so the OM escapes from oxidation that results in good preservation. A positive correlation of SOC with clay ($r^2 = 0.62$; $p < 0.001$) and silt ($r^2 = 0.64$; $p < 0.001$) demonstrate that a strong influence of grain size of sediment on the OM preservation in the lower estuary. Therefore, grain size of sediment rather controls SOC accumulation in the Godavari estuary than the biological production in the surface. Very recently, Gireeshkumar et al. (2013) also reported that sediment

grain size is the major controlling factor for preservation of OM in surface sediments of the Cochin estuary, southwest coast of India.

Possible sources of OM to the surface sediments

The range of $\delta^{13}\text{C}_{\text{SOC}}$ observed in the upper (-28.6 to -24.4‰) and lower estuaries (-27.0 to -22.2‰;) are close to the $\delta^{13}\text{C}$ range of terrestrial OM (-29.5 to -24.4‰; Kao and Liu 1999), freshwater algae (-33.2 to -27.5‰; Kao and Liu 1999), estuarine phytoplankton (-25.3±0.6; Sarma et al. 2013) and marine phytoplankton (-23.2‰, Dehairs et al. 2000; -23.1‰, Sarma et al. 2013) indicating that SOC is a broad mixture of OM derived from both terrestrial and in-situ sources. Similarly, the range of $\delta^{15}\text{N}_{\text{sed}}$ found in the upper (1.0 ‰ to 16.6‰) and lower (3.4 to 9.0‰) estuaries also suggest that OM contribution from terrestrial (1.8‰, Wada et al. 1987; 1.9‰, Thornton and Mcmanus 1994; 5.4±0.3, Sarma et al. 2013) and in-situ produced OM by phytoplankton (5 - 7‰; Altabet 1996; Brandes and Devol 2002; Lamb et al. 2006). However, enriched $\delta^{15}\text{N}_{\text{sed}}$ ratios observed in the upper estuary could be due to intense transformation of OM in the upper estuary, because preferential removal of labile nitrogenous compounds during transformation of OM results in enrichment of N isotopic signatures in the residual OM. Moreover, very high OC:N ratios (>100) in sediments also support that occurrence of intense degradation of OM in the upper estuary as OC:N ratio increases with the transformation of OM due to preferential loss of N than C. The results of $\delta^{13}\text{C}_{\text{SOC}}$, $\delta^{15}\text{N}_{\text{sed}}$ and elemental OC:N ratios suggests that contribution of OM from both terrestrial and in-situ sources to the sediments of upper and lower estuaries. Contribution of terrestrial OM (C_3 and C_4 plants and soil) to sediments during study period can be explained by the transport of huge amount of terrestrial OM to the Godavari estuary (2.81×10^6 tonnes year⁻¹; Gupta et al. 1997) through river discharge during southwest monsoon (discharge period), as surface sediments store integrated signals of both the water column production and the river transported terrestrial OM during previous discharge periods. Surface sediment in the estuary preserves signatures of both processes; terrestrial OM brought to the estuary during discharge period and in-situ OM produced by biological production during no-discharge period. Therefore, SOC in surface sediments of the estuary represents modern environment, in contrast to the particulate organic matter which represents the prevailing conditions at the time of sample collection.

Proportional contributions of OM from major sources

The model output showed that particulate OM in the upper estuary is produced mostly by freshwater phytoplankton with a contribution of ~85% (Fig. 5a). Major contribution of OM from freshwater

phytoplankton could be due to prevailing conducive conditions for biological production in the upper estuary. Decreased contribution from freshwater phytoplankton (~60%) with an additional contribution from estuarine phytoplankton (~25%) and terrestrial C₃ plants (~10%) in the lower estuary, (Fig.5b) suggests the influence re-suspension of surface sediment particles. Minor contribution from terrestrial OM (~10%) in the POM of the lower estuary during no-discharge period is attributed to tidal induced re-suspension of surface sediment particles that contain terrestrial OM imported to the estuary during discharge period, as vertical mixing in the lower estuary is evidenced by relatively cooler and high salinity water in the surface and high TSM concentrations. Our results indicate that suspended particulate OM in the Godavari estuary is predominantly (>80%) of in-situ origin during no-discharge period. In contrast to our estimates, based on simple two end member mixing model, Sarma et al. (2013) reported that terrestrial OM contributes ~46% to the suspended particulate matter in the Godavari estuary. This is attributed to temporal variability in proportional contributions from different sources as Sarma et al. (2013) collected samples during southwest monsoon (June-September) when river discharge brings huge amount of terrestrial OM from the drainage basin (Gupta et al. 1997).

On the other hand, the model output revealed that SOC is a mixture of OM derived from both in-situ (produced by freshwater, estuarine and marine phytoplankton) and terrestrial (derived from C₃ and C₄ land plants and soils) pools with slight dominance of the former in the upper estuary (60%; Fig. 8a) and nearly equal contribution of ~50% from each pool (in-situ and terrestrial) in the lower estuary (Fig. 8b). No significant contribution from terrestrial C₄ plants was observed in the upper estuary, while the lower estuary received minor (~10%) contribution. Contribution of OM from in-situ sources to SOC is attributed to dominant in-situ biological production during no-discharge period supported by the conducive conditions for phytoplankton to grow. On the other hand, contribution from terrestrial sources could be due to riverine transport of huge amount of terrestrial OM during discharge period, as surface sediments provide integrated signals of recent past.

Conclusions

In order to understand possible sources of OM and its preservation in sediments of the monsoonal Godavari estuary, we studied content, elemental and stable isotope ratios of organic carbon and nitrogen in suspended particulate matter and surface sediments. Our data and isotope mixing model (SIAR) results demonstrate that particulate OM is derived predominantly from freshwater phytoplankton in both upper and lower estuaries, with some contribution from estuarine phytoplankton and terrestrial C₃ plants in the lower estuary. On the other hand, sediment OM is a

mixture of autochthonous OM produced by freshwater, estuarine and marine phytoplankton, and allochthonous OM produced by terrestrial C₃ plants and soils. About half of the sediment OM in the Godavari estuary is contributed by the in-situ biological sources while remaining half by the terrestrial sources. Despite, relatively higher production in the upper than the lower estuary was found, relatively lower SOC in the former than the latter region, suggest that preservation processes rather controls the sediment OM in the estuary than the surface biological production. This could be due to prevailing favourable conditions for degradation of OM, such as relatively high residence times of particles and water, dominance of relatively fresh OM and sandy nature of sediments. Degradation of OM results in dilution of residual OM with sand in the upper estuary because SOC was reported as wt%. In contrast, existing conditions such as relatively high suspended matter, which helps OM to sink down faster, and high clay and silt content in sediments of the lower estuary are not favourable for degradation of OM resulting in well preservation of OM in the in the lower estuary.

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Figure Captions:

Fig.1: a) Location of the study region (shown by dash lined rectangle), AS: Arabian Sea, BoB: Bay of Bengal; b) Enlargement of the rectangle (dashed line) in Fig.1a; Sampling stations were shown by filled dark circles. Lower estuary was defined as up to the distance of 10km from mouth of the estuary and upper estuary as >10 km

Fig.2: Spatial distribution of (a) surface salinity and (b) surface temperature ($^{\circ}\text{C}$) in the Godavari estuary during study period

Fig.3: Spatial distribution of (a) Chlorophyll-a (mg m^{-3}), (b) particulate organic carbon (mg l^{-1}), (c) POC:Chl-a ratio (d) total nitrogen (mg l^{-1}), in suspended matter and (e) total suspended matter (mg l^{-1}) in the Godavari estuary during study period

Fig.4: Spatial variability in (a) $\delta^{13}\text{C}$ of particulate OM, (b) $\delta^{15}\text{N}$ of total nitrogen and (c) elemental OC:N ratios in particulate matter of the Godavari estuary.

Fig.5: Proportional contributions from source materials, terrestrial C_3 (TC_3), and C_4 (TC_4) plants, soils, freshwater (FP), estuarine (EP) and marine phytoplankton (MP) to the suspended particulate matter of the (a) upper estuary and (b) lower estuary during study period. Boxes indicate credibility internals of 95% and 75% for contribution from each source.

Fig.6: Spatial distribution of (a) organic carbon (%), (b) total nitrogen (%), (c) $\delta^{13}\text{C}$ of organic carbon (‰), (d) $\delta^{15}\text{N}$ of total nitrogen (‰) and (e) elemental OC:N ratios in surface sediments of the Godavari estuary.

Fig.7: Distribution of (a) sand (%), (b) silt (%) and (c) clay (%) content in surface sediments of the Godavari estuary.

Fig.8: Proportional contributions from source materials, terrestrial C_3 (TC_3), and C_4 (TC_4) plants, soils, freshwater (FP), estuarine (EP) and marine phytoplankton (MP) to the sediment organic matter of the (a) upper estuary and (b) lower estuary during study period. Boxes indicate credibility internals of 95% and 75% for contribution from each source.

Fig.9: (a) Variation of POC/Chl-a with salinity and (b) seaward enrichment of $\delta^{13}\text{C}_{\text{POM}}$ in particulate matter of the Godavari estuary during study period, and (c) correlation between SOC(%) and sand (%) content in surface sediments of the upper Godavari estuary

Table caption:

Table 1: Details and their stable isotope ratios of terrestrial end members (C_3 and C_4 plants and soils) collected from the drainage basin of the river Godavari, and in-situ end members (freshwater, estuarine and marine phytoplankton) collected from within the river Godavari.

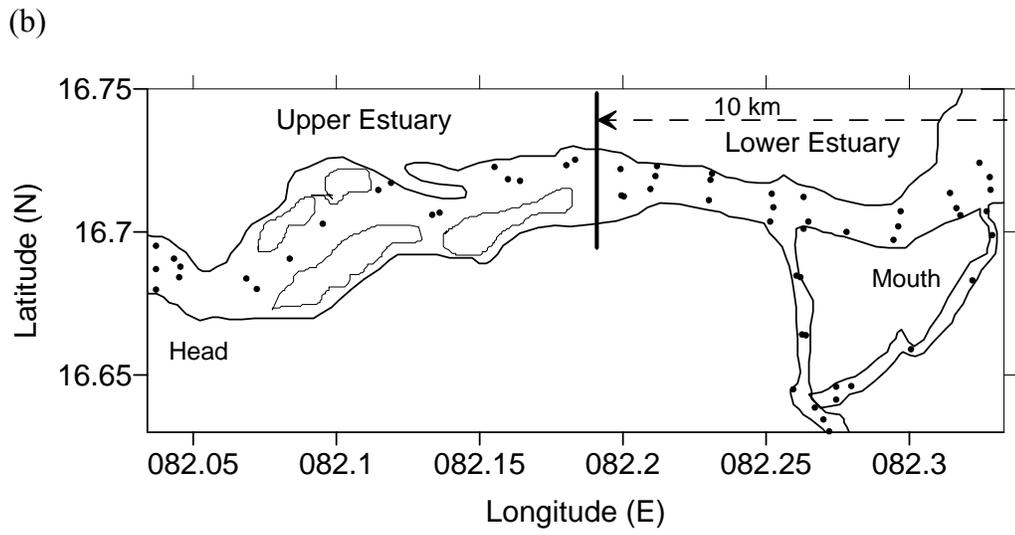
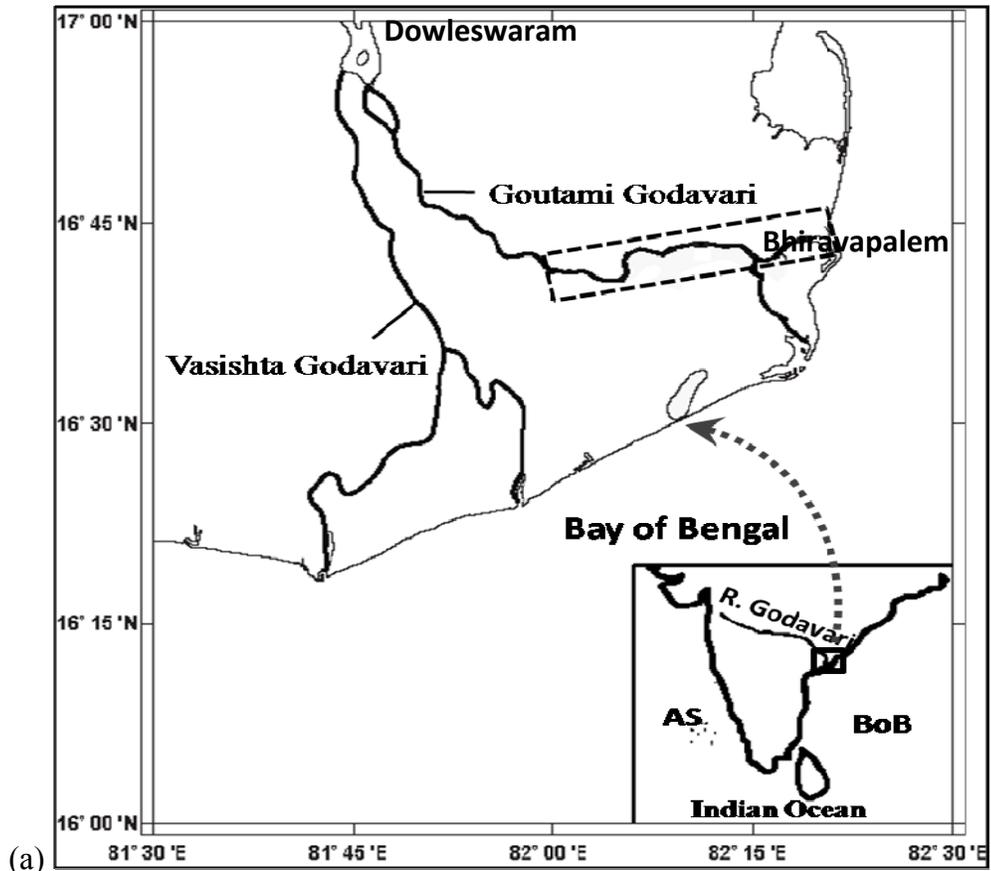
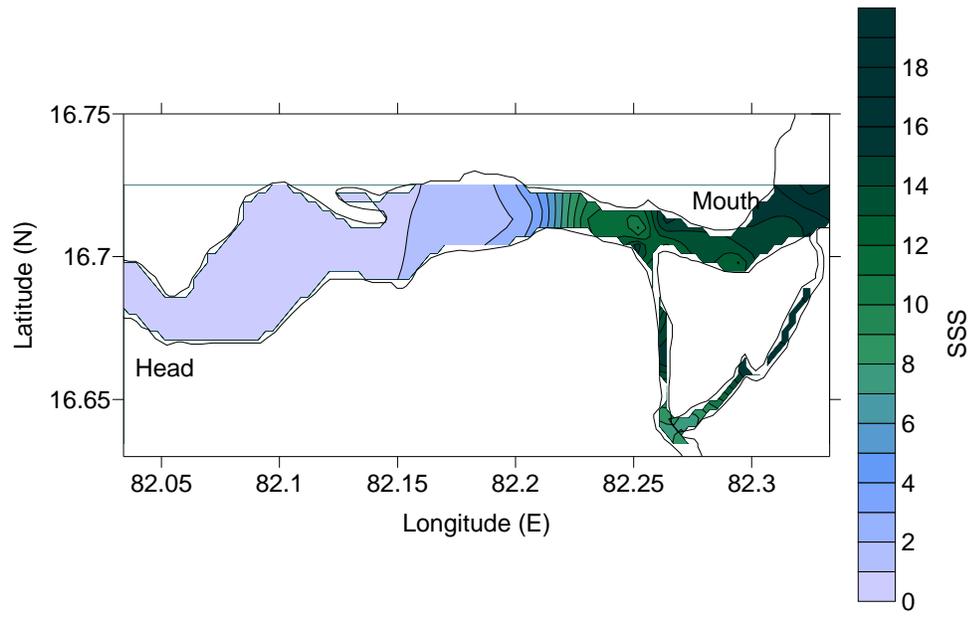


Fig 1

(a)



(b)

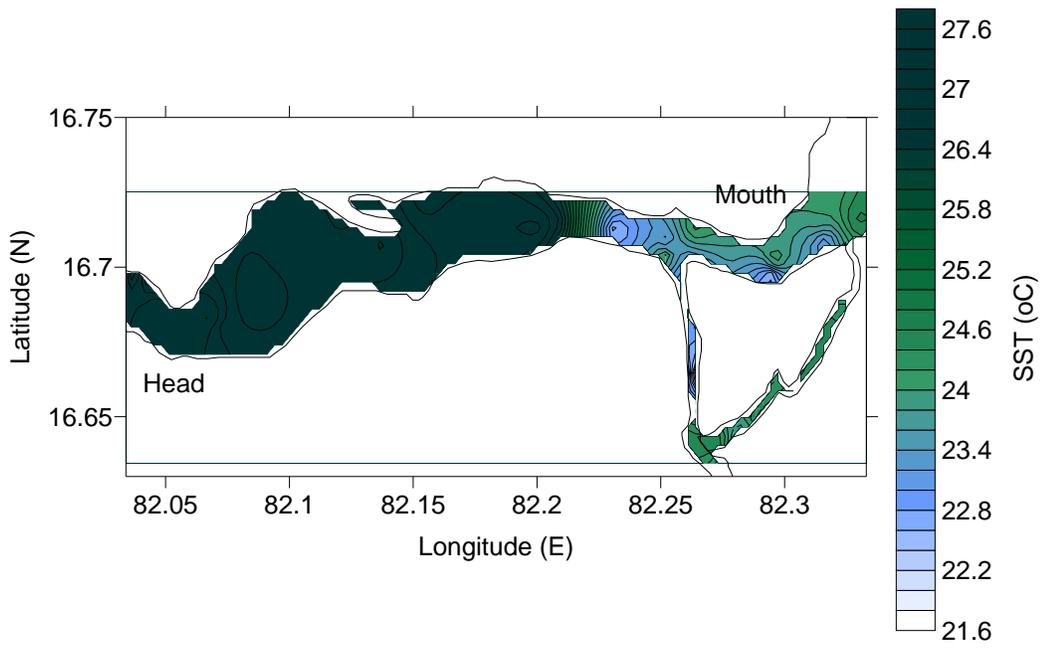
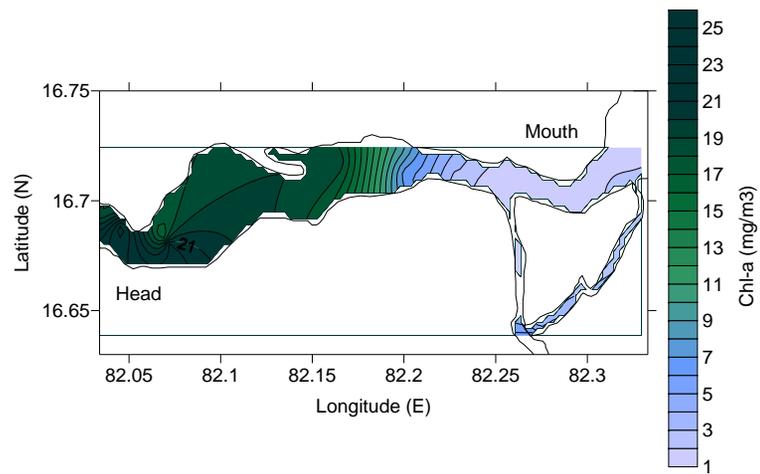
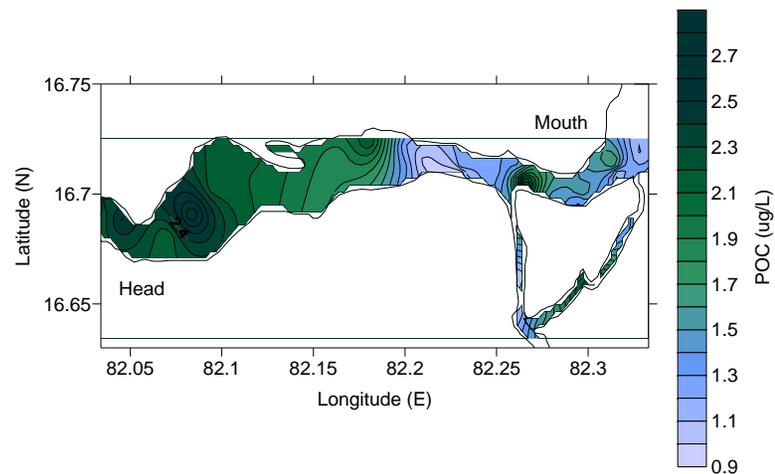


Fig. 2

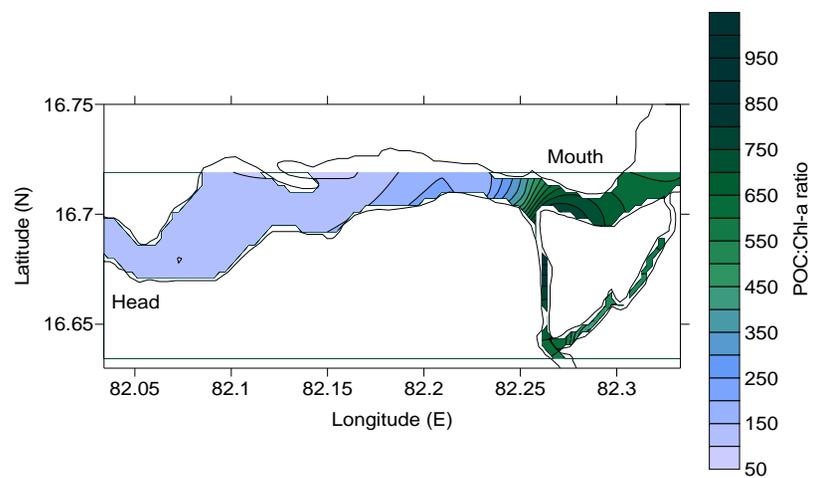
(a)



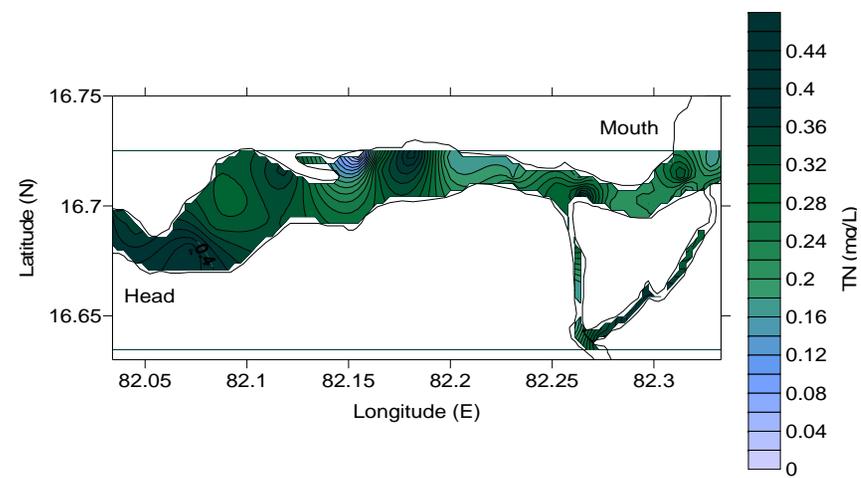
(b)



(c)



(d)



(e)

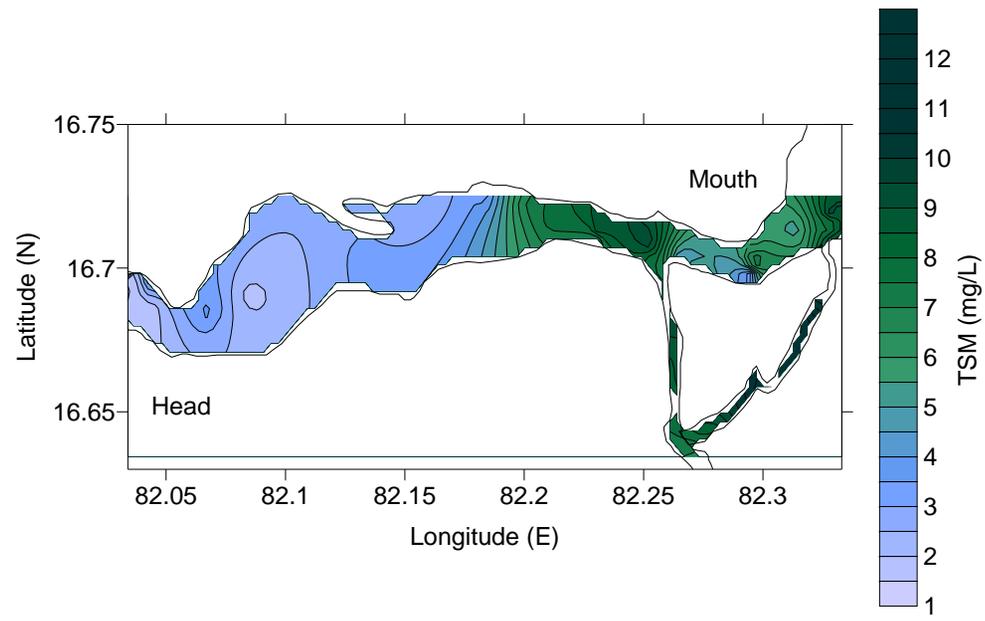


Fig. 3

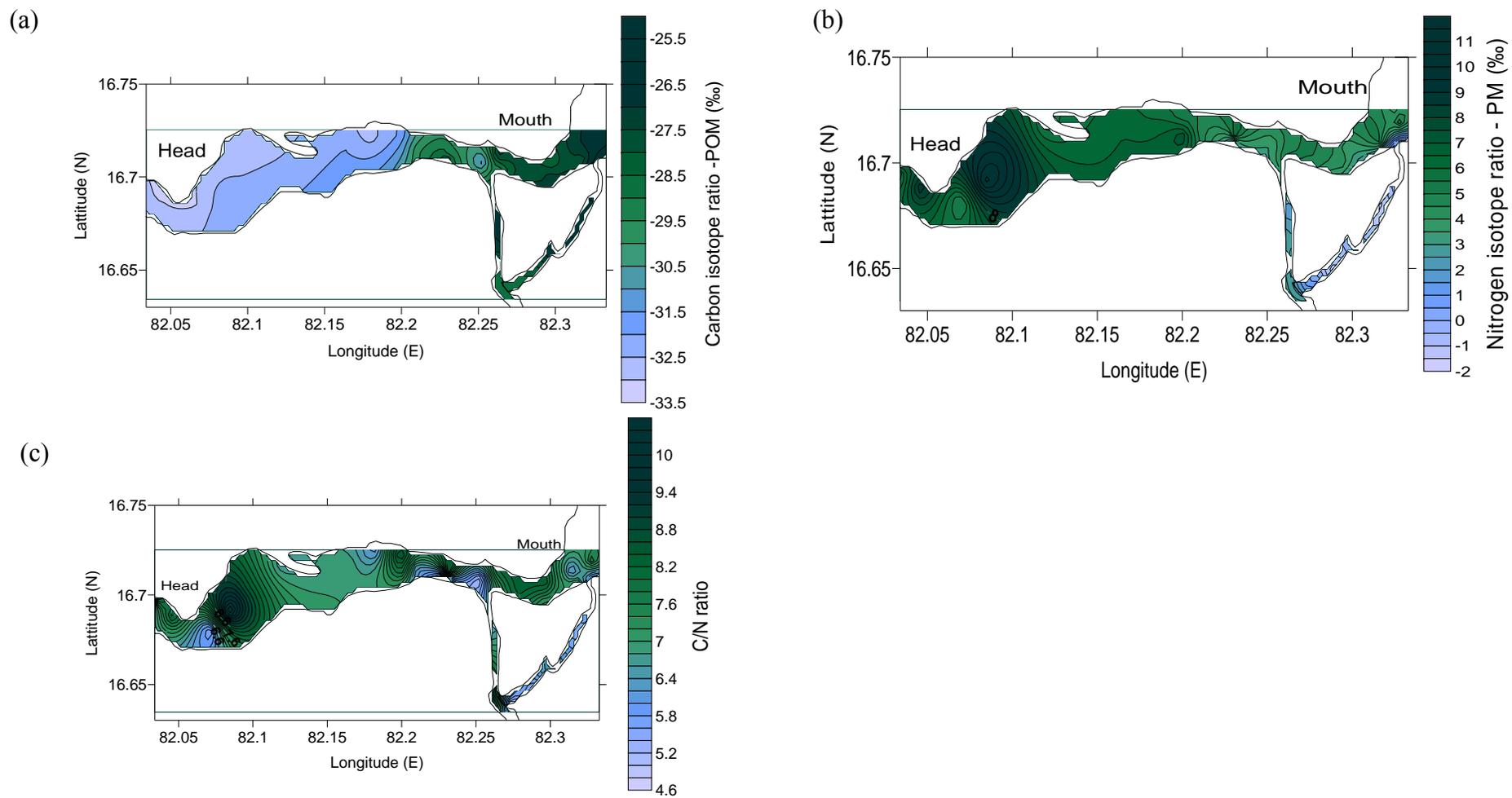


Fig.4

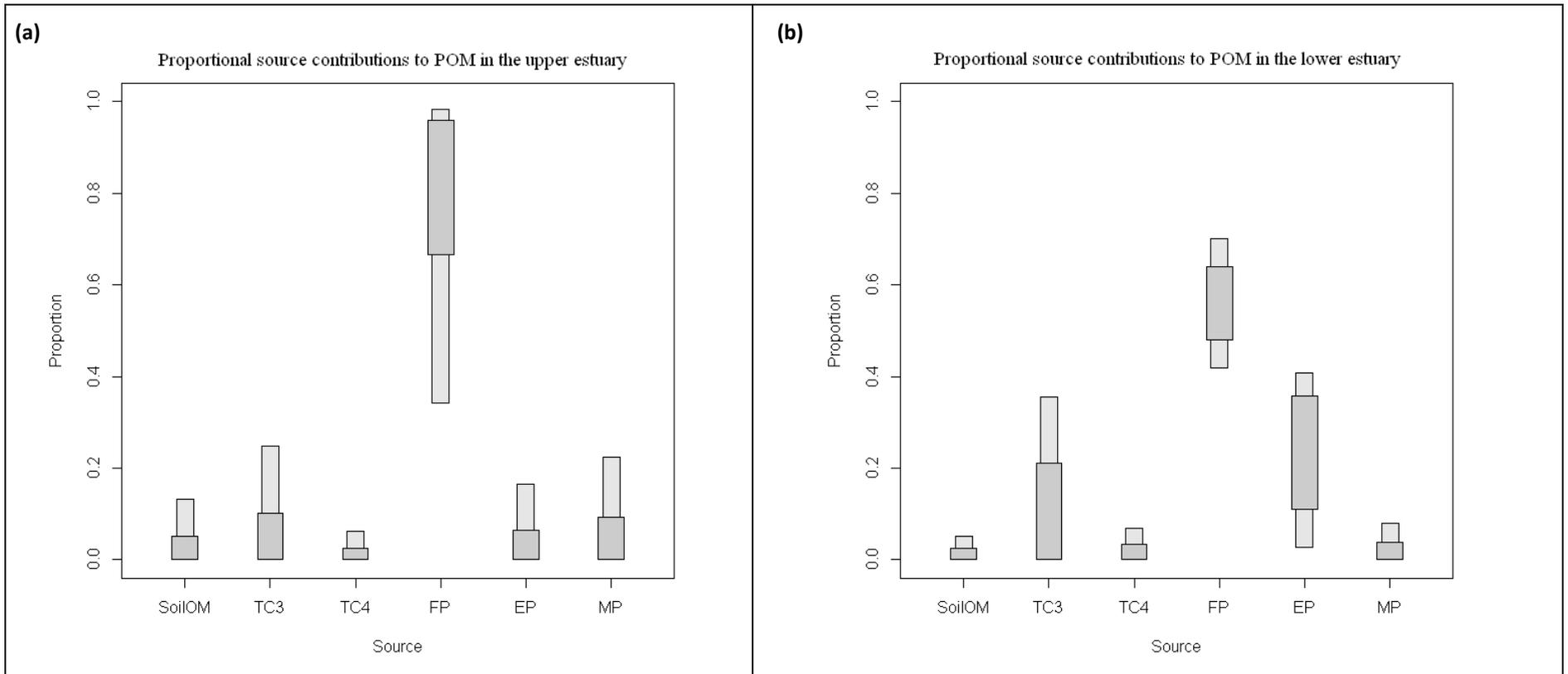
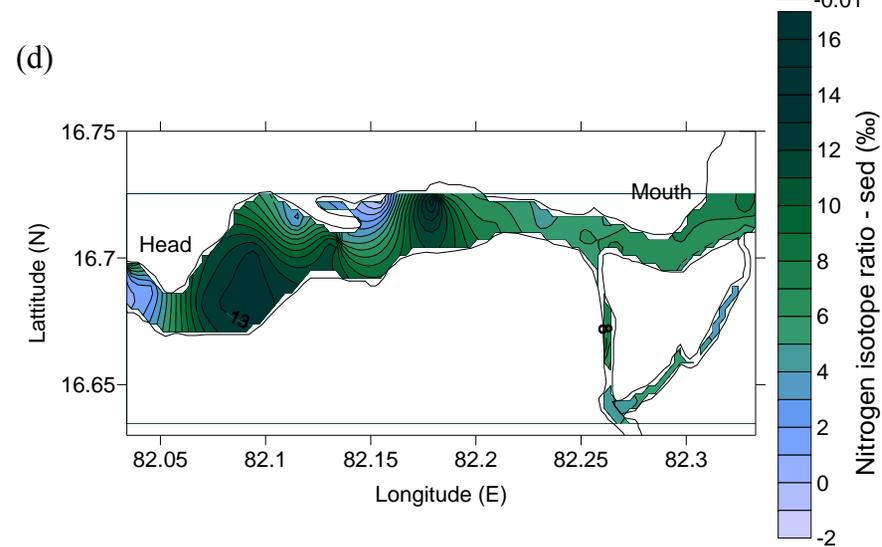
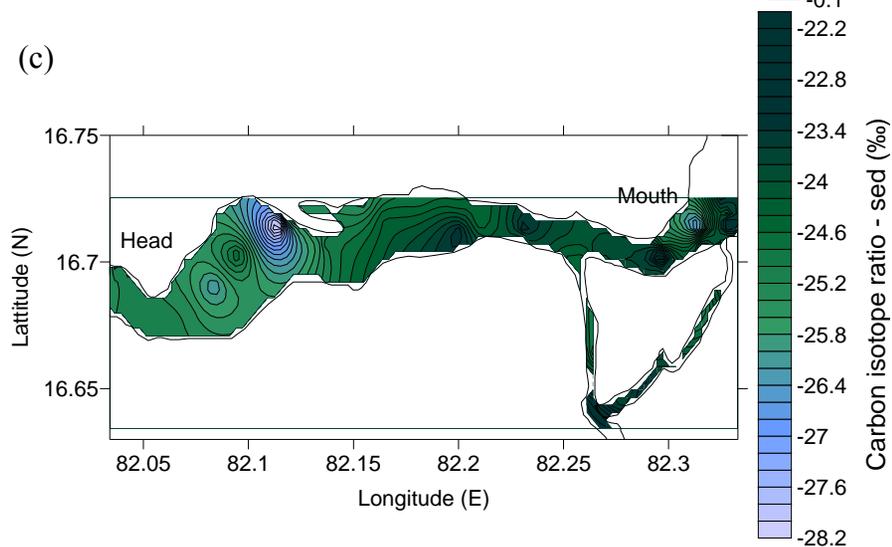
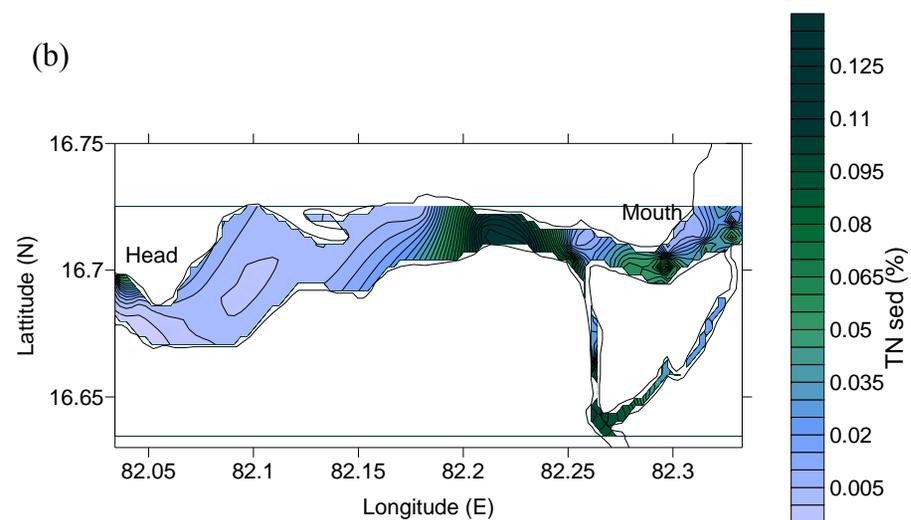
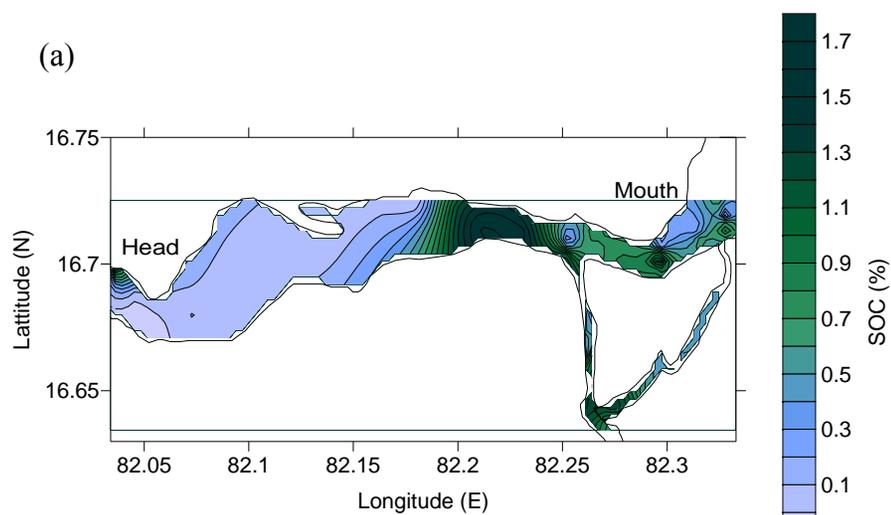


Fig. 5



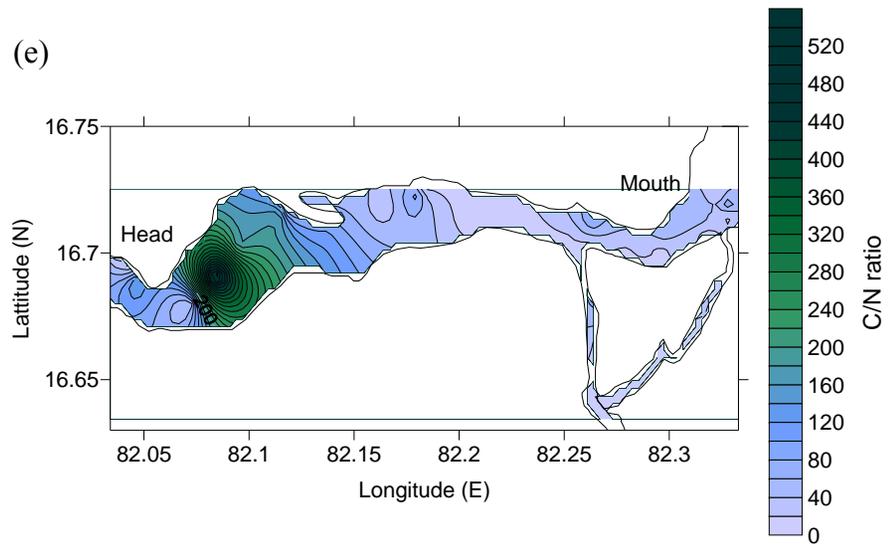


Fig. 6

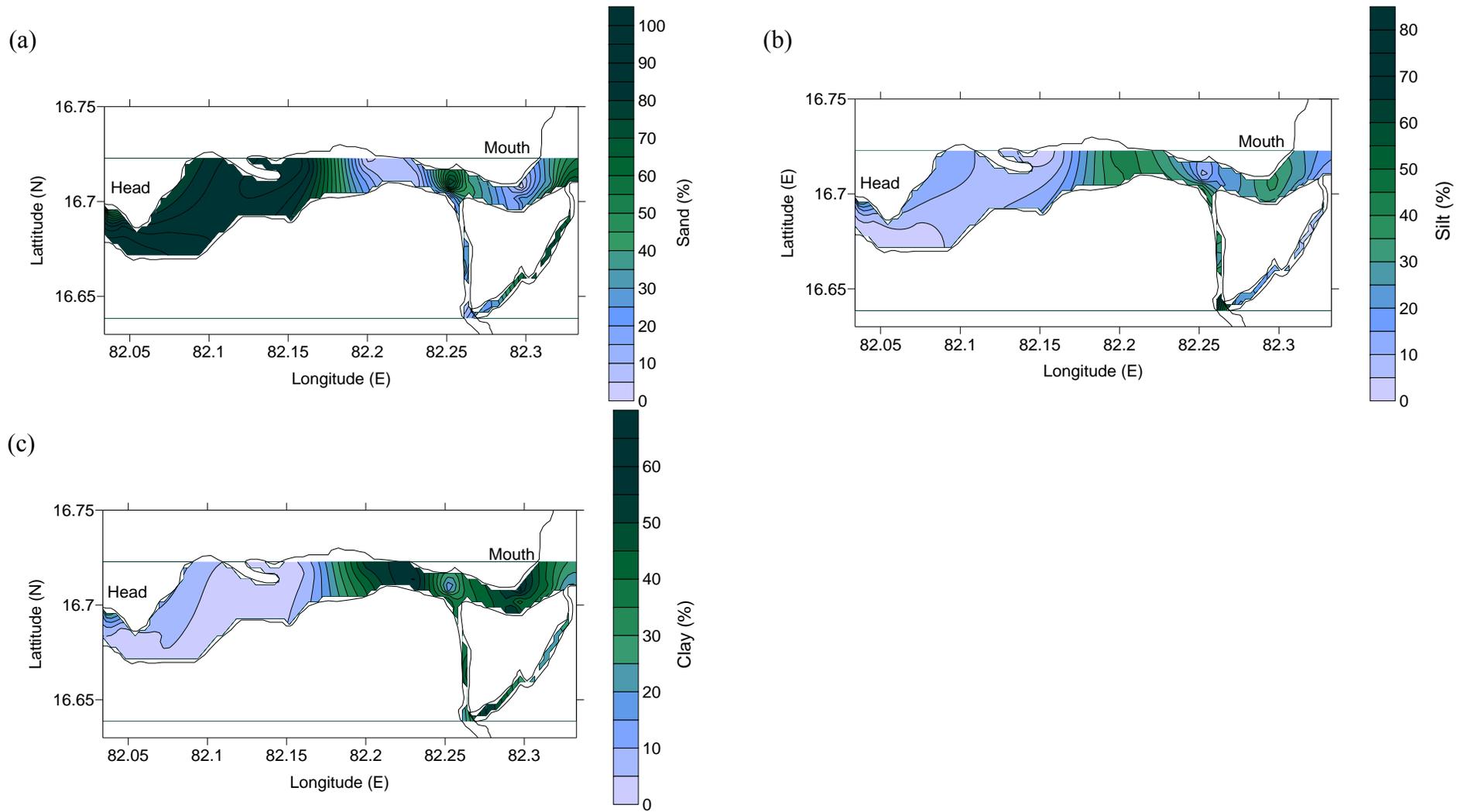
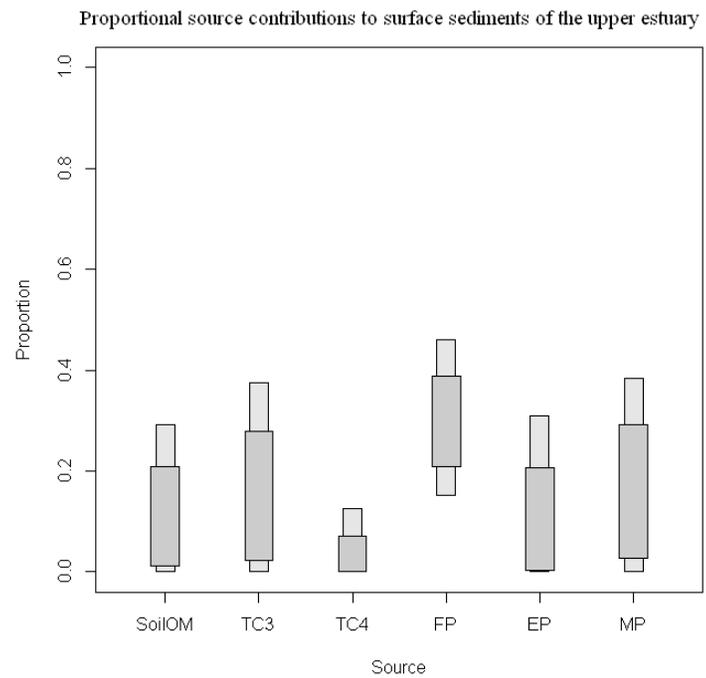


Fig. 7

(a)



(b)

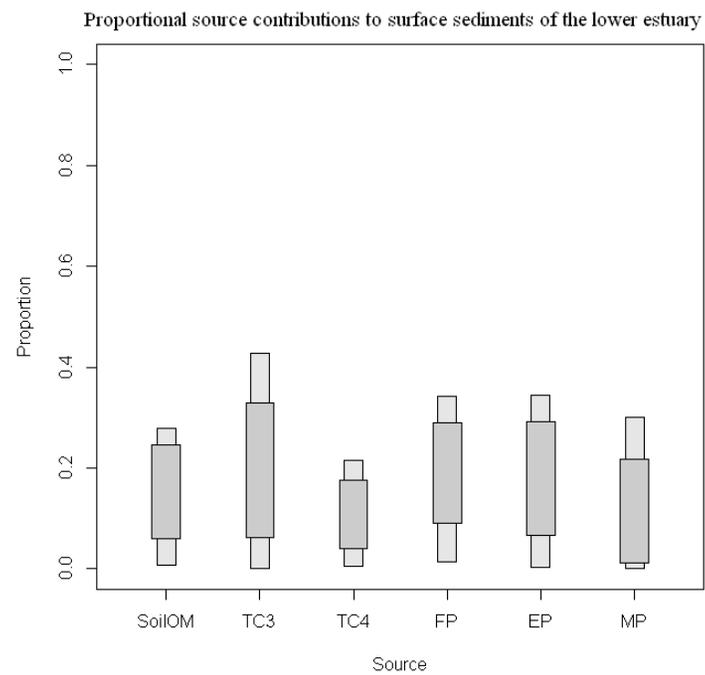


Fig. 8

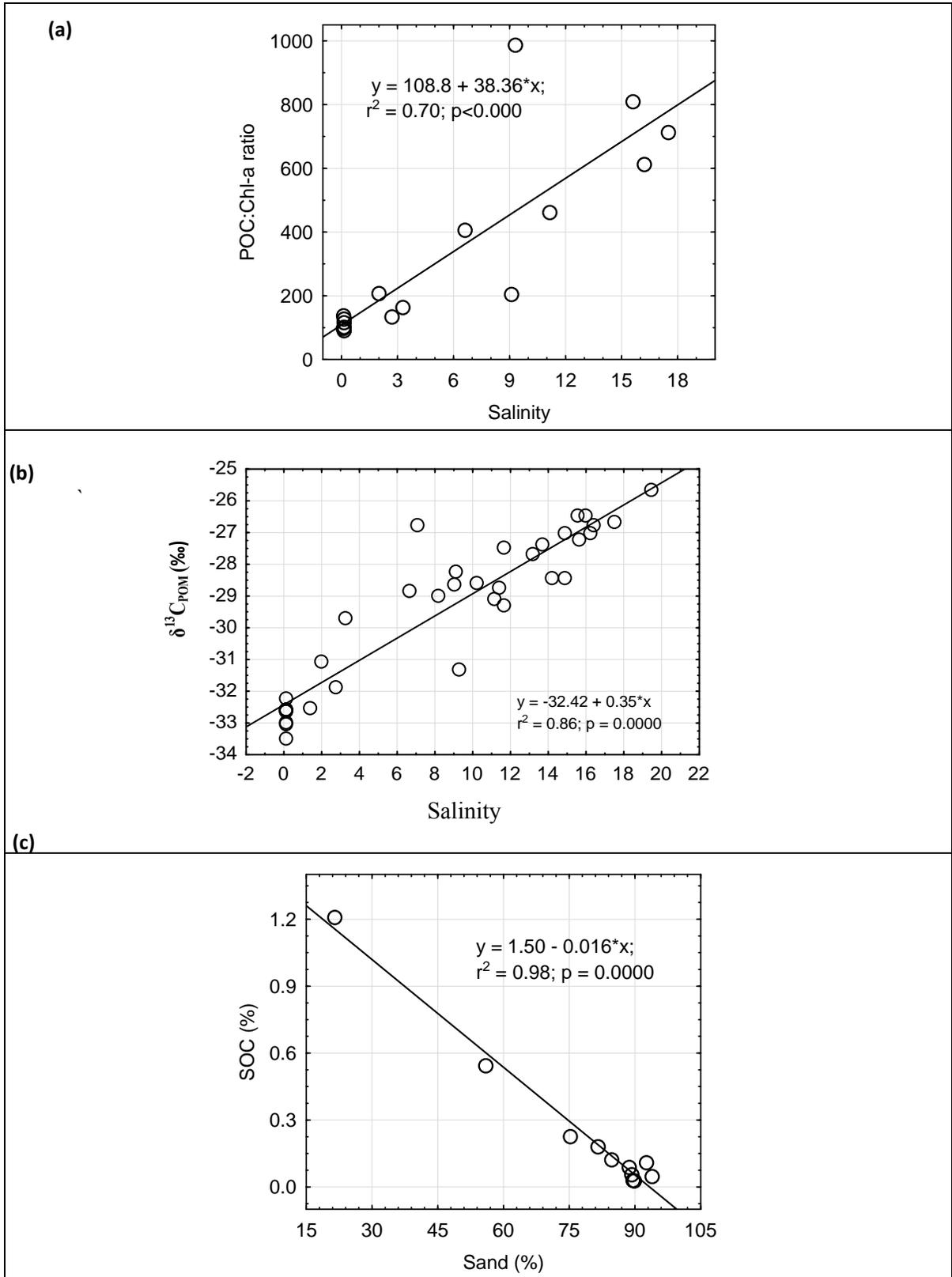


Fig. 9

Type of sample	Latitude ($^{\circ}$ N)	Longitude ($^{\circ}$ E)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
Terrestrial C₃ plants				
Rice (leaf)	17.676	80.889	-26.4	6.1
Rice (root)	17.676	80.889	-26.7	8
Cotton (leaf)	18.873	79.849	-24.0	2.6
Cotton (stem)	18.873	79.849	-24.7	7.5
Turmeric (leaf)	19.017	78.654	-25.3	3.6
Turmeric (root)	19.017	78.654	-26.0	3.7
Turmeric (Stem)	19.017	78.654	-24.6	4.9
Wheat (leaf)	20.009	74.133	-27.4	2.5
Wheat (stem)	20.009	74.133	-27.2	7.8
Wheat (root)	20.009	74.133	-26.9	5.0
Terrestrial C₄ plants				
Sugarcane (leaf)	19.534	74.533	-13.0	1.3
Sugarcane (stem)	19.534	74.533	-13.0	2.9
Maize (corn) leaf	19.282	76.162	-13.2	2.3
Maize (corn) stem	19.282	76.162	-16.3	4.7
Bajra (leaf)	19.071	76.481	-13.4	4.2
Bajra (stem)	19.071	76.481	-13.0	6.4
Bajra (root)	19.071	76.481	-12.7	5.6
Sorghum (leaf)	18.805	77.784	-12.6	4.0
Sorghum (stem)	18.805	77.784	-12.1	8.8
Sorghum (root)	18.805	77.784	-11.7	3.6
Soils				
Surface soil	19.931	73.859	-20.8	7.4
Surface soil	20.023	73.729	-17.0	6.7
Surface soil	20.005	73.631	-15.5	7.4
Surface soil	19.994	73.906	-18.6	8.9
Surface soil	20.011	74.005	-18.1	11.2
Surface soil	20.009	74.133	-17.2	10.9
Surface soil	19.886	74.487	-21.4	11.6
Surface soil	19.771	74.615	-19.9	13.3
Surface soil	19.534	74.533	-23.4	7.9
Surface soil	19.555	74.925	-17.4	10.3
Surface soil	19.64	74.901	-18.8	14.4
Surface soil	19.623	75.026	-17.7	14.8
Surface soil	19.306	75.981	-17.4	11.3
Surface soil	19.282	76.162	-15.3	6.9
Surface soil	19.225	76.364	-17.0	12.0
Surface soil	19.071	76.481	-17.2	7.3

Surface soil	19.019	76.727	-16.0	9.2
Surface soil	18.805	77.784	-20.3	7.4
Surface soil	18.863	77.959	-20.2	9.4
Surface soil	19.017	78.654	-22.1	9.0
Surface soil	19.106	78.789	-23.4	12.9
Surface soil	18.873	79.849	-23.5	7.3
Surface soil	18.859	79.961	-20.0	12.2
Surface soil	18.288	80.483	-19.4	11.8
Surface soil	17.676	80.889	-21.3	15.3
Freshwater Phytoplankton				
At Kotipalli*	16.697	82.033	-31.2±0.6	6.2±0.5
Estuarine Phytoplankton				
At Yanam*	16.715	82.209	-24.4±0.4	3.5±0.3
Marine Phytoplankton				
At off Yanam *	16.761	82.535	-23.6±0.3	9.2±0.8

*: 4 samples were collected from the same region and mean values were given Table 1: