Sources and fate of organic matter in suspended and bottom sediments of the Mandovi and Zuari estuaries, western India

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Organic carbon (OC), total nitrogen (TN) and stable carbon and nitrogen isotopic compositions were measured in suspended particulate matter (SPM) and surface sediment along estuaries of Mandovi and Zuari rivers, two small mountainous river systems in western India during wet and dry seasons, to characterize the sources of organic matter (OM) in these systems. Unlike major rivers, SPM concentrations increase seaward with a general trend of decreasing particulate organic carbon (POC) in these rivers, mostly due to the presence of estuarine turbidity maximum (ETM) located downstream of the estuaries. POC and particulate nitrogen (PN) were higher in the Mandovi than in the Zuari estuary. Except during wet season in the Mandovi, POC/PN and δ^{15}N were altered by biogeochemical processes in both the estuaries and are not indicators of source organic matter. PN/POC and $\delta^{13}C_{org}$ indicated the dominance of terrestrial plant-derived OM and terrestrial soil-derived OM respectively, in the Mandovi and Zuari estuaries during wet season. The $\delta^{13}C_{org}$ versus salinity plot indicated increasing proportions of marine OM seaward in both estuaries during dry season. OC and TN in the sediments of both estuaries were much lower than in the overlying suspended matter. The mean $\delta^{13}C_{org}$ in the sediment and SPM were similar in both the seasons in Mandovi and only during wet season in Zuari estuary. Uniform mean values of $\delta^{13}C_{org}$ in the lower estuary and bay of Zuari indicated efficient mixing of sediments during wet season. Sediments with relatively high $\delta^{13}C_{org}$ and low δ^{15}N in the upper estuary of Zuari were related to anthropogenic contamination by sewage effluents during dry season. It is estimated that each river contributed at least ~20% terrestrial organic carbon (TOC) to the coastal system during wet season and received similar quantity of TOC during dry season. Since there are more than 10,000 small rivers originating from monsoon-dominated and/or mountainous regions globally, it must be appreciated that their total TOC contribution to the coastal system must be substantial.

Keywords: Carbon and nitrogen isotopes, estuaries, sediments, suspended particles.

Introduction

RIVERS transport sediment as bed load and in suspension, and bed load is usually <10% of the total load[1]. Milliman and Meade[2], and Degens *et al.*[3] estimated the annual global river discharge reaching the seas and oceans at 13.5×10^{15} and 16×10^{15} g respectively. Data gathered by the SCOPE/UNEP International Carbon Project indicate that the particulate organic carbon (POC) in world rivers varied between 1% and 8% of the total suspended matter (TSM). Rivers with low TSM concentrations (<15 mg/l) exhibit the highest relative POC contents, whereas those with high TSM concentrations (500–1500 mg/l) display the lowest relative POC contents[4]. Although POC from major rivers is mostly from allochthonous sources, the sources of POC in the medium (<200 km length) and minor (<100 km length) rivers[5] are yet to be precisely determined. Since there are numerous small mountainous rivers (more than 10,000), Milliman and Syvitski[6] suggested that the sediment contribution from them is grossly underestimated and more research is needed to appreciate their role in discharging sediment. Except the Indus and Narmada–Tapi rivers, all other rivers bringing sediment load to the coastal eastern Arabian Sea are moderate and minor-sized and originate in mountainous regions[5]. Run-off from these rivers is high during wet season (monsoon) and negligible during dry (non-monsoon) season. Circulation in the estuaries of these rivers is dominated by tidal and wind-driven currents during dry season. In view of the contrasting seasonal hydrodynamic conditions in these tropical rivers, the river estuaries are expected to show relatively high suspended particulate matter (SPM) and reduced production during wet season, and autotrophic production and active biological and geochemical processes during dry season. Here we report organic carbon (OC), total nitrogen (TN)

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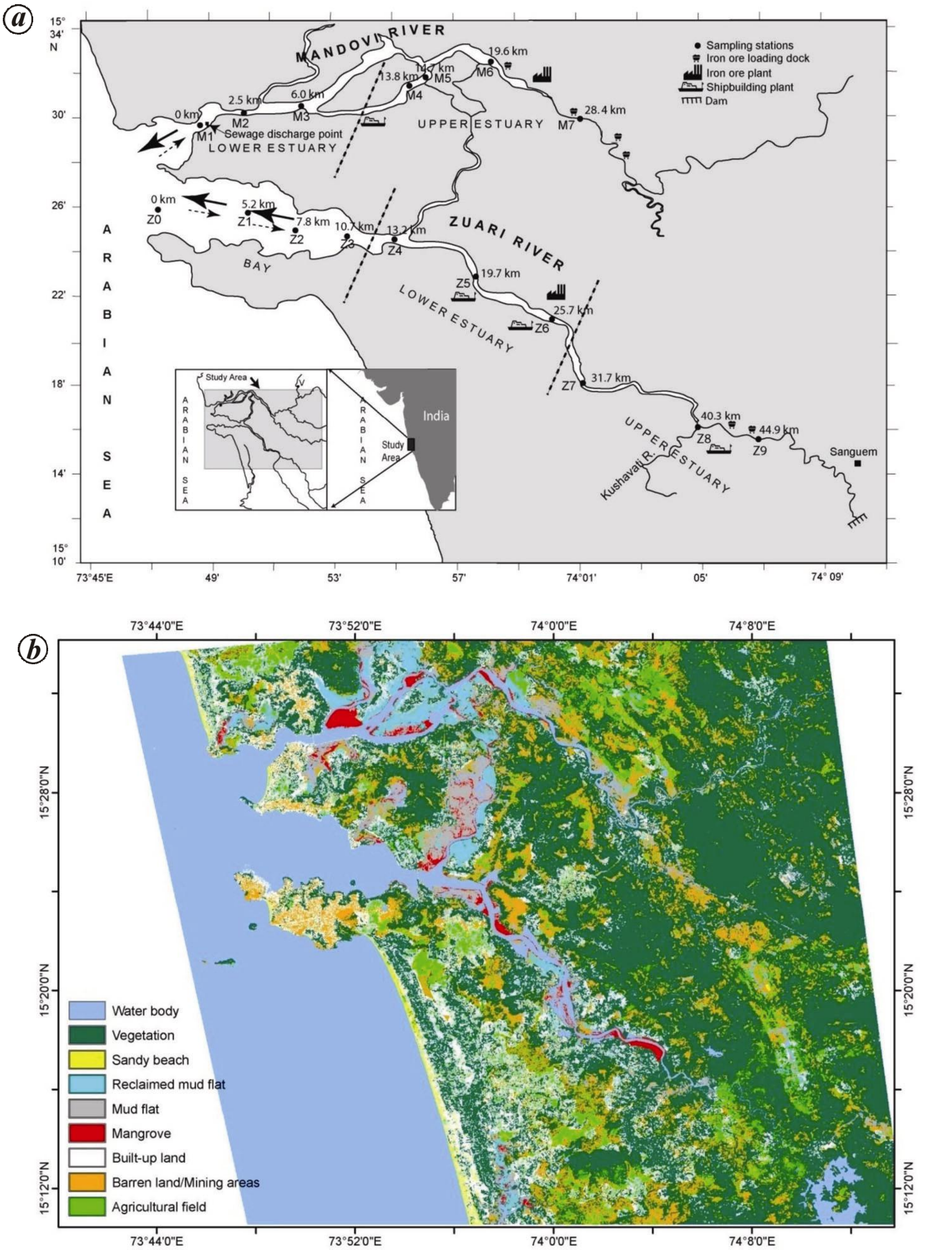

Figure 1. ***a***, Location of stations in the Mandovi and Zuari estuaries, central west coast of India. Zonations, upper estuary, lower estuary and bay are also shown. Dark thick arrow shows the direction of river flow during wet season, while dashed thin arrow shows the dominant current direction during dry season. Indiscriminate disposal of untreated sewage at many unchecked points by both hoteliers and residents, river cruises for tourists, ship-building activity, disposal of mining waste, ore transport, sand mining, etc. contaminate the estuarine waters from time to time. ***b***, Map showing land use surrounding the Mandovi and Zuari estuaries. Mangroves (C3 plant) occupy larger area along the Mandovi (1107 ha) than the Zuari (735 ha) estuary[67]. Agriculture is the major land use in the regions adjacent to both rivers. Seasonal crops, including rice (C3 plant), sugarcane (C4 plant), corn (C4 plant) and vegetables are cultivated in the lowlands.

and their stable isotopic compositions ($\delta^{13}C_{org}$, $\delta^{15}N$) in SPM and bed sediments from the estuaries of the Mandovi and Zuari (Ma–Zu) rivers, two small systems delivering materials from coastal mountainous watersheds in western India into the Arabian Sea. The purpose of the study is to identify the sources and fate of organic matter (OM) in these estuaries in two distinct seasons and controls on the OM transported to the coastal environment.

Study area and previous work

The Ma–Zu are two adjacent rivers of Goa in the central west coast of India (Figure 1 *a*). They originate in the mountain regions and drain through a narrow coastal plain with estuarine lengths nearly identical (~50 km each). The river run-off of Mandovi[7] measured at the head during June–October is ~258 $m^3 s^{-1}$ and during November–May it is ~6 $m^3 s^{-1}$. The discharge of the Zuari River into the estuary was regulated by a dam in the upper reaches and the run-off measured at Sanguem and Kushavati tributaries (Figure 1 *a*) during wet (June–September) and dry seasons (October–May) is ~147 $m^3 s^{-1}$ and 8.1 $m^3 s^{-1}$ respectively. General features such as locations of industries, Fe–Mn ore loading points, sewage discharge point and the presence of a dam along river estuaries are shown in Figure 1 *a*. A map showing land use in the study area is given in Figure 1 *b*. Agriculture is the major land use in the regions adjacent to both the rivers. The river estuaries are meso-tidal; the tidal ranges[8] are ~2.3 and 1.5 m during the spring and neap tides respectively. During dry season tidal circulation dominates and saline waters penetrate ~45 km upstream from the river mouth in both rivers. The rivers are connected to the sea through bays. The Aguada Bay off Mandovi is semi-circular and is at least one-fourth the size of the funnel-shaped, Mormugao Bay off Zuari.

Previous studies on Ma–Zu estuaries include seasonal distribution of nutrients[9–12], SPM[13] and phytoplankton diversity[14,15]. Fernandes[16] reported C/N ratios, $\delta^{13}C_{org}$ and amino acids, and Maya *et al.*[17] reported $\delta^{13}C_{org}$ and $\delta^{15}N$ of SPM at a few downstream stations in the Mandovi estuary. Stable isotopic composition of OM in the Zuari estuary has not yet been studied. The present study deals with seasonal and spatial variations of the isotopic composition of OM in SPM and sediments from the Ma–Zu estuaries.

Material and methods

Five litres of surface water in two sets and bottom sediment was collected every month at each station along transects of the Mandovi estuary during July 2007–May 2008 and Zuari estuary during June 2008–May 2009 (Figure 1 *a*). Detailed sampling procedure given elsewhere[18] was followed. We have sampled at five and six stations respectively, in the Mandovi and Zuari estuaries during the monsoon, and seven and ten stations respectively, during the non-monsoon season. The water samples from the first set were filtered through 0.4 μm Millipore filter paper and SPM retained on the filter paper was dried and weighed. SPM at each station (Table 1; Figures 2 and 3) is an average value for four months representing seasons, i.e. June–September (wet season) and February–May (dry season). The water samples from the second set were used for stable isotope analyses. Water samples and bottom sediment collected during

Table 1. Organic matter parameters in suspended particulate matter (SPM) of the Mandovi and Zuari rivers estuaries

	Station																
	Mandovi estuary							Zuari estuary									
	Lower estuary			Upper estuary				Bay				Lower estuary			Upper estuary		
Parameter	M1	M2	M3	M4	M5	M6	M7	Z0	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9
Wet season																	
Salinity (average)	8.3	6.6	1.9	1.0	0.1				14.9	13.5	9.8	7.7	2.9	1.0			
SPM (mg/l; average)	21.9	16.0	12.2	6.3	8.4				11.0	11.2	16.1	18.6	22.0	17.3			
POC (%)	11.3	11.1	11.2	21.2	11.4				10.6	10.1	8.8	7.3	7.6	7.4			
PN (%)	0.8	0.9	0.8	1.5	0.8				1.2	1.1	0.9	0.7	0.9	0.8			
POC/PN	14.1	12.2	14.6	14.6	14.2				8.7	9.1	10.1	9.7	8.7	9.3			
$\delta^{13}C$ (‰)	–22.1	–25.2	–22.6	–24.8	–28.4				–25.0	–25.0	–25.5	–25.7	–26.0	–26.9			
$\delta^{15}N$ (‰)	6.4	5.8	6.6	4.8	5.6				9.8	8.8	9.4	10.1	9.3	7.5			
PN/POC	0.07	0.08	0.07	0.07	0.07				0.11	0.11	0.10	0.10	0.12	0.11			
Dry season																	
Salinity (average)	33.9	33.1	30.4	24.3	22.8	18.6	10.7	35.2	34.3	33.1	32.3	31.3	27.3	21.2	15.1	4.8	0.9
SPM (mg/l; average)	16.1	16.4	10.9	8.3	6.8	5.2	3.4	3.5	11.4	19.7	29.0	19.3	16.7	14.1	10.3	8.9	9.0
POC (%)	8.5	11.3	10.1	10.1	15.5	16.3	25.5	8.9	8.0	6.7	5.2	7.7	8.0	8.7	7.2	9.6	12.3
PN (%)	0.6	0.9	0.7	0.9	1.3	1.4	2.2	0.9	0.7	0.6	0.4	0.6	0.7	0.8	0.7	0.9	1.3
POC/PN	13.2	12.9	14.3	11.6	12.0	12.0	11.8	10.0	11.7	11.1	13.7	13.0	11.0	10.9	10.4	11.2	9.3
$\delta^{13}C$ (‰)	–23.5	–23.5	–25.2	–26.9	–26.9	–27.6	–28.0	–23.2	–23.3	–22.0	–23.4	–23.7	–25.3	–25.5	–26.4	–27.6	–28.6
$\delta^{15}N$ (‰)	10.0	8.8	10.0	9.7	10.7	10.0	9.1	6.7	9.1	8.9	9.4	9.3	8.4	8.6	8.4	7.6	5.1
PN/POC	0.07	0.08	0.07	0.09	0.08	0.09	0.09	0.10	0.09	0.09	0.08	0.08	0.09	0.09	0.10	0.09	0.11

POC, Particulate organic carbon; PN, Particulate nitrogen.

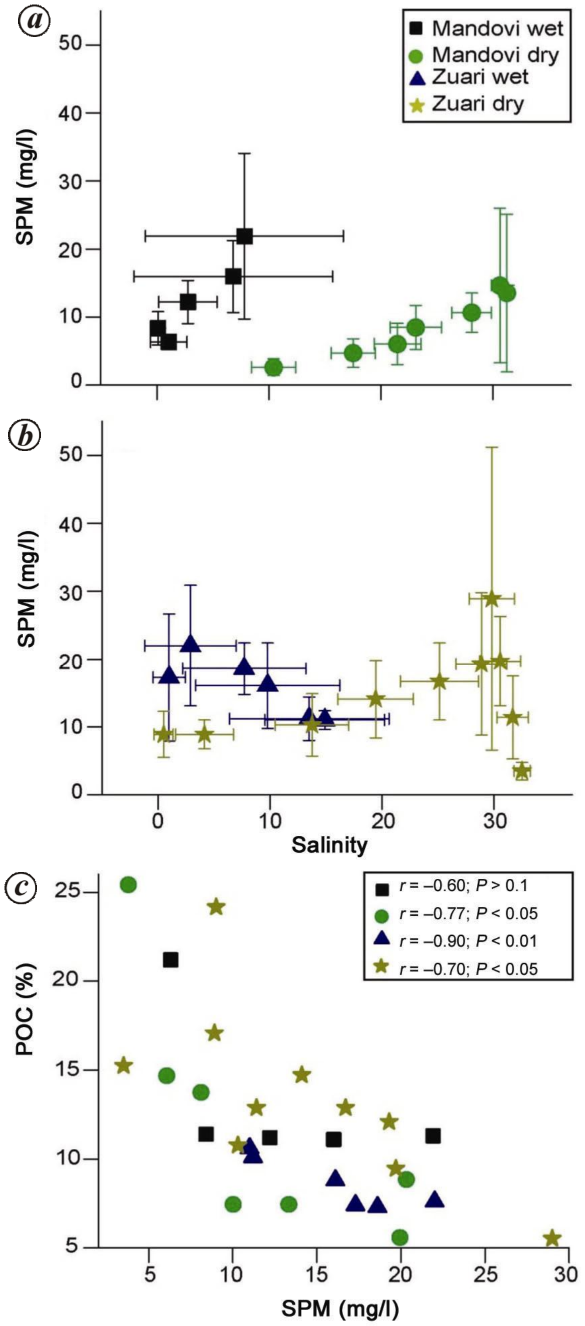

Figure 2. Plots showing the relationship between mean salinity and suspended particulate matter (SPM) with standard deviation (bars) in the (***a***) Mandovi (Ma) and (***b***) Zuari estuaries. The mean salinity and SPM are obtained by averaging their values at different stations from June to September (wet season) and from February to May (dry season) during spring tide. ***c***, Plot showing relationship between SPM and particulate organic carbon (POC) in the Mandovi–Zuari estuaries.

spring tide and from a representative month for the wet (August) and dry (April) seasons were selected along transects of the Mandovi and Zuari estuaries for measuring OC, TN, $\delta^{13}C_{org}$ and $\delta^{15}N$. Sample preparation given elsewhere[19] was followed. The GF/F filters were pre-combusted at 300°C for 6 h, and then the water samples were filtered and the SPM retained was dried at < 45°C. We used <2 μm fraction of the sediment in order to maintain uniformity in all our studies (mineralogy, geo- and isotope chemistry of sediments). The <2 μm fraction of the sediment was separated by Stoke's settling velocity principle and filtered through the pre-combusted GF/F filter and dried. Calcium carbonate content was removed by exposing the GF/F filters with sample to concentrated HCl fumes in a desiccator for 12 h. OC, TN, $\delta^{13}C_{org}$ and $\delta^{15}N$ were measured on dried samples on the filters, using the elemental analyser coupled with isotope ratio mass spectrometer (EA-IRMS-Delta V, Thermo Fisher Scientific, Germany) at the Regional Centre, National Institute of Oceanography (NIO), Visakhapatnam, India. $\delta^{13}C_{org}$ and $\delta^{15}N$ are expressed as per mil (‰) against PDB and air standards respectively. The precision is ±0.2‰ for $\delta^{13}C_{org}$ and $\delta^{15}N$. Here we use POC and PN while referring to organic carbon and total nitrogen in suspended matter, and OC and TN while referring to them in sediments.

Results

Concentration and composition of suspended matter

For convenience of description of the results, the sampling transects of both estuaries were divided into upper estuary, lower estuary and bay, based on the distance from the mouth of the estuary (Figure 1 *a*). SPM, POC and PN concentrations and $\delta^{13}C_{org}$ and $\delta^{15}N$ in SPM (Table 1) displayed strong spatial and seasonal variations in both estuaries. The mean SPM concentrations ranged from 3.4 to 21.9 mg/l in the Ma–Zu river estuaries (Table 1) with the lowest concentrations coinciding with low salinities in the upper estuary of both the rivers. In contrast to the major rivers, SPM concentrations in the Ma–Zu estuaries increased seaward with increase in salinity in the lower estuary both during the wet and dry seasons (Figure 2 *a* and *b*). In the bay of Zuari, SPM concentration decreased seaward with increase in salinity (Table 1). POC concentration was higher in the Mandovi (8.5–25.5%) than in the Zuari estuary (7.2–12.3%; Table 1) and displayed moderate inverse relationship with SPM both in wet and dry seasons (Figure 2 *c*). PN concentration ranged from 0.6% to 2.2% in the Mandovi and from 0.4% to 1.3% in the Zuari estuary, and displayed similar distribution to that of POC; both were linearly correlated during wet and dry seasons (Figure 3 *a* and *b*). POC concentration showed no significant change with increase in salinity seaward in the Mandovi during wet season. In dry season, POC concentration was high in the upper estuary and decreased seaward with increase in salinity in the lower estuary (Figure 3 *c*). In Zuari POC showed minor variations (7.3–7.6%) with salinity change of 1.0–7.7 in the lower estuary (Table 1), but increased linearly with

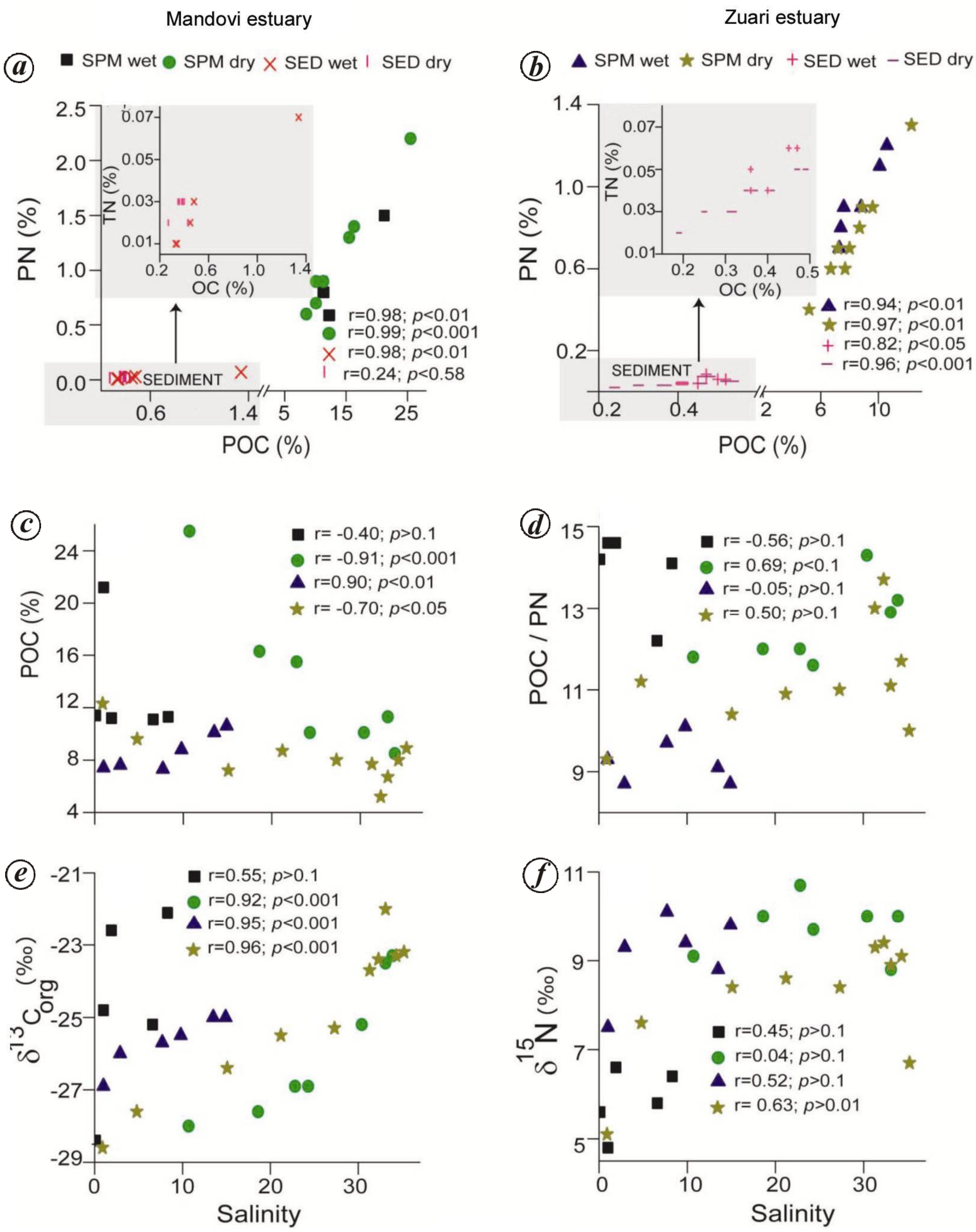

Figure 3. Organic matter parameters in SPM of the Mandovi–Zuari estuaries. ***a***, ***b***, Relationship between POC and particulate nitrogen (PN) in SPM of the Mandovi and Zuari estuaries respectively. (Inset) Relationship between organic carbon (OC) and total nitrogen (TN) in sediments of the same estuaries. ***c–f***, Relationship between salinity and POC, POC/PN, $\delta^{13}C_{org}$ and $\delta^{15}N$ respectively, in the Mandovi–Zuari estuaries during wet and dry seasons. Symbols are common for all figures: square and circle represent wet and dry seasons respectively, for Mandovi estuary, whereas triangle and star represent wet and dry seasons respectively, for Zuari estuary.

salinity in the bay during wet season (Figure 3 *c*). POC decreased seaward in the upper and lower estuary and increased in the bay stations during dry season (Figure 3 *c*). Local variations along transect, i.e. elevated concentrations of POC associated with low SPM in Mandovi during both seasons, and depleted concentrations of POC with high SPM at intermittent stations in Zuari were seen (Table 1). POC/PN ratios were higher in the Mandovi (11.8–14.6) than in the Zuari estuary (9.07–13.73; Table 1). POC/PN displayed moderate negative correlation with salinity in the Mandovi during wet season and positive correlation during dry season (Figure 3 *d*). In Zuari POC/PN displayed no correlation with salinity during wet season and positive correlation during dry season (Figure 3 *d*).

$\delta^{13}C_{org}$ in SPM of the Ma–Zu estuaries increased seaward and was strongly correlated with increase in salinity. $\delta^{13}C_{org}$, however, showed a moderate correlation during wet season in Mandovi (Figure 3 *e*; Table 1). $\delta^{15}N$ of SPM in the Mandovi estuary was lowest in wet season (4.8–6.6‰) and highest in dry season (9.1–10.7‰). In Zuari, $\delta^{15}N$ of SPM ranged from 7.5‰ to 10.1‰ and from 5.1‰ to 9.4‰ during wet and dry seasons respectively (Table 1). $\delta^{15}N$ and salinity showed moderate correlation during wet season in both estuaries (Figure 3 *f*). They showed no correlation in Mandovi and positive correlation in the Zuari estuary during dry season.

Concentration and composition of OM in sediments

OC and TN contents of surface sediments in the Mandovi estuary (0.27–1.34% and 0.01–0.07% respectively) were close to those of the Zuari estuary (0.24–0.52% and 0.02–0.06% respectively; Table 2). OC and TN of sediments were much lower than those in suspended matter of the same estuaries. They showed strong correlation with each other in wet season and no correlation during dry season in the Mandovi estuary (Figure 3 *a*) and strong correlation in both seasons in the Zuari estuary (Figure 3 *b*). The OC/TN ratios in the Mandovi (11.9–24.3) were higher than those in Zuari (8.57–12.5). Textural analyses showed that the sediments were sandy in both estuaries. Clay (<4 μm) content of the sediments in the Mandovi estuary at different stations varied from 9% to 31% and from 10% to 25% during the wet and dry seasons respectively. In Zuari, clay content varied from 9% to 34% in wet season and 9% to 51% in dry season.

$\delta^{13}C_{org}$ of sediments in the Mandovi during wet (–27.2‰ to –21.6‰) and dry (–28.4‰ to –24.1‰) seasons was within the range of values reported for SPM (–28.4‰ to –22.1‰ and –28.0‰ to –23.5‰ respectively; Tables 1 and 2) and displayed similar distribution as that of SPM. $\delta^{15}N$ of sediments varied in the range 4.0–10.0‰ and 6.8–8.9‰ in the wet and dry seasons respectively. $\delta^{13}C_{org}$ of sediments in Zuari (–26.5‰ to –25.2‰) showed an increasing trend in the lower estuary during wet season, but the mean value in the lower estuary and bay was similar (Table 2). $\delta^{15}N$ of sediments ranged from 0.01‰ to 6‰, with the lowest values in the upper estuary (Table 2). During dry season, sediments of the Zuari were characterized by low $\delta^{15}N$ (–5.3‰ to +5.3‰) and relatively high $\delta^{13}C_{org}$ (–26.3‰ to –24.5‰) in the upper estuary and uniformly high $\delta^{15}N$ in the lower estuary and bay during dry season (Table 2).

Discussion

Distribution of SPM and POC

Low SPM associated with low salinities in the upper estuary, and increase in SPM concentration with increase in salinity seaward are consistent features of both rivers during the wet and dry seasons (Figure 2 *a* and *b*). Despite high river discharge into the estuaries during wet season and negligible discharge during dry season, low SPM concentrations in the upper estuary of both rivers indicate that most of the SPM in river discharge settled upstream before reaching the estuarine part and therefore there was no seasonal contrast in SPM at river end

Table 2. Organic matter parameters in sediments of the Mandovi and Zuari river estuaries

	Station															
	Mandovi estuary							Zuari estuary								
	Lower estuary			Upper estuary				Bay			Lower estuary			Upper estuary		
Parameter	M1	M2	M3	M4	M5	M6	M7	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9
Wet season																
OC (%)	1.34	0.33	0.34	0.45	0.48			0.41	0.41	0.45	0.41	0.50	0.52			
TN (%)	0.07	0.01	0.01	0.02	0.03			0.04	0.05	0.04	0.04	0.06	0.06			
OC/TN	19.48	22.31	24.27	17.96	14.43			10.92	8.86	11.60	11.02	9.09	8.57			
$\delta^{13}C$ (‰)	–24.5	–21.6	–25.8	–27.2	–26.4			–25.2	–25.5	–26.1	–24.9	–26.0	–26.5			
$\delta^{15}N$ (‰)	8.4	9.5	10.0	5.8	4.0			6.1	1.0	6.0	5.6	1.9	–0.01			
TN/OC	0.05	0.03	0.03	0.04	0.06			0.10	0.12	0.09	0.10	0.12	0.12			
Dry season																
OC (%)	0.40	0.38	0.27	0.39	0.36	0.35	0.43	0.42	0.36	0.24	0.52	0.46	0.37	0.30	0.54	0.40
TN (%)	0.03	0.03	0.02	0.03	0.03	0.03	0.02	0.04	0.03	0.02	0.05	0.04	0.03	0.03	0.05	0.04
OC/TN	11.88	13.45	15.28	14.35	14.31	13.53	21.32	9.48	12.50	9.48	10.09	10.92	11.02	11.69	10.53	11.20
$\delta^{13}C$ (‰)	–24.1	–26.4	–24.8	–25.9	–27.1	–26.9	–28.4	–25.6	–25.9	–24.4	–24.5	–25.1	–26.1	–26.3	–25.4	–24.5
$\delta^{15}N$ (‰)	8.1	7.0	8.9	7.5	6.8	7.0	6.8	5.0	5.6	3.7	5.9	5.7	5.2	5.3	–2.3	–5.1
TN/OC	0.08	0.08	0.07	0.08	0.08	0.09	0.05	0.10	0.08	0.08	0.10	0.09	0.08	0.10	0.09	0.10

OC, Organic carbon; TN, total nitrogen.

stations. The seaward increase of SPM in the lower estuary is attributed to the estuarine turbidity maximum (ETM)[13] located at the mouth of the estuaries. Rao *et al.*[13] suggested that the morphology of the bays and tidal- and wind-induced currents at the mouth played an important role in developing ETM at seaward stations of the estuary. Although salinity and SPM concentrations increase seaward, POC concentrations do not vary significantly in the Ma–Zu estuaries during wet season (Table 1). Moreover, POC showed an inverse relationship with SPM during both seasons (Figure 2 *c*). At least one sample from Mandovi showed elevated POC with relatively low SPM and one sample from Zuari showed low POC associated with relatively high SPM (Table 1). This suggests significant spatial and temporal heterogeneity in the composition of particles. The ETM developed at the mouth may have resulted in re-suspension of particulates from the seabed and affected both SPM and POC concentrations.

Sources of OM in SPM during wet season

POC and PN are moderately correlated in the Mandovi estuary (Figure 3 *a*). POC/PN ratios (12.2–14.6) are within the range (5.8–22) reported in the same estuary[16]. Hedges *et al.*[20] reported OC/TN ratios of soil material (9–12), vascular plant tissues (20–200) and marine plankton (~7). The POC/PN ratios of mangrove (C3) plants and sediments from low latitudes[21–24] range from 14.1 to 25. Mangroves occur on the banks of the estuary. The POC/PN ratios suggest that the terrestrial OM dominated by plant material is characteristic of Mandovi in wet season.

The POC/PN ratios in the Zuari estuary (8.7–10.0; Table 1) are within the range of values (9–12) reported for soil OM[25]. Lower POC/PN ratios in Zuari than in Mandovi could be due to the following: (a) The existence of large drainage basin of Zuari in coastal plains. It is likely that the fine-grained soil material from coastal plains was quickly transferred into the estuary during heavy monsoon rains and resulted in POC/PN ratios similar to those in soils. Kessarkar *et al.*[26] reported that the minerals in the lower zone are largely the weathering products of hinterland formations in coastal plains. (b) As mangroves occupy smaller area in Zuari (735 ha) compared to that in Mandovi (1107 ha; Figure 1 *b*), less POC may have been received from mangrove vegetation. POC/PN ratios can be lower if inorganic nitrogen occurs presumably as ammonia (NH_4^+) adsorbed onto clay particles[27,28]. POC and PN showed strong covariance (Figure 3 *b*) and the values plot on the regression line passing through the origin, suggesting that PN is largely nitrogen-bound organic matter.

$\delta^{13}C_{org}$ in the Mandovi estuary (–28.4‰ to –22.1‰) is at a higher end than that reported (–32.1‰ to –25.1‰) in the same estuary[16]. Several workers reported $\delta^{13}C_{org}$ from rivers (–25‰ to –28‰), marine plankton (–18‰ to –22‰), C3 (–23‰ to –34‰) and C4 plants (–9‰ to –17‰) and mangrove plants and sediments from low latitude regions (–25.4‰ to –32‰)[20,23,29–34]. The $\delta^{13}C_{org}$ values reported here are in the range of OM from terrestrial soils and mangrove plants at river end station (M5) and marine OM at sea end stations (M3 and M1). Since $\delta^{13}C_{org}$ increases abruptly by 5.8‰ between stations M5 and M3 and by 3.1‰ between stations M1 and M2 with little/minor change in salinity (Figure 3 *e* and Table 1), there may be no increase of marine organic carbon seaward. Devassy and Goes[14], based on phytoplankton cell counts, reported scarcity of marine OM and more of terrigenous OM in this estuary during wet season. As ETM occurs at sea end stations (Figure 2 *a*), the increased $\delta^{13}C_{org}$ could be due to mixing of material which is transported with the re-suspended matter (previously deposited OM), or domestic sewage (see discharge point in Figure 1 *a*) discharged into the lower estuary, or a mixture of OM from C4 and C3 plants (Figure 1 *b*) resulting in OM with a $\delta^{13}C$, which isotopically resembles marine plankton[20]. It is likely that the plant materials and grasses belonging to C4 plants are transported from the adjacent fields and reclaimed mud flats (Figure 1 *b*) which got mixed up with mangrove material (C3 plant) in the estuary during heavy monsoon rains. In other words, high $\delta^{13}C_{org}$ at sea end stations in wet season should represent a mixture of fresh terrestrial and reworked organic matter. As POC showed linear relationship with PN, we plotted the values of PN/POC and $\delta^{13}C_{org}$ on the diagram (Figure 4 *a*) of Goni *et al.*[35] to identify the source of OM. The values plot midway between C3 vascular plants and riverine and estuarine algae (Figure 4 *a*) for the samples collected at the river end and slightly away for the samples at the sea end suggesting little contribution from C4 terrestrial plant sources. The $\delta^{15}N$ values (4.8–6.6‰; Table 1) are higher than those reported (2.4 ± 0.7‰) in the same estuary[17], but comparable with the global freshwater and estuarine particulate organic nitrogen (4.3–6.3‰)[34–37]. Weak correlation between $\delta^{15}N$ and salinity (Figure 3 *f*) and moderate correlation between $\delta^{15}N$ and $\delta^{13}C$ (Figure 4 *b*) may be due to the mixing of OM which is in suspension along with re-suspended OM from the seabed due to turbidity maximum.

Unlike in Mandovi, the $\delta^{13}C_{org}$ values in the Zuari estuary (–26.9‰ to –25‰) are within the range reported for terrestrial sediments and support the interpretation based on POC/PN ratio. PN/POC and $\delta^{13}C$ values plot midway between C3 vascular plants and riverine and estuarine algae, more towards the latter (Figure 4 *d*), confirming the dominant character of soil-derived OM. The strong correlation of $\delta^{13}C_{org}$ with salinity (Figure 3 *e*) indicates decreasing influence of terrigenous OM towards the bay. $\delta^{15}N$ (7.5–10.1‰) showed weak correlation with salinity (Figure 3 *f*), and weak or no correlation with $\delta^{13}C$ and POC/PN (Figure 4 *e* and *f*). Moreover, the peak high

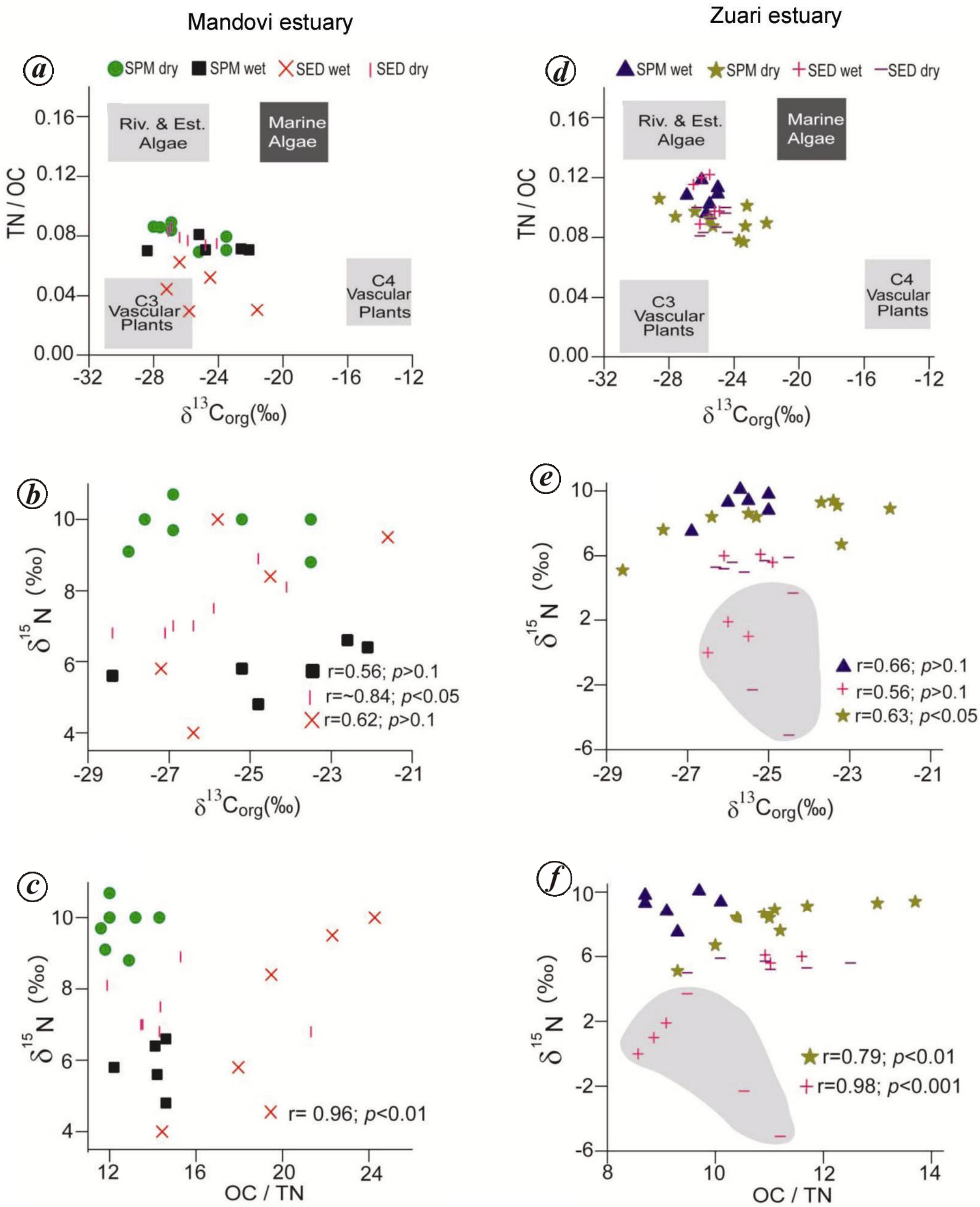

Figure 4. ***a***, ***d***, Relationship between TN/OC and $\delta^{13}C_{org}$ in SPM and sediments of the Manadovi and Zuari estuaries respectively plotted on the diagram of Goni *et al.*[35] to differentiate the source of organic matter. ***b***, ***c***, Relationships between $\delta^{15}N$ and $\delta^{13}C_{org}$ as well as OC/TN ratio in SPM and sediment respectively of the Mandovi estuary. ***e***, ***f***, Relationship between $\delta^{15}N$ and $\delta^{13}C_{org}$ as well as OC/TN ratio in SPM and sediment respectively, of the Zuari estuary.

$\delta^{15}N$ coincides with peak high POC/PN ratio in the lower estuary (Table 1). Since increased SPM in the lower estuary was attributed to the ETM, it is likely that the particulate organic matter (POM) was subjected to alteration due to turbidity. Owens[36] reported that the POM entrained in the turbidity maximum undergoes enhanced chemical and microbial activity that results in relative increase in $\delta^{15}N$. The low nitrogen and high $\delta^{15}N$ at stations in the lower estuary of Zuari (Table 1) indeed attest microbial mineralization of OM. Thus $\delta^{15}N$ in the Zuari estuary does not merely reflect hydrodynamic mixing of the freshwater and seawater source particulates but intense biogeochemical processes, even during wet season.

Sources of OM in SPM during dry season

The POC/PN ratios in the Mandovi (11.8–14.3) and Zuari (9.34–12.97) estuaries indicate the dominance of terrestrial organic matter during dry season. This inference is not in agreement with other evidences: (a) Since the river discharge is negligible during dry season, one would expect little terrigenous POC directly from land. (b) The phytoplankton cell counts at different stations in the dry season range from 1.5 to 4.5×10^5 l^{-1} and from 0.5×10^5 to 4.5×10^5 l^{-1} in the Mandovi and Zuari estuaries respectively[15]. This indicates high *in situ* production and increase of marine OM. Both estuaries showed almost similar range of $\delta^{13}C_{org}$ (Table 1), which strongly correlates with increase in salinity, suggesting significant increase in marine organic matter seaward. The plot of TN/OC and $\delta^{13}C_{org}$ on the diagram of Goni *et al.*[35] indicates that the samples from the upper estuary of both rivers plot midway between C3 vascular plants and fluvial and estuarine algae (Figure 4 *a* and *d*), while those from the lower estuary plot slightly away and a distinct source cannot be revealed for these samples. The low $\delta^{13}C_{org}$ (~–28.6‰ to –26.9‰) in the upper estuary of both rivers is associated with low salinity water. $\delta^{13}C_{org}$ from woody tissues from C3 tropical plants is in the range –28‰ to –25‰, while that of tropical leaves[32] range from –32‰ to –29‰. The variations in $\delta^{13}C_{DIC}$ can also contribute significantly[38] to depletion in $\delta^{13}C_{org}$ (ref. 38). $\delta^{13}C_{DIC}$ has not been measured in these estuaries so far, but one would expect its contribution to $\delta^{13}C_{org}$ because of salinity variations in the upper and lower estuary. Therefore, $\delta^{13}C_{org}$ in the upper estuary was rather contributed by a mixture of *in situ* plankton-derived and reworked terrestrial carbon, plant tissues and depleted isotopic composition of DIC.

$\delta^{15}N$ values do not correlate with salinity (Figure 3 *f*), $\delta^{13}C_{org}$ or POC/PN (Figure 4 *b* and *c*) in the Mandovi, but exhibit only moderate correlation with these parameters in the Zuari estuary (Figures 3 *f* and 4 *e*, *f*). These indicate that POC/PN and $\delta^{15}N$ along transect of both estuaries were modified by metabolic processes and represent degraded/altered organic matter during dry season. $\delta^{15}N$ of OM can be modified by different processes, including nutrient utilization, nitrification and/or denitrification and organic diagenesis[39–43]. $\delta^{15}N$ of OM can become heavier if regeneration and consumption are unbalanced or if there are external inputs of ammonium. Microbial assimilation of nitrate can alter $\delta^{15}N$ of OM[44]. Denitrification causes loss of the lighter isotope, while residual nitrate is ^{15}N-enriched. The high $\delta^{15}N$ in the Delaware (up to 18.7‰) and Schelde (up to 15‰) estuaries was attributed to preferential removal of ^{15}N in the uptake of ammonia by phytoplankton and other processes such as nitrification and denitrification[36,45,46].

Different biogeochemical processes can be envisaged along transects in both estuaries during dry season: (a) Organic-rich mangrove sediments are an important source of NH_4^+ in these estuaries[11,12] and the benthic NH_4^+ efflux sustains high estuarine productivity. Elevated $\delta^{15}N$ values may have been caused by the uptake of ammonium with heavy isotopic ratio. If the riverine-derived ammonium is consumed by nitrifiers[47], the ammonium remaining in solution enriches $\delta^{15}N$ due to preferential uptake of ^{14}N (refs 48 and 49). Incorporation of such heavy ammonium by algae[45] and heterotrophic bacteria[46] may lead to elevated $\delta^{15}N$ values. (b) Ore mining is an important activity in Goa. De Souza *et al.*[10] reported that the mining rejects that end up in the estuaries can serve as a source of nitrates, because the explosives used in mining operations contain nitrates that end up in mining rejects. Nitrate concentrations were indeed high at upstream stations during dry season[11]. Nitrate can be an important nitrogen substrate for heterotrophic bacteria in a nitrate-rich estuary[41] and microbial assimilation of nitrate has been shown to result in elevated $\delta^{15}N$ of organic matter[41]. (c) Sediments in the upper estuary of Zuari are affected by sewage (see later in the text) and sewage-derived NH_4^+ could be a source of ^{15}N-enriched particulate matter. (d) ETM is a characteristic feature in both estuaries. Microbial mineralization of OM in the zone of ETM[36] results in preferential loss of ^{14}N and enrichment of ^{15}N. (e) Because of longer residence times of water in both estuaries (more than 50 days)[9] during dry season, OM may have undergone significant microbial transformations and attained high $\delta^{15}N$ values[43,48]. Fernandes[16] reported degraded OM rich in amino acids in the Mandovi estuary during dry season; degraded OM may be responsible for elevated $\delta^{15}N$. Therefore, high $\delta^{15}N$ could be due to the cumulative effect of different processes in the estuaries during dry season.

Sources of sedimentary organic matter during the wet season

The OC and TN contents in sediments are much lower and OC/TN ratios are higher than those in SPM of both rivers. High OC/TN ratios may be due to sandy sediments, which will have increased access to bacteria and increased mineralization of nitrogenous compounds. As we have measured OC and TN in <2 μm fraction of sediment the values must have been higher than in the total sediment. Zhou *et al.*[40] reported high OC and TN in finer fractions of sediment. $\delta^{15}N$ in the Ma–Zu estuaries is moderately correlated with $\delta^{13}C_{org}$ (Figure 4 *b* and *e*) and strongly correlated with OC/TN (Figure 4 *c* and *f*). Moreover, peak high OC/TN ratio coincides with peak high $\delta^{15}N$ during wet season (Table 2); this may indicate microbial mineralization of OM that resulted in progressive enrichment of ^{15}N. In other words, sedimentary organic matter (SOM) may have been subjected to early diagenetic changes and OC/TN and $\delta^{15}N$ of sediments are not indicators of source OM.

The mean $\delta^{13}C_{org}$ (–26.8 ± 0.6‰) in the sediments of the upper estuary of Mandovi indicates that terrigenous OM is the dominant component. As in SPM, the $\delta^{13}C_{org}$

values abruptly increased from –25.8‰ to –21.6‰ in the lower estuary (Table 2). Since domestic discharge point is located in the vicinity of M2 station (Figure 1 *a*) and ETM occurs in the lower estuary, $\delta^{13}C_{org}$ may represent a mixture of OM from degraded terrestrial and sewage effluents. Similarly, $\delta^{13}C_{org}$ (–26.5‰ to –25.2‰) in the lower estuary of Zuari (Figure 4 *c*) indicates that terrestrial OM is the dominant component. The mean $\delta^{13}C_{org}$ values in sediments of the lower estuary (–25.8 ± 0.8‰) and bay (–25.6 ± 0.4‰) are uniform. This indicates that dynamic processes are operating in these parts of the estuary, causing efficient mixing and redistribution of sediments. Graham *et al.*[50] reported uniform $\delta^{13}C_{org}$ in sediments of the Forth estuary, Scotland, and attributed this to the efficient mixing of sediments. Larger differences between the mean $\delta^{15}N$ of SPM and sediments in the upper (8.9 ± 1.3‰ and 2.5 ± 2.8‰ respectively) and lower estuary (9.4 ± 0.4‰ and 4.4 ± 2.9‰) of Zuari indicate significant isotopic fractionation of organic nitrogen in SPM.

Sources of SOM during dry season

High OC/TN ratios (11.9–21.3) and $\delta^{15}N$ (6.8–8.9‰) in the Mandovi estuary indicate that SOM was subjected to early diagenetic changes. However, moderate correlation of $\delta^{13}C_{org}$ in sediments and SPM ($r = 0.72$; $P < 0.01$; not shown in figure) and plot of TN/OC and $\delta^{13}C_{org}$ values in Figure 4 *a* suggest coupling between the two, and particulate matter from water column is found to settle in the bottom sediments. $\delta^{13}C_{org}$ in sediments (Table 2) suggests dominant terrigenous plant-derived OM in the upper estuary and increase in the percentage of marine OM towards the lower estuary.

The sediments in the upper estuary of Zuari exhibit high $\delta^{13}C_{org}$ (–26.3‰ to –24.5‰) and low $\delta^{15}N$ (–5.1‰ to 5.3‰). Depleted $\delta^{15}N$ values (0–1.9‰) also occur in sediments of the lower estuary and bay during wet season (Table 2). The low $\delta^{15}N$ values plot distinctly on the $\delta^{13}C_{org}$ vs $\delta^{15}N$ graph (Figure 4 *e*) and on $\delta^{15}N$ vs OC/TN graph (Figure 4 *f*). As river discharge is negligible during dry season, SOM with high $\delta^{13}C_{org}$ and low $\delta^{15}N$ may not be related to river source. The $\delta^{15}N$ values (–5.3‰ to –2.3‰), especially at stations Z8 and Z9 (Table 2) are much lower than the OM from continental sources[48] (~ 1.5‰) and freshwater sediments[51] (2.3 ± 0.9‰). The low $\delta^{15}N$ in sediments could result from atmospheric nitrogen fixation by cyanobacteria and/or from sludge or raw sewage discharge[52]. Low $\delta^{15}N$ (–2.3‰ to 0.9‰) in suspended matter of the Brantas River estuary was attributed to nitrogen fixation by cyanobacteria[53]. Sweeney *et al.*[54] reported $\delta^{15}N$ of the effluent particulates (2–3‰) and contaminated sediments (1.8–3.6‰) on the shelf of San Pedro, California. Liu *et al.*[55] identified the mean $\delta^{13}C$ (–23.6 ± 0.7‰) and $\delta^{15}N$ (–3.0 ± 0.1‰) of POM in highly polluted waters in Danshuei estuary, Taiwan. Barros *et al.*[56] reported $\delta^{13}C$ (–22‰) and $\delta^{15}N$ (1.2‰) of the sewage in the Babitonga Bay, Brazil. Although the $\delta^{13}C$ values (–23.3‰ to –26.8‰) fall within the range inferred for anthropogenic end-member[55] (–26.7‰ to –16.5‰), the values of $\delta^{15}N$ (–5.1‰ to 5.3‰; Figure 4 *d*) fall within the sludge values (–1.1‰ to 3.3‰)[52,57] and also lower values (–2.3‰ to –5.1‰; Figure 4 *e*) than that of sludge. Liu *et al.*[55] reported very low $\delta^{15}N$ values (–16.4‰ to +3.8‰) for particulate nitrogen in the Danshuei estuary, which was attributed to nitrate uptake that may occur in the early stage of nitrification. In view of dense human population and hectic mining activities surrounding this part of the river, we suggest the sewage waste released to this part of the estuary may be responsible for low $\delta^{15}N$ and high $\delta^{13}C$ of SOM and thus indicate anthropogenic contamination.

The gradual increase in $\delta^{13}C_{org}$ in the lower estuary of Zuari (Table 2) may be related to the increase in marine organic carbon, whereas its decrease in bay stations could be due to effective mixing of organic materials at the bottom due to turbidity.

Contribution of terrestrial organic carbon to the coastal system

The net export of terrestrial organic carbon (TOC) to the coastal system in event-dominated watersheds and in the regions of estuarine turbidity maximum is largely controlled by effective discharge, estuarine turbidity maximum and energy conditions of the tidal currents at the mouth[58–60]. Here we have estimated the TOC content at the mouth of the Ma–Zu estuaries in August (peak monsoon month – representative of wet season) when river discharge was at its peak and in April (representative month for dry season) when river discharge was negligible and tidal and wind-induced currents play a major role in transporting sediments. The contribution of TOC discharged into the coastal system can be calculated using the equation[61]

$$\text{Percentage of TOC} = [(\delta^{13}C_{marine} - \delta^{13}C_{sample})/(\delta^{13}C_{marine} - \delta^{13}C_{terrestrial})] \times 100.$$

This equation requires end-member $\delta^{13}C$ values for terrestrial and marine organic carbon. Here, we used $\delta^{13}C$ of –28.6‰ and –22‰ respectively, as end-member values for terrestrial and marine organic carbon. These values represent the lowest and highest $\delta^{13}C_{org}$ of SPM in the Mandovi estuary during wet and dry season respectively. Using the mean value of $\delta^{13}C_{org}$ (–23.3‰) for SPM in the lower estuary (Table 1), <20% TOC was found to be transported to the bay. This estimate includes OM re-suspended from bottom sediments due to ETM at sea end stations. This estimate would be the lowest as it does not take into account events of peak discharges that occur frequently during wet season.

Following similar criteria, a maximum of ~18% TOC was found to be exported to the coastal system through the Zuari estuary. This estimate also includes OM re-suspended from bottom sediments due to ETM. Despite distinct river run-off values, both rivers contributed similar amount (18–20%) of TOC to the coastal system. This is due to the occurrence of ETM downstream of the rivers, which was influenced by the size and morphology of bays off the rivers and associated physical processes[13].

During dry season we found that <20% of TOC was brought into suspension at sea end stations due to the occurrence of ETM and this amount was transported into the estuarine channel by the prevailing dominant tidal and wind-induced currents. In other words, the amount of TOC discharged during wet season is the same as that received by the estuaries during dry season. Several investigators estimated TOC content of the major and minor rivers. TOC content of the Yangtze River varied from 61% in the river to 45% at the mouth[62]. TOC content in the Pearl River varied from 50% to 10%, with low values at the mouth[63]. Sarma *et al.*[19] reported 46% TOC at the mouth of the Godavari River estuary. TOC content of the sediments of the Gulf of Marthaban was 70%, transported by Ayeyarwady River[64]. TOC content of the minor rivers discharging into Bohai Bay, China[65] ranged from 20% to 13%. In the tropical Periyar River, SW India, it ranged from 74% to 13% with low values at the mouth[66]. TOC values reported here agree well with those of small rivers. Since there are numerous small rivers originating from monsoon-dominated and/or coastal mountainous regions globally, their total TOC contribution to the coastal system must be substantial and appreciated.

Conclusions

This study reported SPM concentration, OC/TN ratios $\delta^{13}C_{org}$ and $\delta^{15}N$ of SPM and bottom sediment in two adjacent, small river estuaries during wet and dry seasons. Unlike the case of major rivers, SPM increases seaward and shows inverse relationship with POC in both estuaries. POC/PN ratios reflect sources of OM only during wet season; these ratios were altered during dry season. In both estuaries, $\delta^{13}C_{org}$ of SPM is largely terrestrial during wet season, and *in situ* estuarine-derived at river end and marine plankton-derived at sea end during the dry season. $\delta^{15}N$ of OM is modified by biogeochemical processes in both estuaries, except during the wet season in Mandovi. The mean $\delta^{13}C_{org}$ values of SPM and sediments were similar in different parts of the estuaries during wet season. The uniform $\delta^{13}C_{org}$ of sediments indicates strong hydrodynamic conditions and mixing of sediments in the lower estuary and bay of Zuari. The sediments in the upper estuary of Zuari showed anthropogenic contamination. In the Ma–Zu estuaries ETM and hydrodynamic conditions control biogeochemical processes. The small mountainous rivers studied here discharged 20% of TOC to the coastal system during wet season and received similar quantity during dry season. Turbidity maximum most probably sustains productivity of the estuaries during dry season.

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