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Sources and implications of particulate organic matter from a small tropical river—Zuari River, India

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Abstract

Transitional ecosystems, estuaries and the coastal seas, are distinctively affected by natural and anthropogenic factors. Organic matter (OM) originating from terrestrial sources is exported by rivers and forms a key component of the global biogeochemical cycles. Most previous studies focused on the bulk biochemical and anthropogenic aspects affecting these ecosystems. In the present study, we examined the sources and fate of OM entrained within suspended particulate matter (SPM) of the Zuari River and its estuary, west coast of India. Besides using amino acid (AA) enantiomers (L- and D-forms) as biomarkers, other bulk biochemical parameters viz. particulate organic carbon (POC), δ^{13}C, particulate nitrogen (PN), δ^{15}N and chlorophyll *a* were analyzed. Surprisingly no significant temporal variations were observed in the parameters analyzed; nonetheless, salinity, POC, δ^{13}C, PN, δ^{15}N, glutamic acid, serine, alanine, tyrosine, leucine and D-aspartic acid exhibited significant spatial variability suggesting source differentiation. The POC content displayed weak temporal variability with low values observed during the post-monsoon season attributed to inputs from mixed sources. Estuarine samples were less depleted than the riverine samples suggesting contributions from marine plankton in addition to contributions from river plankton and terrestrial C_3 plants detritus. Labile OM was observed during the monsoon and post-monsoon seasons in the estuarine region. More degraded OM was noticed during the pre-monsoon season. Principal component analysis was used to ascertain the sources and factors influencing OM. Principally five factors were extracted explaining 84.52% of the total variance. The first component accounted for 27.10% of the variance suggesting the dominance of tidal influence whereas, the second component accounted for heterotrophic bacteria and their remnants associated with the particulate matter, contributing primarily to the AA pool. Based on this study we ascertained the role of the estuarine turbidity maximum (ETM) controlling the sources of POM and its implications to small tropical rivers. Thus, changes in temporal and regional settings are more likely to affect the natural biogeochemical cycles of small tropical rivers.

Key words: Zuari River, estuarine turbidity maximum (ETM), suspended particulate matter (SPM), organic matter (OM), amino acids (AA), degradation index (DI)

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1 Introduction

Continental margins are dominated by inputs from rivers which play an important role in influencing the global biogeochemical cycles as they receive significant amounts of terrigenous and marine materials. These regions are characterized by highly dynamic physical, chemical and biological processes (Hedges et al., 1997; Bianchi and Allison, 2009). Pathway of the transport of organic matter (OM) from the land to the sea provides valuable insights into the natural processes and anthropogenic disturbances occurring within the drainage basin (Ke et al., 2017; Ni et al., 2016; Mai-Thi et al., 2017). In this regard, small tropical rivers are very sensitive and vulnerable to significant environmental changes and socio-economic problems, thus acting as indicators of change on spatial and temporal scales (Syvitski et al., 2014). Small tropical rivers transport the same or nearly the same amounts of solutes, suspended particulates and sediments as large rivers in response to extreme catastrophic events such as cyclones, floods, or earthquakes (Hilton et al., 2008; Milliman et al., 2017). Additionally, these rivers possess unique characteristics as they are predominantly seasonal and dynamic in nature. The factors controlling the sources composition, distribution and transport of solutes, particulates and sediments in these rivers is governed by the seasonal (Jennerjahn et al., 2008; Wu et al., 2013) and geomorphological features (meandering river loops) (Fernandes et al., 2019) along with tides, rainfall and river discharge (Goldsmith et al., 2015).

Estuaries are transition zones acting as conduits for transferring both dissolved solutes and particulate matter from the terrestrial environs to the marine regions (Abril and Borges, 2005; Abril et al., 2007). Freshwater discharge, tidal forcing coupled with physical processes such as gravitational circulation and salinity stratification forms the estuarine turbidity maxima (ETM)

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within estuaries. The distribution and concentration of suspended particulate matter (SPM) within the ETM can be directly related to its location and physical processes (Geyer, 1993). The ETM behave differently as they have dual characteristics. Both the allochthonous and autochthonous sources of OM exist due to the hydrodynamic function of the tidal pumping and estuarine circulation (Suzuki et al., 2010; Uncles et al., 2006). The ETM is an important feature as it influences primary productivity, pollutant flushing, fish migration, and anthropogenic activities (dredging) (Mitchell et al., 1999). Additionally, the ETM are important sites where mineralization of particulate organic nitrogen (PON) takes place (Abril et al., 2000). The non-conservative mixing behavior of the particulate components and their active transport by the estuary influences the quality and quantity of OM. The OM entrained within SPM plays a vital role in the lateral and vertical transport of material from the river to the sea. Therefore, in the recent years the estuarine systems have received considerable attention as they are impacted by nutrients influx and pollutants from agricultural, industrial sources, and waste water runoff from their watersheds (Rao et al., 2011).

The origin and diagenetic state of OM entrained within suspended particles has been studied using number of techniques mainly taking into consideration the bulk parameters (C:N ratio and stable isotope composition) and organic biomarkers (pigments, lipids, lignin phenols and amino acids) (Cowie and Hedges, 1994; Wu et al., 2007; Veuger et al., 2012; Pradhan et al., 2014). Most conventional studies have taken into consideration the C:N ratio coupled with stable isotopes in order to distinguish between the terrestrial and marine sources of OM (Gordon and Goñi, 2003). Components used as biomarkers are derived from terrestrial plants, marine plankton and bacteria provide specific and complementary data to trace the origins of OM (Zhang et al., 2014). Amino acids (AA) are the basic building blocks of all organisms, and are often used as biomarkers. They act as a promising tool as they have specific biological sources and are relatively well preserved during diagenesis (Eglinton and Eglinton, 2008). Being ubiquitous in the environment, they are often used to provide insights about OM sources and diagenetic alterations (Dauwe and Middelburg, 1998; Kaiser and Benner, 2008). Additionally, the D-enantiomers of some AA are used as tracers to identify sources and degradation status of organic nitrogen (ON) (Wu et al., 2007). The AA such as alanine, glutamic acid, aspartic acid, serine and arginine provide information about bacterial sources (Lomstein et al., 2009; Wu et al., 2007).

Previously, most studies focused on the bulk characteristics of OM in relation to the origin, distribution and its role in affecting the environment (Gupta et al., 1997; Jørgensen et al., 2014; Ke et al., 2017). The Zuari River system (ZRS) is a small tropical river located on west coast of India which is affected by natural (rainfall, tides) and anthropogenic (agriculture, aquaculture, mining, land reclamation, sewage discharge) stressors. The occurrence of ETM is a consistent feature of this river and it persists throughout the year at the mouth of the estuary. However, most studies conducted in this river distinguished between the sources of organic carbon (OC), geochemistry of major and trace metals (Kessarkar et al., 2013), and bacterial production (Bhaskar and Bhosle, 2008) from SPM. The distribution and speciation of trace metals in surface sediments was investigated by Dessai and Nayak (2009). Number of biomarkers have been used to study various aspects of riverine and estuarine environment, however there are limited studies focusing on the use of AA as the biomarker approach to explain the composition and diagenetic status of OM from this river. Considering the importance of the ETM in influencing the distribution and transformation of OM, we conducted this study to understand the sources, contributions, quality and factors controlling POM within this small tropical river. Detailed investigations were carried out for the AA biomarkers (L- and D- enantiomers) entrained within particulate matter along with the ancillary parameters so as to determine the provenance, contributions, and the controlling factors such as seasons, zone, and geomorphological settings (wide mouth of the estuary). We hypothesize the composition and diagenetic status of POM trapped within the estuarine region is influenced by the ETM.

2 Materials and methods

2.1 *Study area*

The ZRS is located in the state of Goa, India between the latitudes 15°20′N and 15°30′N, and longitudes 73°45′E and 74°10′E (Fig. 1a) and has a catchment area of approximately 550 km^2 (Bardhan et al., 2015). It is a highly seasonal river originating at Hemad–Barshem hills in the Western Ghats escarpments. The river flows approximately 145 km before draining into the Arabian Sea at Mormugao. The Zuari River and its basin experience a humid tropical monsoon type of climate. The Ghats presents a topographical barrier to the southwest monsoon (SWM) winds and thus creates one of the world's highest orographic gradients (Hibbert et al., 2015). Approximately 85% of the seasonal precipitation and runoff occurs during the monsoon months (June–September). The maximum rainfall that the region experiences during the monsoon season for any day could range from 70 to 200 mm/d (India Meteorological Department (IMD), 2013). The fresh water discharge of ZRS is regulated by a dam (Selaulim dam) in the upstream that has a storage capacity of 227×10^6 m^3/a (i.e., ~10% of total annual runoff: 2 190×10^6 m^3/a; Suprit and Sankar, 2008). Most of the river discharge is during the monsoon with negligible discharge during the other (post- and pre-monsoon) seasons (Kessarkar et al., 2013). The runoff measured in the upstream for the monsoon, post-monsoon and pre-monsoon were ~147, 7.3 and 0.8 m^3/s, respectively (Kessarkar et al., 2013). The river flows steeply down the Western Ghats across the low-lying coastal plains, which are mainly composed of heavily weathered rocks and covered by laterites. Due to low elevation of the coastal plains, the tidal effect are observed ~45 km inland and it is forced out seawards during the monsoons by high amounts of river discharge (Shetye et al., 2007). The tides are of mixed semi-diurnal type and the river experiences a meso-tidal range of about ~2.3 and 1.5 m during the spring and neap tides as it is situated along the central west coast of India (Sundar and Shetye, 2005; Shetye et al., 2007). The river experiences vertical mixing of the water column due to strong flood and ebb tides (Manoj and Unnikrishnan, 2009). The river forms an estuarine system at the mouth (Shetye et al., 1995) and is classified as a "monsoonal estuary" (Vijith et al., 2009). A characteristic feature of this estuary is the occurrence of ETM in the channel during the monsoon and post-monsoon season and it moves to the bay region near to the mouth during the pre-monsoon season. The formation of the ETM results from the interaction of tidal currents, river flow and wind induced currents (Rao et al., 2011). The estuarine region of the Zuari River is fringed with mangroves along its banks serving as nursery grounds to organisms such as prawn, fish and many other invertebrate species thereby supporting diverse flora and fauna (Bhosle, 2007). The sediments of the river are primarily composed of sand (58.6%±34.7%) while silt+clay fractions account for 42%±34.1% (Rao et al., 2015). Dominant land use practices include plantations within the degraded forest lands (jack-

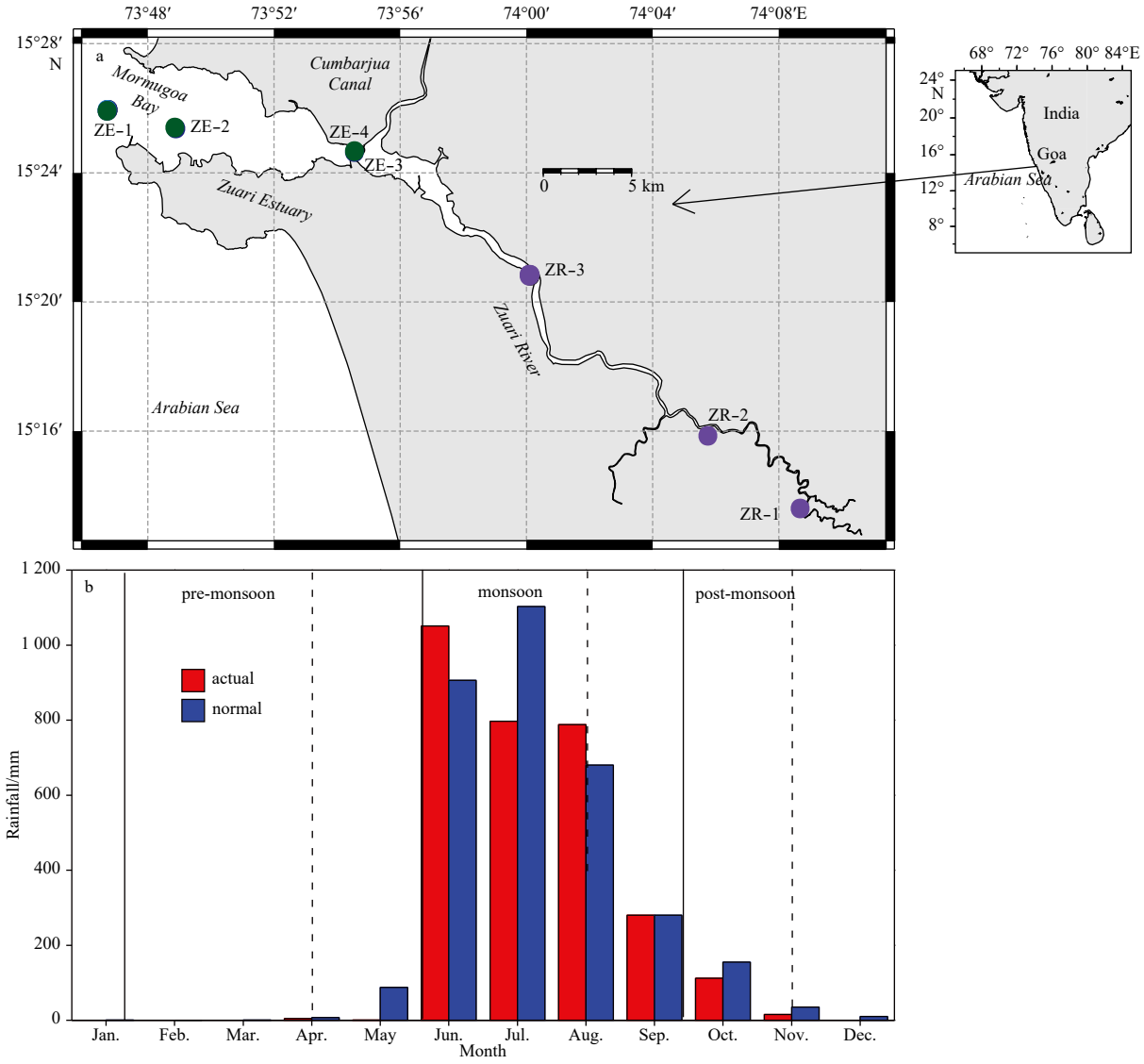

Fig. 1. The location of sampling stations within the Zuari River (station marked in dark green are the estuarine stations and the ones in violet are the riverine stations) (a), and average monthly rainfall (mm) for the year 2011–2012 (the red color columns indicate actual rainfall and the blue color the predicted rainfall) (b). Source is from the India Meteorological Department (IMD, 2013). The solid lines demarcate the three seasons and the dashed lines the sampling period.

fruit and coconut) and areas of mineral ore mining. This area is associated with moderately dense human settlements over the basin (population density of Goa is 394 inhabitants per km^2; Census Organization of India, 2011). A major shipping port is located in close proximity to the river mouth and is affected by anthropogenic activities such as mine tailings, discharge of partially treated or untreated sewage from municipal sources (Bardhan et al., 2015).

2.2 *Sampling sites and sample collection*

Surface water samples were collected from the riverine and estuarine region from predetermined locations along the Zuari River during the SWM of 2011 (August–September), post-monsoon season of 2011 (November–December) and pre-monsoon season of 2012 (April–May) (Figs 1a, b). The sampling stations Zuari River 1 and 2 (ZR-1 and ZR-2) are located in the main channel of the river, whereas the stations Zuari Estuary 1, 2, 3 and 4 (ZE-1, ZE-2, ZE-3 and ZE-4) were positioned within the estuarine region of the river. River water was collected using a clean bucket lowered from the top of a bridge into the river channel. Surface water samples from the estuarine region were collected using a 5 L Niskin water sampler (General Oceanic, USA) from a mechanized boat. The collected water samples were transferred to acid cleaned polyethylene carboys and were preserved with ice in an icebox and transported to the local laboratory (National Institute of Oceanography, Goa, India) for preliminary analyses and subsampling. The water samples were then sub-sampled, processed and preserved at –20°C before shipping them to SKLEC, ECNU, Shanghai for further analyses.

2.3 *Hydrographic measurements*

In-situ measurements of temperature, pH, and salinity were done using a multi-parameter system provided with a probe (Inolab multi-720). The average precision for temperature, salinity, and pH measured by the probe system was 0.01°C, 0.01 and 0.01 pH units, respectively.

2.4 *Suspended particulate matter (SPM), chlorophyll a and dissolved organic carbon (DOC)*

Water samples were filtered through pre-combusted (450°C, 5 h) GF/F fiber filters (nominal pore size 0.7 μm; 47 mm diameter; Whatman) under moderate vacuum for analyses of bulk and trace level contents from SPM. The filters were stored in pre-combusted aluminum foils (450°C, 5 h) at –20°C until further analysis of the contents was done for the isotopic measurements of the stable isotope of carbon (δ^{13}C), nitrogen (δ^{15}N) (Krishna et al., 2018), chlorophyll *a* and AA. The SPM was measured as the difference of weight after drying the filters at 40°C for 48 h. Chlorophyll *a* concentration was determined using Whatman 47 mm Ø GF/F fiber filters (0.7 μm nominal pore size). The contents were extracted using 90% acetone, refrigerated (4°C) in dark for 20–24 h, centrifuged and the absorbance was measured at 750, 664, 647 and 630 nm using a spectrophotometer (Shimadzu UV 1800) according to Strickland and Parsons (1972). Analysis of DOC from filtered water samples was done using the high-temperature catalytic oxidation (HTCO) method [Shimadzu TOC analyzer (model: TOC-CPH)]. The relative standard deviation of the method was less than 2% (Wu et al., 2013).

2.5 *Elemental and stable isotope analyses*

About one quarter of the dried filter membrane containing SPM was weighed, cut and acidified with excess 1 mol/L HCl for 24 h in order to completely remove the inorganic carbon. These filters were then dried at 45°C in an oven for 24–36 h to remove the traces of acid and moisture, and were later packed in tin cups for analyses. The content of particulate organic carbon (POC) and δ^{13}C were measured by an elemental analyzer (Finnigan EA1112) interfaced with a continuous flow isotope ratio mass spectrometer (Finnigan Delta plus XP). The results are expressed as per mille (‰) deviation relative to the Vienna–Pee Dee Belemnite (V-PDB) standard calculated using the equation below:

$$\delta^{13}\mathrm{C}\ (‰) = \left[\left(\left({}^{13}\mathrm{C}/{}^{12}\mathrm{C}\right)_{\mathrm{sample}}/\left({}^{13}\mathrm{C}/{}^{12}\mathrm{C}\right)_{\mathrm{PDB}}\right) - 1\right] \times 1\,000. \quad (1)$$

Particulate nitrogen (PN) and nitrogen isotope composition (δ^{15}N) were measured form un-acidified filter membranes. The δ^{15}N was determined using a Thermo Finnigan Delta plus XP gas isotope ratio mass spectrometer (IRMS) after high temperature combustion in a Flash 1112EA elemental analyzer. The δ^{15}N values are presented as per mille (‰) deviation from atmospheric N_2 isotope composition and were calculated using the equation below:

$$\delta^{15}\mathrm{N}\,(‰) = \left[\left(\left({}^{15}\mathrm{N}/{}^{14}\mathrm{N}\right)_{\mathrm{sample}}/\left({}^{15}\mathrm{N}/{}^{14}\mathrm{N}\right)_{\mathrm{atmospheric\ N2}}\right) - 1\right] \times 1\,000. \quad (2)$$

The standard deviations based on replicate analyses of laboratory standard was <10% for OC content, <1% for N content, ±0.3‰ for δ^{13}C and ±0.2‰ for δ^{15}N. Standards were analyzed every ten samples and had a mean analytical error of 0.05%.

2.6 *Amino acid analyses*

Digestion of OM (proteins) to its monomers (AA) was done by acid hydrolysis, as it is an ideal method (Nunn and Keil, 2005). Total hydrolysable amino acids (THAA) were analyzed according to Fitznar et al. (1999) and Wu et al. (2007). In brief, approximately one quarter of the filter membranes were hydrolyzed with HCl (16%, 10 mL) in pre-combusted glass ampoules (450°C, 5 h), sealed in a nitrogen (N_2) environment and incubated in an oven for 22–24 h at 110°C. The samples were cooled and neutralized with boric acid buffer. The pH was adjusted to pH 8.5 by adding NaOH solution. Samples were analyzed using a slightly modified method that incorporated a Phenomenex™ Hyperclone column (5 μm particle diameter, BDS C18, 250 mm length, 4 mm inner diameter) with a guard column (4 mm×2 mm). The mobile phases were: (A) 125 mmol/L sodium acetate with 2% methanol (pH 6.8, adjusted with acetic acid), and (B) HPLC grade 100% methanol. The gradient began at 99% A and 1% B and was gradually changed to 100% B at 110 min (held for 3 min), before being shifted back to the initial conditions. External AA enantiomer standards (Fluka, Switzerland; Aldrich, USA; Sigma, USA) were used for calibration. Deamination reaction results in the degradation of glutamine (Gln) and asparagines (Asn) during hydrolysis. Therefore in the results we represent Asx and Glx as the sum of aspartic acid (Asp) + asparagines (Asn) = (Asx) and glutamic acid (Glu) + glutamine (Gln) = (Glx), respectively. The L- and D-enantiomers of the individual amino acids in the hydrolyzates were determined fluorometrically by a high performance liquid chromatography (HPLC) system (Agilent 1100 series). The relative standard deviation for the individual amino acids for triplicate analysis was <3.5% (Wu et al., 2007). The contribution of racemerized D-amino acid content during hydrolysis is very small as compared to the naturally occurring D-amino acid as discussed in study conducted by Dittmar et al. (2001). The relative abundance of individual AA was used to calculate the degradation index (DI) of the samples following the equation based on Dauwe and Middelburg (1998) and Dauwe et al. (1999), given below as follows:

$$\mathrm{DI} = \sum_i \left[\frac{\mathrm{var}_i - \mathrm{AVGvar}_i}{\mathrm{STDvar}_i}\right] \times \mathrm{fac.coef.}_i \quad (3)$$

where var_i is the molar percentage of AA i in the sample, $\mathrm{fac.coef.}_i$, AVGvar_i and STDvar_i are the principal component analysis factor coefficient, mean molar percentage and standard deviation of AA i in the dataset of Dauwe et al. (1999).

2.7 *Statistical analyses*

Data were tested for normality using Shapiro–Wilk test and homogeneity of variance using Levene's test. One way analysis of variance (ANOVA) followed by Tukey's post hoc test and the independent *t* test were applied to the temporal and spatial data, respectively so as to determine the significant differences. Pearson's correlation coefficient was calculated to assess the inter-relationships and associations among the parameters investigated. A p value of $\leqslant 0.05$ was considered statistically significant for all the statistical tests, unless otherwise stated. The R-mode factor analysis (FA) with Varimax-normalized rotation by means of principal components extraction method (Kara, 2009) was applied to the physical and bio-chemical variables of the data set. The data were normalized by subtracting the mean of all values and dividing each variable by its standard deviation (Unger et al., 2013). All statistical analyses were done using the IBM SPSS 20 software (IBM, Armonk, NY, USA).

3 Results

3.1 *Physical, biological and ancillary parameters*

The highest average rainfall was recorded during the mon-

soon season ((730±280) mm) followed by the post-monsoon ((30±45) mm) and pre-monsoon ((1±2) mm) seasons, respectively during the period of this study (IMD, 2013). Rainfall during the monsoon was significantly higher than the other two seasons (post- and pre-monsoon) (p<0.05). No significant difference was observed between the recorded actual rainfall and the predicted normal rainfall (p>0.05, Fig. 1b). Surface water temperature and pH values varied from 28.0°C to 33°C and 6.6 to 8.2 with an average of 30.6°C and 7.7, respectively. Significantly lower temperatures (p<0.05) were observed during the monsoon season as compared to the post- and pre-monsoon season. Significantly higher pH (p<0.05) was observed in the estuarine region as compared to the riverine region. Salinity values measured ranged from 0 to 35, with the highest value recorded during the pre-monsoon season in the estuarine region (Table 1). Significantly higher salinities (p<0.05) were recorded in the estuarine region as compared to the riverine region. The SPM values varied from 1.3 to 165.6 mg/L (Table 1, Fig. 2a), with no significant spatial or temporal variations (p>0.05). Chlorophyll *a* values ranged from 2.0 to 9.5 mg/m^3 with an average of 4.1 mg/m^3. The highest values were observed in the riverine region during the pre-monsoon season (Table 1) with no significant spatial or temporal variations (p>0.05). Although higher values of DOC are observed in the riverine region, no significant differences were observed spatially and temporally (p>0.05, Table 1).

3.2 *Bulk geochemical parameters*

The POC and PN content expressed on the basis of the whole weight varied from 1.4% to 38.8% and from 0.1% to 5.2% with an average of 6.7% and 0.9%, respectively with no significant temporal differences in both the estuarine and riverine regions (p>0.05, Table 1). The POC and PN content of the riverine stations were significantly higher than that of the estuarine stations (p<0.05). The C:N_{atomic} ratio and N:C_{atomic} ratio varied from 1.9 to 19.8 and 0.05 to 0.53 with an average of 11.0 and 0.12, respectively with no significant temporal or spatial variation (p>0.05). The δ^{13}C values of SPM varied from –34.1‰ to –20.4‰ with an average of –26.4‰ and the values were significantly different spatially with more depleted values in the riverine region (p<0.05, Fig. 2b). The δ^{15}N values of SPM varied from 1.0‰ to 9.3‰ with an average of 5.6‰ (Table 1). Significantly higher δ^{15}N values were measured in the estuarine region as compared to the riverine region (p<0.05). Furthermore, the POC:Chl *a* ratio and DOC:POC ratio varied from 49.4 to 610.6 and 0.4 to 3.5 with an average of 182.7 and 1.8, respectively (Table 1). Apparently these ratios did not show any significant variability spatial or temporal (p>0.05).

3.3 *Biomarkers and allied indices*

The THAA content varied from 0.1 to 0.5 μmol/g with an average of 0.2 μmol/g with no significant differences spatially and temporally (p>0.05). Highest values were measured in the estuarine region during the pre-monsoon season (Table 2). The contribution of THAA to carbon (AA-C%) varied from 0.1% to 10.0% with an average of 2.4% and was significantly different for the two regions, with higher values in the estuarine region (p<0.05). The contribution of THAA to nitrogen (AA-N%) varied from 0.5% to 51.2% with an average of 10.7% with no significant spatial or temporal differences (p>0.05). Based on functional groups, neutral AA was the most abundant ones and varied from 73.4% to 81.4% with an average of 77.7%. Acidic AA accounted for almost 27.1% to 30.9% with an average of 29.8%. Significantly lower amounts of acidic AA were found in the riverine region as compared to the estuarine region (p<0.05). Hydroxylic AA accounted for about ~16% (Table 2). Aromatic and basic AA accounted for about 5.7% to 7.5% and 3.7% to 4.9% with an average of 6.4% and 4.4%, respectively with no significant spatial and temporal differences (p>0.05, Table 2).

A total of 18 monomers of AA were detected from SPM for the three seasons (Table 3). The average mol percentage (mol%) composition of individual AA from SPM for the two regions with significant differences is presented in Fig. 3a. The most abundant AA were Gly, Ala, Glx, Asx, Ser and Val. The basic AA—Arg varied from 2.7% (mole pencentage) to 3.6% with an average of 3.3%. No significant differences were observed between the AA data collected for the three seasons. Hence the data was analyzed spatially (estuarine and riverine samples). Glx, Ser, Ala, Tyr and Leu displayed significant spatial differences (p<0.05) with higher values of Glx and Tyr were observed in the estuarine region as compared to the riverine region. Likewise, higher values of Ser, Ala and Leu were observed in the riverine region as compared to the estuarine region. The contribution from non protein AA—gamma (γ)-aminobutyric acid (GABA) was low and varied from 0.4% to 1.2% with an average of 0.6% for the three seasons with no significant spatial or temporal variations. The contribution from Tyr+Phe was slightly above 5% (Table 3).

Furthermore, the contributions from the D-enantiomers of AA, namely, D-Asx, D-Glx, D-Ser and D-Ala, varied between 2.2% to 9.6% with an average of 6.6% for the three seasons (Table 3). The percentage contribution of D-Arg was higher as compared to the other D-AA and accounted for more than 13% with no significant spatial or temporal differences (p>0.05). The percentage contributions from D-AA were comparatively higher in the estuarine region as compared to the riverine region (Fig. 3b). Only D-Asx showed significant differences (p<0.05) with higher values observed in the estuarine region as compared to the riverine region. The D/(D+L)AA ratio varied from 2.9 to 7.2 with an average of 4.3 and was significantly different for the two regions (p<0.05) with higher ratios observed in the estuarine region as compared to the riverine region. The DI values varied from –0.23 during the monsoon season to 0.19 during the post-monsoon season with an average of –0.03. The Glx:GABA ratio varied from 8.5 to 28.9 with an average of 18.7 (Fig. 4). No significant spatial or temporal differences were observed with DI and Glx:GABA ratio (p<0.05).

3.4 *Correlation and principal component analyses (PCA)*

Correlation analyses indicated contrasting results with some parameters depicting positive correlations while others presented negative correlations (Table S1). Significant positive correlation was observed between salinity and δ^{13}C (r=0.89, p<0.01), acidic AA (r=0.72, p<0.01) and D-Asx (r=0.57, p<0.05). Similarly, strong positive correlations were observed between SPM with THAA, D-Asx (r=0.84, p<0.01; Fig. 5), D-Glx, D/(D+L)AA ratio, D-Ala, and GABA. D/(D+L) ratio and GABA were strongly positively correlated with the individual monomers of D-AA (Table S1). Likewise, D-Asx correlated positively with all the other D-AA, namely, D-Ala, D-Arg, D-Glx (p<0.01) and D-Ser (p<0.05), suggesting a common source of D-AA (Table S1). Furthermore, significantly strong negative correlation was observed between OC and δ^{13}C (r=–0.72, p<0.01). Strong negative correlations were observed between acidic AA and chlorophyll *a* (r=–0.75, p=0.01) and between hydroxylic AA and DI (r=–0.78, p=0.01) (Table S1).

Unbiased variables from the data set were subjected to principal components (PC) analyses. Five leading PC were extracted based on the Eigen values (>1) and accounted for 85.5% of the total variance. The PC analyses showed that the first principal

Table 1. Station locations, physical and bulk biochemical parameters of water and suspended particulates of the Zuari River, west coast of India

Season /station name	Distance from estuary/km	North latitude	East longitude	Temperature /°C	pH	Salinity	SPM /mg·L^{-1}	Chl *a* /mg·m^{-3}	POC /%	PN /%	δ^{13}C/ ‰	δ^{15}N/ ‰	C:N atomic	N:C atomic	POC:Chl *a*	DOC /μmol·L^{-1}	DOC:POC
Monsoon																	
ZE-1	–4	15.43°	73.78°	29.4	8.1	18.9	13.6	2.2	3.3	0.3	–22.8	7.7	11.4	0.09	204.4	60.1	1.6
ZE-2	0	15.42°	73.82°	29.3	8.1	18.4	17.7	3.5	2.8	0.3	–22.8	7.8	12.9	0.08	143.1	58.9	1.4
ZE-3	13	15.41°	73.91°	29.2	7.5	7.5	10.9	2.0	3.2	0.4	–28.4	6.4	9.1	0.11	175.6	43.9	1.5
ZR-2	46	15.35°	74.00°	28.0	7.0	0.0	9.7	4.3	8.5	5.2	–28.5	1.0	1.9	0.53	191.6	50.7	0.7
ZR-1	56	15.23°	74.14°	29.2	6.6	0.0	1.3	3.0	38.8	2.3	–34.1	2.5	19.8	0.05	172.3	39.7	0.9
Average				29.0	7.5	9.0	10.7	3.0	11.3	1.7	–27.3	5.1	11.0	0.17	177.4	50.7	1.2
SD				0.6	0.7	9.4	6.0	0.9	15.5	2.1	4.7	3.2	6.5	0.20	23.1	9.0	0.4
Post-monsoon																	
ZE-1	–4	15.42°	73.82°	30.4	8.2	33.7	16.5	3.8	1.9	0.2	–20.4	8.1	9.4	0.11	82.6	65.9	2.5
ZE-2	0	15.43°	73.78°	30.5	8.1	33.7	18.5	2.7	1.5	0.2	–21.0	9.3	10.6	0.09	105.9	69.9	2.9
ZE-4	12	15.41°	73.91°	31.7	7.8	24.8	27.5	3.6	1.4	0.2	–24.7	4.9	9.5	0.11	104.3	75.3	2.4
ZE-3	13	15.41°	73.91°	31.1	8.0	31.1	44.4	3.5	1.4	0.1	–23.0	5.6	11.8	0.08	177.6	85.4	1.6
ZR-2	46	15.35°	74.00°	30.6	7.0	10.4	27.3	4.8	2.8	0.2	–27.3	5.4	13.7	0.07	156.7	149.0	2.4
ZR-1	56	15.23°	74.14°	29.1	6.9	0.0	11.0	3.7	9.4	0.8	–29.4	4.3	13.7	0.07	278.2	138.9	1.6
Average				30.6	7.7	22.3	24.2	3.7	3.1	0.3	–24.3	6.3	11.5	0.09	150.9	97.4	2.3
SD				0.9	0.6	14.0	11.8	0.7	3.1	0.3	3.5	2.0	1.9	0.01	71.8	36.8	0.5
Pre-monsoon																	
ZE-1	–4	15.43°	73.78°	31.0	8.1	35.0	165.6	5.6	2.1	0.2	–23.4	6.2	13.6	0.07	610.6	124.8	0.4
ZE-2	0	15.42°	73.82°	31.3	7.9	35.0	14.4	3.2	1.9	0.2	–21.3	8.2	10.9	0.09	84.9	78.3	3.5
ZR-3	27	15.27°	74.11°	33.0	7.6	17.6	22.1	3.4	3.6	0.5	–29.6	5.6	9.0	0.11	231.2	45.5	0.7
ZR-2	46	15.35°	74.00°	33.0	7.2	0.0	8.3	6.3	11.7	1.5	–31.5	3.0	9.4	0.11	155.0	55.4	0.7
ZR-1	56	15.23°	74.14°	32.2	7.0	0.0	3.5	9.5	13.4	1.7	–33.6	3.8	9.4	0.11	49.4	119.8	3.1
Averege				32.1	7.6	17.5	42.8	5.6	6.5	0.8	–27.9	5.4	10.5	0.10	226.2	84.8	1.7
SD				0.9	0.5	17.5	69.0	2.6	5.6	0.7	5.3	2.0	1.9	0.02	225.9	36.3	1.5

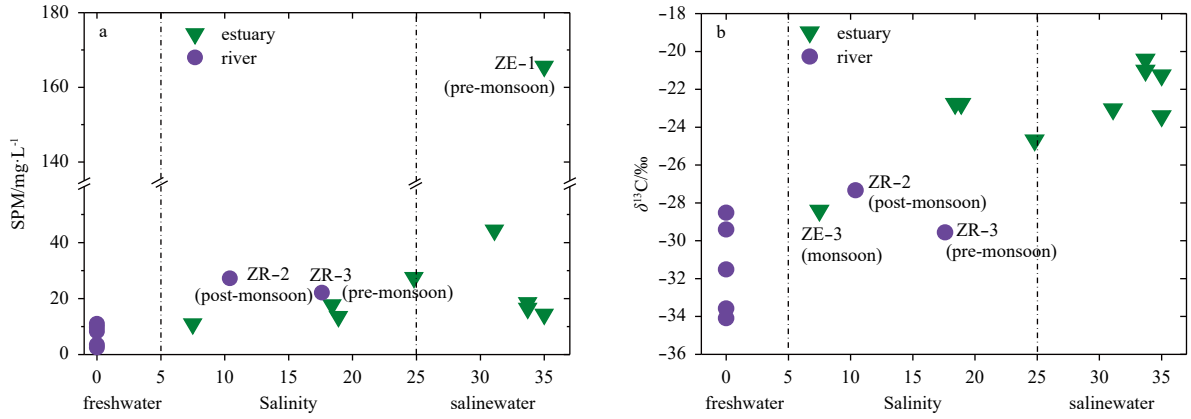

Fig. 2. Plots of suspended particulate matter (SPM, mg/L) with salinity (a), and δ^{13}C (‰) with salinity (b) of the Zuari River and estuary.

Table 2. Bulk concentrations of amino acids (AA) from suspended particulates of the Zuari River, west coast of India

Season/station name	THAA/μmol·g^{-1}	AA-C/%	AA-N/%	Neutral/%	Acidic/%	Hydroxylic/%	Aromatic/%	Basic/%	D/(D+L)AA
Monsoon									
ZE-1	0.2	1.8	7.8	79.8	30.9	16.0	6.2	3.7	4.5
ZE-2	0.2	2.2	10.5	80.3	29.9	16.2	6.7	3.9	3.4
ZE-3	0.1	1.5	5.3	77.8	30.3	16.6	6.2	4.4	3.8
ZR-2	0.1	0.6	0.5	81.4	28.7	17.7	5.9	4.6	4.4
ZR-1	0.1	0.1	0.8	74.7	28.6	17.2	6.1	4.8	4.2
Average	0.1	1.2	5.0	78.8	29.7	16.7	6.2	4.3	4.1
SD	0.0	0.9	4.4	2.6	1.0	0.7	0.3	0.5	0.5
Post-monsoon									
ZE-1	0.1	2.5	8.8	75.2	30.7	16.1	6.7	4.2	3.8
ZE-2	0.1	2.9	11.6	75.1	29.9	16.0	7.5	4.3	3.7
ZE-4	0.1	3.6	13.1	76.0	29.9	16.5	6.1	4.6	5.0
ZE-3	0.2	4.7	21.5	79.0	30.1	17.4	5.8	4.4	4.9
ZR-2	0.2	2.8	14.7	78.6	29.3	17.0	5.7	4.4	4.4
ZR-1	0.2	1.0	5.2	73.4	29.0	17.4	6.0	4.6	5.2
Average	0.2	2.9	12.5	76.2	29.8	16.7	6.3	4.4	4.5
SD	0.1	1.2	5.5	2.2	0.6	0.6	0.7	0.2	0.6
Pre-monsoon									
ZE-1	0.5	10.0	51.2	79.1	29.8	17.2	7.1	4.6	7.2
ZE-2	0.1	1.8	7.6	77.4	30.4	16.2	6.4	4.9	5.1
ZR-3	0.2	2.2	7.5	78.0	28.7	16.2	6.2	4.5	2.9
ZR-2	0.2	0.8	2.9	80.1	27.6	16.3	6.9	4.5	3.0
ZR-1	0.1	0.4	1.5	77.8	27.1	15.9	6.3	4.5	3.8
Average	0.2	3.0	14.1	78.5	28.7	16.4	6.6	4.6	4.4
SD	0.2	3.9	20.9	1.1	1.4	0.5	0.4	0.2	1.8

component represents up to 27.1% of the total variance of the observations with strong positive loading of acidic AA, δ^{13}C and salinity with negative loading of chlorophyll *a*. The positive values on component one corresponds to important inputs and the negative values to low inputs. The first component can be characterized as the tidal factor. The second component accounted for 19.6% of the variance, with strong positive loading of GABA, D-Asx and SPM, together with moderate positive loading of hydroxylic AA (Fig. 6; Table S2). The second component favors the characterization of microbial inputs attached to SPM. The third component accounts for 14.1% of the variance with positive loading of pH and moderate positive loading of POC and PN, and strong negative loading of DOC. The variances accounted by component four and five were 13.3% and 10.4%, respectively (Table S2).

4 Discussion

4.1 *The sources of OM in the Zuari River and estuary*

In our study, the POC and PN values of the estuarine region were significantly lower than the values found in the riverine region, whereas the C:N $_{atomic}$ ratio was >9 for most stations except Sta. ZR-2 (monsoon season) displayed a very low value (Table 1). These values are within the range of values observed for terrestrial (plant detritus and soils) and marine sources. Terrigenous plants are rich in lignin whereas, phytoplankton are rich in protein and thus have a C:N$_{atomic}$ ratio of >15 and 4–10, respectively and this ratio is often used to distinguish sources arising from

Table 3. Concentration of L-enantiomer of AA in mole percentage, percentage contribution of D-AA and diagenetic indices of suspended particulates of the Zuari River, west coast of India

Season /station name	Asx /%	Glx /%	Ser /%	Thr /%	Gly /%	Arg /%	Ala /%	GABA /%	Tyr /%	Val /%	Phe /%	Ile /%	Leu /%	D-Asx /%	D-Glx /%	D-Ser /%	D-Ala /%	D-Arg /%	DI (Dauwe)	Glx: GABA
Monsoon																				
ZE-1	11.1	11.3	6.6	5.1	26.5	2.7	12.9	0.8	0.5	7.7	4.0	5.5	5.1	6.3	4.6	5.5	5.7	23.9	–0.04	15.11
ZE-2	10.3	11.3	6.8	4.9	26.8	2.9	12.7	0.6	0.6	7.4	4.3	5.5	5.5	4.8	3.8	5.1	3.7	15.4	0.11	19.09
ZE-3	10.9	11.3	7.1	5.1	25.9	3.2	13.1	0.7	0.6	7.3	3.9	5.3	5.4	5.1	4.5	4.9	4.7	18.7	–0.03	16.91
ZR-2	10.6	10.0	7.7	5.0	27.5	3.3	13.5	0.7	0.2	7.1	4.0	4.8	5.4	4.6	6.1	3.4	6.2	23.8	–0.23	14.39
ZR-1	10.8	10.8	7.5	5.5	23.7	3.6	14.4	0.7	0.4	7.4	4.3	4.9	5.6	4.6	5.9	4.6	4.1	20.2	–0.13	15.08
Average	10.8	11.0	7.1	5.1	26.1	3.1	13.3	0.7	0.5	7.4	4.1	5.2	5.4	5.1	5.0	4.7	4.9	20.4	–0.1	16.1
SD	0.3	0.6	0.5	0.2	1.4	0.4	0.7	0.1	0.2	0.2	0.2	0.3	0.2	0.7	1.0	0.8	1.0	3.6	0.1	1.9
Post-monsoon																				
ZE-1	11.0	12.0	7.1	4.9	24.6	3.1	13.4	0.5	1.0	7.2	4.1	5.2	5.6	4.5	4.7	7.5	3.4	15.6	0.11	26.72
ZE-2	11.1	11.4	7.1	4.9	24.6	3.2	13.3	0.4	1.3	7.2	4.4	5.3	5.7	4.7	4.9	4.9	4.2	14.5	0.19	28.91
ZE-4	10.7	11.5	7.4	4.9	24.6	3.5	14.3	0.9	0.6	7.2	4.0	4.8	5.4	5.7	5.8	7.7	5.9	21.4	–0.11	13.28
ZE-3	11.3	10.6	7.7	4.9	26.7	3.2	13.3	0.6	0.4	7.2	3.9	4.8	5.2	6.0	6.5	6.4	4.9	23.7	–0.21	17.10
ZR-2	10.9	10.6	7.5	5.0	25.8	3.2	13.4	0.7	0.2	7.4	4.0	5.2	5.6	5.1	5.1	5.0	5.1	21.5	–0.09	15.59
ZR-1	11.0	11.0	7.9	5.3	23.1	3.5	14.2	0.9	0.5	7.2	4.0	4.9	5.7	4.5	5.7	8.4	4.9	25.4	–0.07	12.38
Average	11.0	11.2	7.5	5.0	24.9	3.3	13.7	0.7	0.7	7.2	4.1	5.0	5.5	5.1	5.4	6.7	4.7	20.3	0	19.0
SD	0.2	0.6	0.3	0.2	1.2	0.2	0.5	0.2	0.4	0.1	0.2	0.2	0.2	0.6	0.7	1.5	0.9	4.4	0.1	7.1
Pre-monsoon																				
ZE-1	11.3	10.1	7.2	5.2	27.1	3.3	12.6	1.2	1.4	7.0	3.7	4.7	4.8	8.4	9.0	8.9	8.6	33.3	–0.16	8.50
ZE-2	10.7	11.7	7.5	4.4	25.9	3.6	12.9	0.6	1.0	7.1	3.7	5.1	5.5	5.2	4.7	6.6	5.8	28.9	0.07	19.43
ZR-3	10.6	10.8	7.0	5.1	25.0	3.4	14.7	0.4	0.3	7.3	4.3	5.1	5.8	4.2	4.5	2.2	3.3	13.0	–0.08	26.83
ZR-2	9.6	10.7	8.0	3.9	26.0	3.3	14.6	0.4	0.2	6.7	4.9	5.0	6.5	3.6	4.3	3.0	3.4	14.5	0.17	24.92
ZR-1	10.0	10.5	7.7	4.4	23.9	3.4	16.0	0.4	0.5	7.6	4.3	5.1	6.0	3.8	5.0	6.7	3.7	16.9	0.00	25.68
Average	10.4	10.8	7.5	4.6	25.6	3.4	14.2	0.6	0.7	7.1	4.2	5.0	5.7	5.0	5.5	5.5	5.0	21.3	0.0	21.1
SD	0.7	0.6	0.4	0.5	1.2	0.1	1.4	0.3	0.5	0.4	0.5	0.2	0.6	2.0	2.0	2.8	2.3	9.2	0.1	7.6

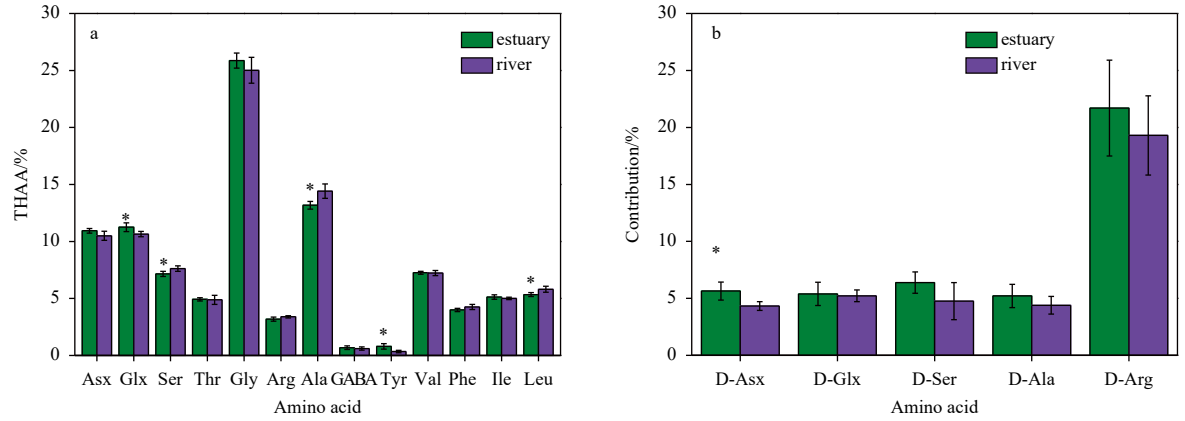

Fig. 3. The average concentration (mol percentage) of individual AA from SPM for the two regions with confidence intervals (p<0.05) (Asx, aspartic acid+aspargine; Glx, glutamic acid+glutamine; Ser, serine; Thr, threonine; Gly, glycine; Arg, arginine; Ala, alanine; GABA, Gamma (γ-)amino butyric acid; Tyr, tyrosine; Val, valine; Phe, phenylalanine; Ile, isoleucine; Leu, leucine) (a); and the percentage contribution of D-enantiomers of the individual AA in SPM of the Zuari River and estuary with confidence intervals (p<0.05) (b). * Significant differences (p<0.05).

marine and/or terrestrial OC (Meyers, 1997; Xu et al., 2018). The δ^{13}C values of OM in the riverine stations were more depleted as compared to the estuarine region and these values were within the range of C_3 plants (–22.0‰ to –35.0‰), soils, marine and river phytoplankton. These results suggest that allochthonous/terrestrial sources (C_3 plant detritus and soil) contribute substantially to OM in the riverine region and autochthonous/marine sources (*in-situ* production) to the estuarine region. The stations located within the salinity range of 5–25 exhibit mixed sources suggesting the role of the ETM in the redistribution and mixing of OM within this region (Figs 2a, b). These results are in agreement with the results obtained by previous studies conducted in the same region wherein only the monsoon season was sampled (Kessarkar et al., 2013). Likewise, the variation in δ^{15}N values can also be used to differentiate the sources of OM. Usually δ^{15}N values for soils range from 2.0‰ to 5.0‰, for plants from 3.0‰ to 7.0‰ and for plankton from –15‰ to 20.0‰ (Wu et al., 2007; Zhang et al., 2007; Maya et al., 2011). In our study, the samples

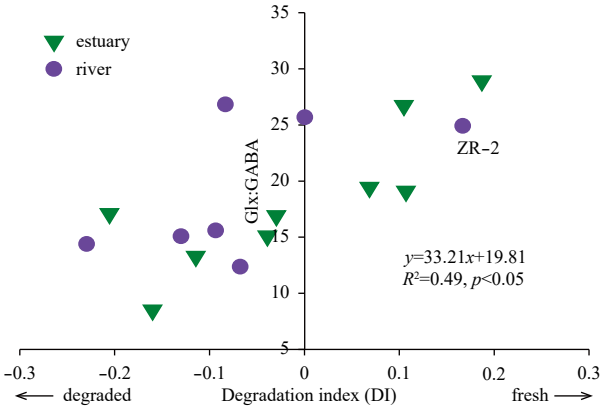

Fig. 4. The relationship between Glx:GABA and degradation index (DI).

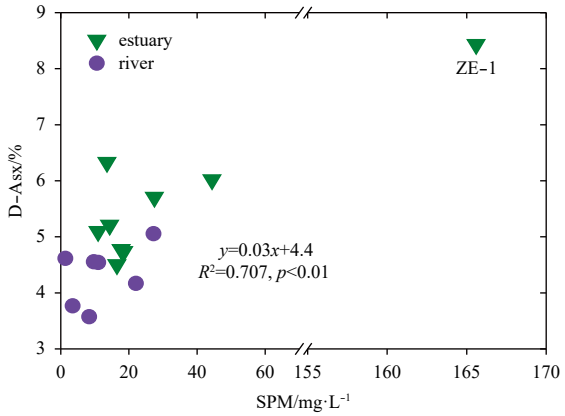

Fig. 5. Plot between D-Asx (%) and suspended particulate matter (SPM) (mg/L) of the Zuari River and estuary.

displayed higher values in the estuarine region and lower values in the riverine region (Table 1). Variations in δ^{15}N values of POM (7‰ to 9‰) collected from the estuarine can be attributed to the isotopic effects associated with nitrate uptake, nitrogen fixation and mixing of different OM sources. The isotopic values of the sampling stations located within the ETM exhibit narrow range suggesting the influence of the estuarine processes in redistributing the OM. A previous study conducted by Bardhan et al. (2015) concluded that the OM in the Zuari Estuary originated from two major pools, namely *in-situ* production and detritus (terrestrial and plankton). Station ZR-2 displays a much lower δ^{15}N isotopic signal during the monsoon season suggesting isotopic fractionation between the nitrogen assimilated by the phytoplankton and nutrients (Bardhan et al., 2015). In addition to the isotopic signatures, the POC:Chl *a* ratio are often used to distinguish the sources of OM from living resources mainly autotrophs and heterotrophs (Cifuentes at al., 1988; Krishna et al., 2018). Usually the POC:Chl *a* ratio of fresh OM produced by marine phytoplankton varies from ~40 (Montagnes et al., 1994) to <200 (Cifuentes at al., 1988) and these variations are attributed to differences in regional temperature, species composition and growth rates. As most of the stations exhibited values <200, it suggests mixed contributions. Some stations exhibited values >200 indicating that POM is dominated by detritus in the estuarine region during the monsoon and pre-monsoon season (Table 1). The possible explanation for this phenomenon can be attributed to the physico-chemical processes occurring within the ETM.

Along with the allochthonous and autochthonous sources, the POM of estuaries and coastal regions originate from anthropogenic sources which is usually consumed by the grazers and/or degraded by heterotrophic organisms. Thus, along with the terrestrial and marine sources, the heterotrophic bacteria and their remnants also contribute to OM, as indicated by the AA data (L- and D-enantiomers). The higher values of glycine (>23 mol%; Table 3) were observed in the estuarine region (Fig. 3a) pointing towards diatoms as a possible source (Keil et al., 2000), in addition to the accumulation of detrital OM (Dauwe and Middelburg, 1998; Wu et al., 2007). The relatively higher mole percentage contributions of Asx and Ala (>10 mol%, Fig. 3a) points towards the contributions from bacteria and its remnants, as cell wall material originating from heterotrophic organisms have an Ala signal (Mayer et al., 1995). The substantial contributions of D-AA in all the SPM samples suggest that bacteria and their remnants contribute substantially to the OM reservoir (Fig. 3b). The D-AA are major the components of bacterial cell wall (peptidoglycan) and are not produced by algae or vascular plants (Jørgensen et al., 2003; Wu et al., 2007). The D-AA are less accessible to biodegradation than the bulk ON (L-enantiomer) (Tanoue et al., 1996; Nagata et al., 1998), thus they accumulate during diagenesis. Interestingly, strong positive correlation is observed between the D-AA monomers, THPAA, D/(D+L) ratio, GABA and SPM (Table S1), which further supports the above statement about contributions from heterotrophic bacterial sources. Although there was no significant difference between the D-AA of the estuarine and riverine stations, the higher values were observed in the estuarine region. An alternative explanation for the occurrence of D-AA in the samples investigated could be from the discharge of treated and untreated effluents from industrial and urbanized areas located within close proximity of the estuarine region. This practice has a negative influence on the water quality. Although, the autotrophic and heterotrophic bacteria were not analyzed, the presence of D-aspartic acid (D-Asx) and D-serine (D-Ser) points towards substantial contributions from heterotrophic sources (Kaiser and Benner, 2008). The values D-Asx reported in the present study are lower than those of the Russian rivers (Dittmar and Kattner, 2003) but were higher than Changjiang River (Yangtze River) (Wu et al., 2007), which is also an estuary that is impacted due to anthropogenic activities. Furthermore, this is in concurrence with a previous study conducted by Nagvenkar and Ramaiah (2009) wherein they reported the presence of bacteria within the estuarine region. Our results match a more recent study conducted by Bardhan et al. (2015) wherein they attribute the poor water quality within the estuarine region to anthropogenic activities such as discharge of untreated or partially treated sewage. Hence, heterotrophic organisms and their remnants contribute substantially to the OM entrained within the SPM of the Zuari River and its estuary along with an overlap of sources observed within the ETM.

4.2 *Quantification of OM in the Zuari River and estuary*

Assuming that different sources have relatively uniform composition and similar preservation (Fry and Sherr, 1989) and based on the δ^{13}C and C:N_{atomic} ratio (Fig. 7a), we applied the three end-member mixing model for quantification OM sources and calculated the percentage contribution. The three end-members were C_3 plants, soils, and river plankton for the river samples, and C_3 plants, river and marine plankton for the estuar-

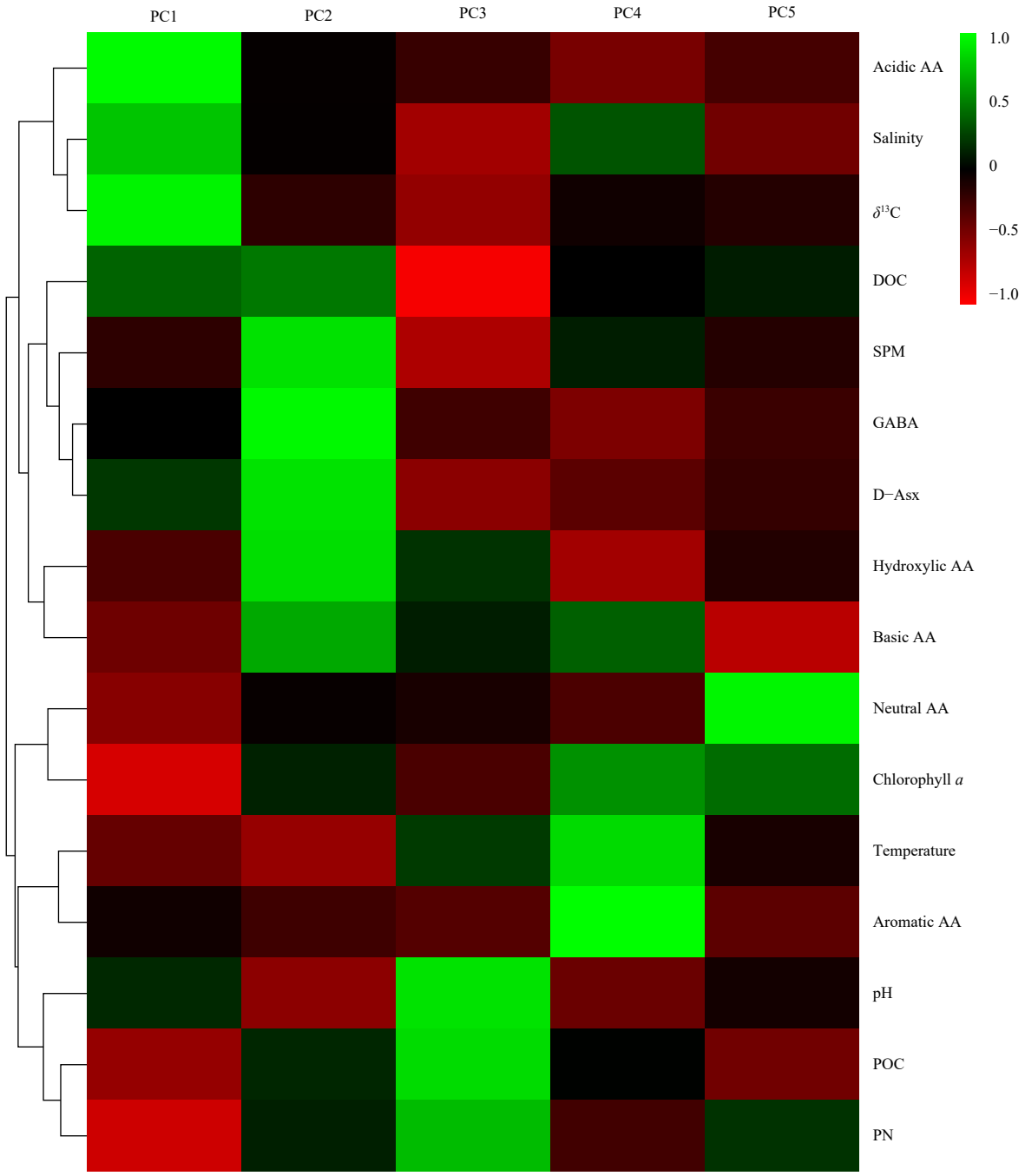

Fig. 6. Heat map of principal components (PC) extracted by R–mode factor analysis with Varimax rotation. The green color indicates positive loadings, black color indicates zero loading, and the red color indicates negative loadings.

ine region. The calculations were done using the Monte Carlo (MC) simulation strategy to track the source distribution in the particulate OC pool taking to consideration the spread of the end-member values (Andersson, 2011; Li et al., 2012). This quantification was based on the δ^{13}C and C:N_{atomic} ratio values of the end-member components adopted from literature and the present data set. We assume that the δ^{13}C and C:N_{atomic} ratio follow normal distribution. The following are the end-member values of δ^{13}C used in our study (C_3 plants (–28.1‰±1.0‰), soil (–21.3‰±1.1‰), marine plankton (–19.8‰±0.9‰) and river plankton (–35.0‰±1.0‰)). The end-member value of C:N_{atomic} ratio used were as follows (C_3 plants (30±10), soil (14.1±2.8), marine plankton (7±1) and river plankton (4±3); Meyers, 1994; Gordon and Goñi, 2003; Pradhan et al., 2014; Nasir et al., 2016). The program was run in Enthought Python Distribution 7.2. Basically, 400 000 out of 40 000 000 random samples from the normal distribution of each end-member were taken in order to simultaneously fulfill the following equations:

$$\text{for riverine samples}: f_{\text{river plankton}} + f_{C_3\text{ plant}} + f_{\text{soil}} = 1, \quad (4)$$

$$f_{\text{river plankton}} \times \delta^{13}C_{\text{river plankton}} + f_{C_3\text{ plant}} \times \delta^{13}C_{C_3\text{ plant}} + f_{\text{soil}} \times \delta^{13}C_{\text{soil}} = \delta^{13}C_{\text{sample}}, \quad (5)$$

$$f_{\text{river plankton}} \times \text{C/N}_{\text{river plankton}} + f_{\text{C}_3\text{ plant}} \times \text{C/N}_{\text{plant}} + f_{\text{soil}} \times \text{C/N}_{\text{soil}} = \text{C/N}_{\text{sample}}, \quad (6)$$

$$\text{for estuarine samples}: f_{\text{river plankton}} + f_{\text{marine plankton}} + f_{\text{C}_3\text{ plant}} = 1, \quad (7)$$

$$f_{\text{river plankton}} \times \delta^{13}\text{C}_{\text{river plankton}} + f_{\text{marine plankton}} \times \delta^{13}\text{C}_{\text{marine plankton}} + f_{\text{C}_3\text{ plant}} \times \delta^{13}\text{C}_{\text{C}_3\text{ plant}} = \delta^{13}\text{C}_{\text{sample}}, \quad (8)$$

$$f_{\text{river plankton}} \times \text{C/N}_{\text{river plankton}} + f_{\text{marine plankton}} \times \text{C/N}_{\text{marine plankton}} + f_{\text{C}_3\text{ plant}} \times \text{C/N}_{\text{plant}} = \text{C/N}_{\text{sample}}, \quad (9)$$

where f represents the fraction of river plankton, C_3 plant, marine plankton and soil OC contribution to the samples, respectively. The contribution of each end-member was calculated based on these 400 000 results (Li et al., 2012). The results of the percentage contributions are presented in Fig. 7b. The percentage contribution from soil to the riverine region varied from approximately 7% to 45% with relatively less contributions during the dry season in the estuarine region. The OM in the estuarine region of the Zuari River appeared to be mainly derived from in-situ marine plankton, terrestrial C_3 plants, and river plankton. Marine plankton contributed to the bulk of the OM in the estuarine region and varied from approximately 35% to 88%. During the post- and pre-monsoon season river phytoplankton was the main source of OM in the riverine region. Higher percentage contributions from autochthonous sources was observed during the dry season due to the dominance of tidal activity, resulting in strong lateral and vertical mixing which aids in the transport of marine OM into the estuary. During the dry season the estuary transforms into an extended part of the sea as there is minimal flow of freshwater (Subha Anand et al., 2014). The lower percentage contribution of allochthonous sources observed in the lower reaches can be explained as a result of reduced flow of freshwater during the dry season. Mixing and transport of OM within the estuary is controlled by water discharge and residence time of the water masses. The residence time of the water masses of the Zuari River and its estuary is known to be longer than its neighboring river (Mandovi River, 5–6 d during the SWM to about ~50 d during the non-monsoon season) (Qasim and Sen Gupta, 1981). The prevalence of the ETM within the estuarine region tends to increase the suspension time of the particles. Physical processes (tidal activity) coupled with longer hydraulic residence time provide ideal conditions for heterotrophic organisms to work and rework the OM suspended in the water column thereby controlling its biochemical status.

4.3 *Diagenesis of POM within the ETM*

In order to understand the diagenetic status of OM, the THAA yields (%OC), DI and Glx:GABA ratio of SPM (Fig. 4) were calculated and examined. The yields and ratios serve as the indicators of diagenesis. The degradation index (DI) developed by Dauwe and Middelburg (1998) provides insights into the diagenetic state of OM. The DI values decrease from positive values (1 to 1.5) for fresh phytoplankton to negative values (<–1) for diagenetically altered OM from deep sea sediments (Dauwe et al., 1999). As the DI values of the SPM in the river investigated varies from –0.21 to 0.19, it indicates a minor to moderate diagenetic alterations. Nonetheless, the DI values of riverine stations investigated were more negative during the three seasons indicating the presence of refractory OM. Except Sta. ZR-2 (pre-monsoon) which displays a positive value of DI suggesting the presence of labile OM coupled with low $C:N_{atomic}$ ratio revealing the occurrence of fresh production. A strong positive correlation observed between the diagenetic indicators (Glx:GABA vs. DI) suggests the reliability of these indicators in assessing the overall status of SPM transported by the Zuari River. Furthermore, the estuarine stations displayed mixed characteristics, with both positive and negative values occurring due to lateral and vertical mixing taking place within the ETM resulting from tides and river discharge. Furthermore, the high D-Asx (%) content as observed in the estuarine region was found to be associated with SPM (Figs 4b and 6). The selective preservation of structural compounds in contrast to preferential degradation of cell wall components is an indicator of the heterogeneous nature of OM (Dauwe and Middelburg, 1998). Low salinity conditions within the estuary facilitate flocculation and adsorption processes thereby allowing the particles to stay in suspension for longer periods during the dry season. Deposition-resuspension processes due to wind driven waves and circulation patterns coupled with the narrowing of the estuarine channel alters the quality of OM within the ETM. Complex processes take place within the ETM (mixing zone) such as particle solute interactions, flocculation, coagulation, re-suspension and sedimentation are responsible for altering the characteristics of OM before they are deposited into the sediments (Kessarkar et al., 2013). From these results we can ascertain the influence of the ETM in controlling the diagenesis of OM.

Another possible explanation for the presence of older material in the estuarine region can be attributed to the funnel shape structure of the estuary resulting in additional turbulence. Lighter particle are re-suspended and remain exposed to oxidative diagenesis as they remain in the water column for longer durations. Gravitational circulation (tides), together with rainfall and freshwater discharge during the monsoon season lead to salinity stratification of the water column at the mouth of the river. This leads to the formation of a salt wedge during the SWM and it extends to about 12 km upstream (Qasim and Sen Gupta, 1981). Salinity measured during the monsoon season from the head of the river to the upstream part of the estuary was almost negligible, which is an outcome of increased fresh water discharge. The quantity of fresh water discharged from the river during the dry season is trifling (about 0.03 km^3/a) (Wagle et al., 1988). It is to be noted that salinity stratification of the water column occurs near the mouth of the river during the monsoon season and remains well-mixed during the non-monsoon season. The tidal surge and geomorphological constriction (funnel shape) enhances the drag and lift forces resulting in resuspension of materials from the surface sediments there by exposing the particles to multiple cycles of suspension and deposition before eventual settling down into the sediments of the coastal region. Thus the impact of tidal activity along with wind induced currents results in flocculation of suspended matter at the saltwater-fresh water interface at the river mouth during the monsoon season. Whereas during the post- and pre-monsoon seasons, the mixing zone moves inwards into the estuary as freshwater discharge decreases, and the well-developed ETM moves into the estuarine region. Thus, OM entrained within the SPM of the ETM displays a mixed character due to lateral and vertical mixing of material in the river before they are deposited into the sediments of the coastal seas.

Unlike the Changjiang River where the turbidity maxima is fed by resuspension and erosion of the river bed (Li and Zhang, 1998), the ETM of the Zuari River results from tidal activity and

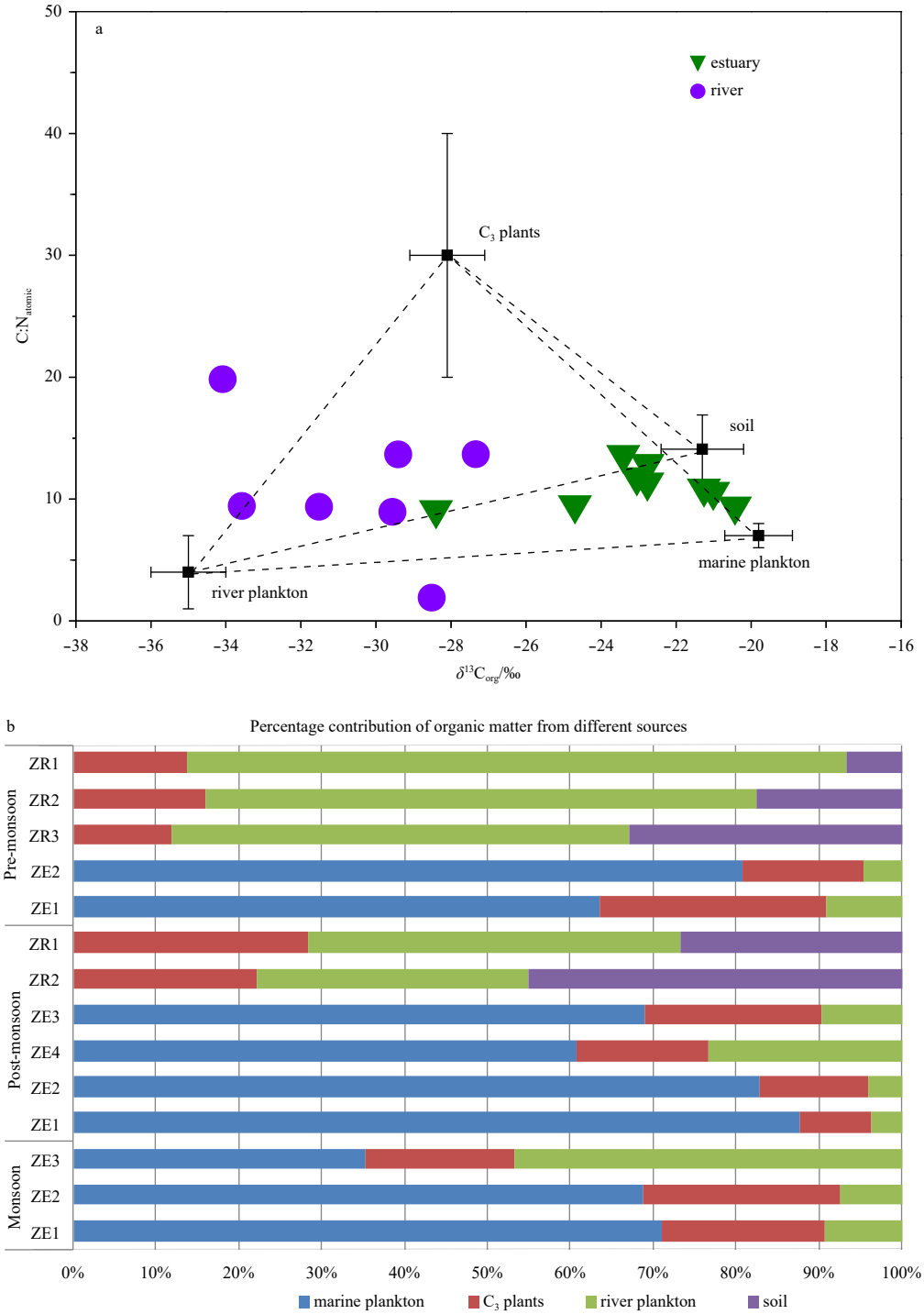

Fig. 7. Property-property plots of $C:N_{atomic}$ ratio vs. $\delta^{13}C_{org}$ values of particulate matter from the Zuari River and estuary along with the potential OM sources (C_3 plants, soils, marine and river plankton) (a); and calculated proportion OM contributed from different sources to the particulates based on the results of end-member mixing model (b).

structural shape of the estuary (funnel shape), thereby causing enhanced turbulence within the estuarine region. During the monsoon season erosion of top soils from the catchment area is a dominant process. Whereas, during the non-monsoon season, the fresh water flow into the river is reduced. This results in the movement of the ETM into the river and alters the composition and diagenetic status of OM. Thus, combination of tidal resuspension and reduced freshwater influx into the estuary results in hydrodynamic sorting of particles along the estuary whereby some marine OM is transported into the estuary during non-monsoon seasons (Fig. 7b).

The sources of OM ascertained qualitatively indicated non-conservative mixing behavior within the estuarine region. Similar observations were noticed with the AA investigated. They also displayed non-conservative mixing behavior within the ETM as no clear trend was observed. Similarly, other labile constituents,

i.e., chromophoric dissolved organic matter (CDOM) show non-conservative behavior within the estuaries as a result of different biogeochemical processes such as adsorption-desorption processes, mixing of terrestrial and marine OM, resuspension, microbial and photochemical degradation which takes place within the ETM (Yang et al., 2013). The non-conservative mixing behavior has been observed with the net fluxes of suspended matter, POC, and total nitrogen (TN) of the Winyah Bay, South Carolina, USA (Goñi et al., 2003).

Furthermore, based on the estuarine mixing diagrams of the nutrients with respect to salinity, the meso-tidal rivers showed greater flushing capacity and act as corridors for the passage and transport of nutrients between the river, estuary and open ocean (Fernandes et al., 2018). The dilution, size and developmental status of the river basin influence the quantity and quality of OM that is transported. Therefore, to increase our knowledge about the complex ecological systems such as ETM, future studies are needed. Additionally, the role of minor rivers and estuaries in modifying the OM trapped within the ETM during transport from river to coastal waters merits special attention as they are influenced and impacted by multiple natural (seasonal changes, tidal cycles) and anthropogenic stressors.

5 Conclusions

In this study, the sources, composition, and factors influencing diagenesis of POM within the Zuari River and estuary were investigated. By analyzing the bulk and ancillary parameters along with the biomarker (AA) of the SPM for the three different seasons we conclude that there was no significant temporal variability. Nonetheless, when the stations were grouped spatially (according to the region) they displayed spatial variability. Temperature, pH, salinity, POC, PN, δ^{13}C, δ^{15}N and AA-C% were significantly different spatially. From the values of POC, δ^{13}C, PN, δ^{15}N, C:N_{atomic} and POC:Chl *a* ratios, and AA (L- and D-enantiomers), the data indicated that the OM mostly originated from terrigenous sources (C_3 plant detritus and soils), *in-situ* production (marine and river phytoplankton) and heterotrophic organisms and their detrital matter. The contribution from marine phytoplankton was the maximum in the estuarine region followed by C_3 plant detritus and soils during the dry season. The average contribution from river phytoplankton during the pre-monsoon season was more than 66%, while the average contribution from soil OM was approximately 19%. River runoff transported refractory and more degraded materials from the head region of the river to the estuarine region during the monsoon season. The diagenetic status of OM is influenced by the formation of the ETM. The funnel shaped structure (geomorphological constriction) of the estuarine region coupled with the meso-tidal cycles experienced by the region play a critical role in altering the OM. The presence of higher proportions of D-AA in the estuary indicates contributions from bacteria and their remnants along with accumulation of older OM. By employing D-AA as a biomarker, bacteria and their remnants act as source indicators pointing towards enhanced contaminations, highlighting the deteriorating water quality of the estuary. Thus, by studying the biomarker (AA), and the other bulk and ancillary parameters of SPM we were able to ascertain the prevailing conditions, thereby contributing to the understanding of the sources, processes and factors controlling the nature OM within the ETM of small tropical rivers.

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Supplementary information:

Table S1. Factor loadings calculated using principal component analysis (PCA) of the physical and biogeochemical parameters of the Zuari River and estuary, west coast of India.

Table S2. Pearson's correlation among the physical and biogeochemical parameters of the Zuari River and estuary, west coast of India.

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