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Sources and preservation dynamics of organic matter in surface sediments of Narmada River, India – Illustrated by amino acids

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ABSTRACT

The preservation process of organic matter (OM) in estuarine environments determines the recycling and sinking of nutrients. This process requires the identification of sources, degradation states and the main processes affecting OM transformations. Unfortunately, our understandingof the sources, degradation and factors affecting OM distribution in tropical rivers experiencing strong seasonality and monsoonal influence is still limited. This study examined the sources, degradation and factors affecting OM distribution along the Narmada River and its estuary during different seasons. Surface waters and sediments were analyzed seasonally for selected physico-chemical parameters and bulk compositions of sediments, together with amino acids (AA, including the bacterial biomarker, D-AA). The sources of OM were soils containing detrital terrestrial plant material, with C_4 and C_3 plants dominating the estuarine and riverine stations, respectively. The other sources of OM were *in-situ* production, together with bacteria and their remnants. Strong seasonality and monsoonal conditions control the sources and distribution of OM in the river. Higher concentrations of total hydrolysable amino acids (THAA) were observed in riverine stations, suggesting the presence of relatively fresher OM. The lower OC:SA ratios recorded in the estuarine sediments indicated a limited OM preservation in the studied river. Positive degradation index (DI) values were obtained during the pre-monsoon season, suggesting seasonal changes in OM diagenesis. Physical (strong tidal currents, rainfall, reduced water flow due to seasonal variations and shallow water depth within the estuary) and geochemical (mineral surface adsorption processes) factors control the distribution and transport of OM. Taken together, the sources, preservation and diagenesis of terrestrial OM along the Narmada River was controlled differentially by the strong seasonal variability of the region. Thus, under variable temporal conditions, tropical estuaries and rivers form important realms for examining, determining, evaluating and assessing OM in order to better interpret nutrient budgets of the seas and oceans.

1. Introduction

Rivers play an important role in providing a wide range of economic and ecological services. They are globally recognized as the most dynamic hydrological agents for transport of major and minor nutrients contained in organic matter (OM) (Garrels et al., 1975). Organic carbon (OC), organic nitrogen (ON), inorganic nutrients and metals make up a major part of dissolved and suspended loads in water column and sediments (Burdige and Martens, 1988; Yao et al., 2012). Amino acids (AA) are ubiquitous organic compounds, which are essential constituents of ON. They represent significant fractions of ON in newly deposited sediments and suspended particles of rivers and coastal marine environments (Cowie and Hedges, 1994). Accordingly, contemporary studies use D-enantiomer of AA to ascertain bacterial contributions to OM in the dissolved phase, suspended particulates and sediments in aquatic environments (Dittmar and Kattner, 2003; Wu et al., 2007; Mai-Thi et al., 2017). The AA are often used as indicators of OM diagenetic states owing to their labile nature (Wakeham et al., 1997; Dauwe and Middelburg, 1998; Ingalls et al., 2006). Also, changes in AA compositions indicate consistent trends in sources and degradation status of cellular OM sinking through the water column and finally getting integrated into the sediments (Ingalls et al., 2003; Yao et al.,

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2012). Moreover, the percentage contribution of AA to OC and ON (AA-C% and AA-N%, respectively), the total hydrolysable amino acids (THAA) and degradation index (DI) are often used as indicators of diagenesis (Cowie and Hedges, 1992; Hedges et al., 1994; Suthhof et al., 2000). Therefore, AA are used as potential indicators of sources and diagenesis of OM in aquatic environments.

Variations in the OM sources, preservation and diagenesis in river sediments and their corresponding factors controlling them have been extensively investigated from several major rivers of the world (Jennerjahn et al., 2004; Zhang et al., 2007). Various sources of OM have been identified in many rivers and settings from different countries such as terrigenous sources in controlled laboratory experiment (Larsen et al., 2013), the Pearl River in China (Zhang et al., 2014), 35 medium and small rivers of India (Pradhan et al., 2014a) and Beibu Gulf in China (Wu et al., 2018). Moreover, autochthonous inputs (Larsen et al., 2013; Wu et al., 2013; Zhang et al., 2014; Pradhan et al., 2014a; Wu et al., 2018) also provide substantial contributions to OM in aquatic environments. Interestingly, heterotrophic bacteria and fungi not only transform OM but also contribute indirectly to OM pool following their senescence and death (Larsen et al., 2013). The OM from the different sources may be diagenized or selectively preserved depending on the presence of living organisms or its interaction with mineral surfaces in the aquatic environments (Van Mooy and Keil, 2002; Lin et al., 2013). The organic carbon to surface area (OC:SA) ratio has been used as a powerful tool for determining the preservation potential of OM in sediments (Nuwer and Keil, 2005). The OC:SA ratio for marine and coastal sediments dominated by rivers inputs ranges from 0.4 to 1.0 mg C m^{-2} (Hedges and Keil, 1995; Keil et al., 1997; Mayer, 1999; Goñi et al., 2005b; Freymond et al., 2018). The diagenetic status of sediments can be evaluated by using the DI, which takes into account the entire proteinaceous AA for its calculation. The diagenetic status of OM has been indicated to range from +1.5 for fresh phytoplankton to negative values −1for diagenetically altered sedimentary OM in deep sea (Dauwe et al., 1999). Several factors control preservation and diagenesis of OM in sediments including physicochemical parameters (Zonneveld et al., 2010) such as dilution and concentration effects of tributary water inflow at different locations such as in the river channel, estuary and seas or oceans (Subramanian, 1983). Moreover, the preservation and diagenesis of OM are controlled by microbial reworking (Ylla et al., 2010) and surface processes including erosion and transport of sediments. The latter factors are dependent on the river velocity, hydrology, rainfall, soil properties and temperature (Pradhan et al., 2017). It is clear that, OM in rivers has multiple sources and ultimately experiences distinct fates depending on various factors, both spatially and temporally.

Rivers and streams in tropical regions have spatial and temporal heterogeneity in terms of physical (Singh and Singh, 2007), chemical (Mukherjee et al., 1993; Riedel et al., 2000), biological (Shruthi and Rajashekhar, 2013; Rajesh et al., 2014) and geological aspects (Jeevanadam et al., 2007). These conditions make rivers and streams in tropical regions ideal settings for studying biogeochemical processes on short time scales (Syvitski et al., 2005). The Narmada River is one of the largest westward flowing rivers of the Indian peninsular. Annually, the region experiences increased occurrence and intensity of droughts and floods due to shifts in precipitation (Varikoden et al., 2015) caused by climate and global changes (Arnell et al., 1996; Goswami et al., 2018). These changes coupled with anthropogenic disturbances such as damming, diversion of river channel for irrigation, industry or power generation (Gupta, 2001; Panda et al., 2011), ultimately affect the river discharge pattern. This has led to considerable changes in mean water discharge, sediment loads (Kathal, 2018), OM accumulation and processing in the rivers (Acuña et al., 2007; Ylla et al., 2010). Indeed, the sediment load of the Narmada River has decreased by approximately 88% (*i.e.*, from 40.7 × 10^9 kg in 1986 to ~5 × 10^9 kg in 2009) (Central Water Commission (CWC), http://www.cwc.nic.in). Despite the decrease in sediment load observed in the Narmada River, its influence on OM sources, preservation, diagenesis is currently unknown. Such data will provide valuable insights into the spatial and temporal variations of sedimentary OM budgets of the north eastern Arabian Sea. We hypothesized that the extreme seasonality of the Narmada River might lead to differences in OM sources, transport and diagenesis within the river and its estuary.

Therefore, to understand the bio-geochemical behavior of OM, we analyzed the surface sediments and ancillary water parameters of the Narmada River. The objectives were to: (1) examine the sources of AA in the sediments of Narmada River based on spatial and temporal variations; (2) determine the preservation of OM in the river; (3) evaluate the degradation state of OM by using AA as biomarkers and (4) assess the factors controlling OM sources, preservation and diagenesis. This was an exploratory research study that provides comprehensive baseline information on AA composition in the surface sediments of Narmada River, which is affected by extreme seasonality and is also highly human-impacted in terms of water and sediment delivery.

2. Materials and methods

2.1. Study area

The western flowing rivers of the Indian peninsular are shorter in length, lithologically heterogenic and experience varied intensities of weathering in comparison to the eastern flowing and the Himalayan Rivers (Gurumurthy and Muguli, 2015). These rivers are extremely seasonal in terms of discharge; nonetheless they form a valuable water realm in their basin and are a major source of sediments and OM transported to the Arabian Sea (Gupta and Chakrapani, 2005). The Narmada River is the seventh largest river in terms of drainage area and flows through the central western part of India (21°20′N–23°45′N; 72°32′E–81°45′E). It has the second largest catchment area of all the rivers draining into the Arabian Sea. The Narmada River originates at roughly 760 m above mean sea level (amsl) in the Amarkantak hills of the Satpura mountain range and has a drainage area of 98.8 × 10^3 km^2. It flows westwards 1310 km through Vindhyan ranges and Deccan basalts before draining into the Gulf of Khambhat, Arabian Sea (Pradhan et al., 2017). The estuarine region of the river experiences the influence of tides up to 32 km above Baruch city. During the neap and spring tides the water level rises between 1 m and 3.5 m, respectively (Kathal, 2018). The average annual freshwater discharge of the Narmada River for the year 2011–2012 was 8.2 × 10^9 m^3 (CWC, http://www.cwc.nic.in). The annual average of sediment load of the Narmada River during the years 1990–2012 was 10.2 × 10^9 kg (CWC, http://www.cwc.nic.in). The combined net delivery of sediment from both Narmada and Tapti river systems to the Arabian Sea was ~95 × 10^6 tons yr^{-1}, approximately 30% of total sediment supply by all the monsoonal rivers of India (excluding Indus, Ganges–Bramhaputra rivers) (Panda et al., 2011).

The average rainfall of the Narmada basin is 1178 mm and the annual rainfall of the entire basin varies from 800 to 1600 mm (Kathal, 2018; India Meteorological Department-IMD, http://www.imd.gov.in). The precipitation mostly occurs during the southwest monsoon (SWM) accounting for approximately 85 to –95% of the annual precipitation (Gupta and Chakarpani, 2005; Gupta et al., 2011). The Narmada River experiences increased runoff during the monsoon season (June to September) due to rainfall. However, during the post- and pre-monsoon seasons the flow of water reduces considerably due to scant rainfall and low discharge, which is regulated by the construction of dams and reservoirs within the drainage basin (Kathal, 2018). In view of the water resource potential of the river, a number of multi-state programs were implemented for the construction of hydropower and irrigation dams, which aims to irrigate 50,000 km^2 of drought prone areas. The Narmada River basin is dominated by humid tropical to arid climatic conditions with maximum temperatures between 40 and 42 °C during May and minimum between 8 and 13 °C in January. The Narmada River

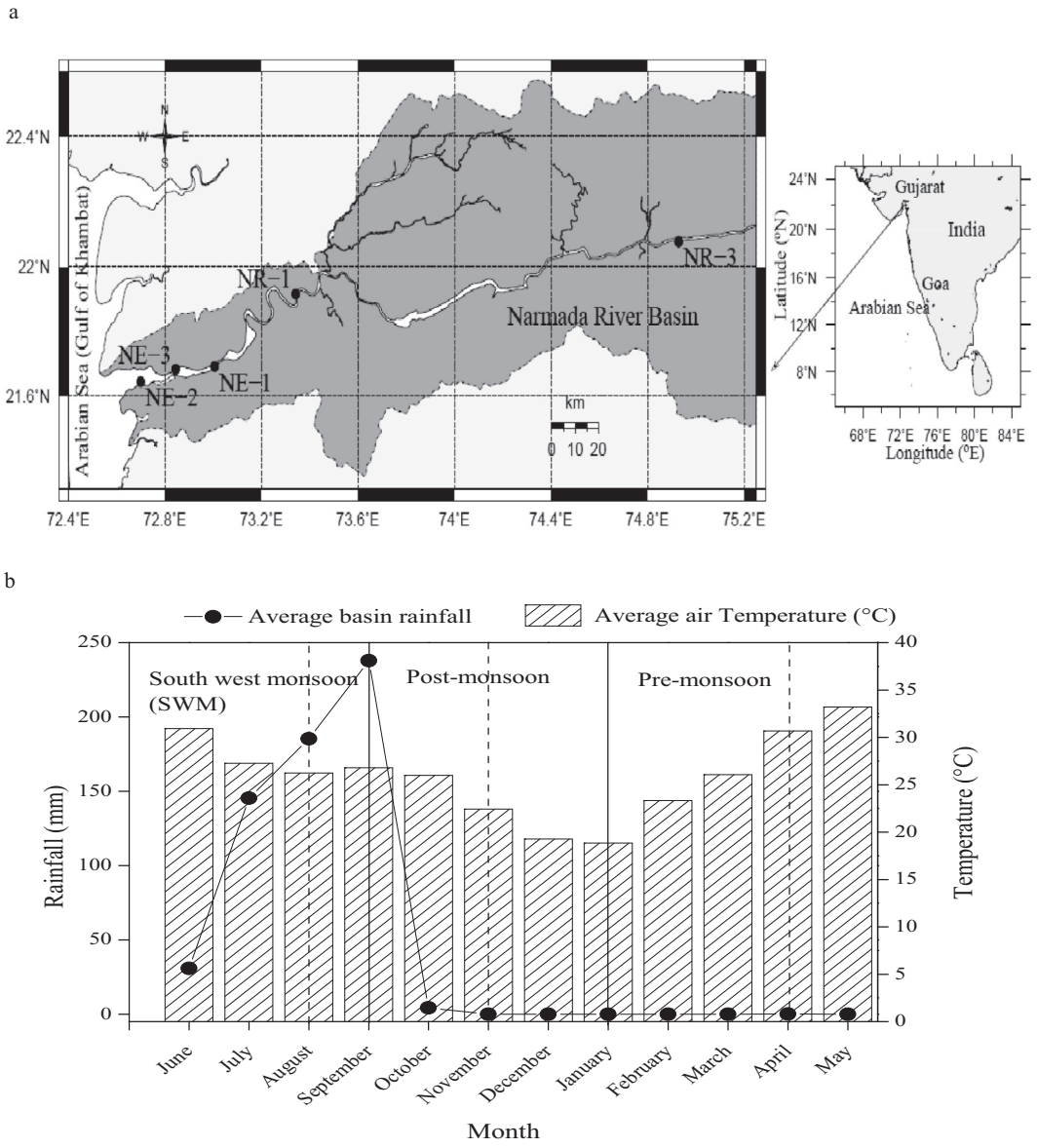

Fig. 1. a: Map of Narmada River and its basin, India surface water and sediment sampling locations are marked as solid circles; b: monthly average rainfall (mm) and air temperature (°C) for the year 2011–2012 (the solid lines demarcate the season and the dashed lines the sampling month).

valley experiences extreme hydrometerological and climatic conditions, supporting diverse vegetations from lush green forests in the upper region to dry deciduous teak forests in the lower region (Kathal, 2018). In the riverine region, agricultural lands together with dry deciduous forest is more dominant mostly comprising of C_3 plants such as *Tectona grandis*, *Terminalia alata*, *Dendrocalamus strictus*and *Acacia* spp. (Murthy, 1978; Pradhan et al., 2019). Along the estuarine region of the study area cultivation of C_4 plant such *Saccharum* spp., *Sorghum* spp. and *Zea mays* takes place (Pradhan et al., 2019). Also the estuarine region contains scrub lands, xerophytes plants (salt marsh vegetation), which usually have less depleted $\delta^{13}C$ values.

2.2. Sampling sites and sample collection

Surface water and sediments samples were collected from pre-determined locations along the Narmada River during the SWM (August to September), post-monsoon (November to December) and pre-monsoon (April to May) seasons in 2011 and 2012 (Fig. 1). Meteorological data were obtained from the India Meteorological Department (IMD) website (http://www.imd.gov.in) for the year 2011 to 2012 (Fig. 1b). The sampling stations - Narmada River 3 and 1 (NR-3 and NR-1) were situated in the main stream, whereas stations - Narmada estuary 1, 3 and 2 (NE-1, NE-3 and NE-2) were located in the estuarine region of the river. River water samples were collected by using clean buckets lowered from the top of a bridge into the river channel. Surface water samples from the estuarine region were collected at a depth of 0.20 to 0.30 m below the water surface by using a 5 L Niskin water sampler (General Oceanic, USA) from a mechanized boat. The collected water samples were transferred into acid cleaned plastic cans and were chilled in an icebox and transported to a make shift laboratory for preliminary sub-sampling, processing and preservation. Further analyses were done at the National Institute of Oceanography (NIO), Goa, India. The sub-sampled water samples and filter membranes were preserved at −20 °C before shipping them to the State Key Laboratory of Estuarine and Coastal Research, East China Normal University (Shanghai, China) for further analyses.

Surface sediments were collected by using a Van Veen grab (15 × 15 cm). After collection, only the top layer of the sediment (0 to 3 cm) was sub-sampled and transferred into clean zip lock polyethene bags and stored in an icebox. The samples were transported to the

National Institute of Oceanography (Goa, India) where they were sub-sampled and oven dried at 45 °C for three to four days. Part of the dried samples were ground by using an agate mortar and pestle and used for bulk elemental and AA analyses.

2.3. Hydrographic parameters

In-situ measurements of salinity were done using a multi-parameter probe (Inolab multi-720). The average precision for salinity measured by the probe was 0.01.

2.4. Suspended particulate matter and chlorophyll a

Water samples were filtered through pre-combusted GF/F Whatman fiber filters (Ø = 47 mm, 0.7 μm nominal pore size) for analysis of suspended particulate matter (SPM). The SPM was measured as the difference of weight after drying the filters at 40 °C for 48 h. Chlorophyll *a* (Chl *a*) concentration was determined by filtering the samples using Whatman 47 mm Ø GF/F fiber filters (0.7 μm nominal pore size). The contents were extracted by using 90% acetone, refrigerated in dark for 20 to 24 h, centrifuged and the absorbance was measured at 750, 664, 647 and 630 nm by using a Shimadzu UV 1800 spectrophotometer according to Strickland and Parsons (1972).

2.5. Elemental and stable carbon isotope analyses

The sediments OC content and its stable isotope ($\delta^{13}C$) were measured by using the elemental analyzer (Finnigan EA 1112) interfaced with continuous flow isotope ratio mass spectrometer (Finnigan Delta plus XP). Homogeneous ground sediments were directly treated with 1 M HCl to remove inorganic carbon and then oven dried at 45 °C for 24 h before the OC and its isotope ($\delta^{13}C$) measurements were carried out. In this study, the analytical precision for carbon isotope ($\delta^{13}C$) measurement was ± 0.1‰ and the results are expressed as per mille (‰) deviation relative to the Vienna–Pee Dee Belemnite (V-PDB) standard calculated using the equation below.

$$\delta^{13}C\ (‰) = [((^{13}C/^{12}C)\ \text{sample}/(^{13}C/^{12}C)\ \text{PDB}) - 1] \times 1000 \quad (1)$$

The sediment total nitrogen (TN) content was measured from ground sediments without acid treatment by using the elemental CHNOS analyzer (Model: Vario EL III).

2.6. Grain size analysis

Part of the unground surface sediments sampled in the previous section was used for grain sizes analysis. The sediment grain sizes analysis was measured by removing the OM using a Coulter laser granular meter (LS-100Q) as previously described by Pradhan et al. (2014b). Briefly, 0.5 g of dry unground sediment was treated with 10% H_2O_2 to remove the OM. The aggregates were dispersed by adding $(NaPO_3)_6$ followed by ultrasonic treatment. The sediment grain sizes were expressed as proportions of clay (< 4 μm), silt (4 to 63 μm) and sand (> 63 μm) with a measurement error of ≤ 1% in the entire dataset (Pradhan et al., 2014b).

2.7. Surface area analysis of sediments

Also, a part of the unground surface sediments sampled in the previous section was oven dried and used for surface area (SA) analysis. The sediments SA was measured by nitrogen adsorption using a five-point Brunauer–Emmett–Teller (BET) method (Keil et al., 1994; Waterson and Canuel, 2008). The unground sediments were combusted at 350 °C for 12 h to remove the OM before measuring the SA ($m^2\ g^{-1}$). The SA values obtained were used to calculate the OC or TN loading, *i.e.*, organic carbon:surface area ratio (OC:SA; mg C m^{-2}, $m^2\ g^{-1}$) and total nitrogen:surface area ratio (TN:SA; mg N m^{-2}), respectively.

2.8. Amino acids analyses

The THAA were analyzed according to Fitznar et al. (1999) and Wu et al. (2007). In brief, approximately 100 to 150 mg of ground sediments were hydrolyzed with HCl (16%, 10 mL) in pre-combusted glass ampoules, sealed in a nitrogen environment and incubated at 110 °C for 24 h in an oven. The samples were cooled and neutralized with boric acid buffer and NaOH solution to adjust the pH to 8.5. Pre-column derivatization was done by using *o*-phthaldialdehyde (OPA) and *N*–i-sobutyryl–L/D-cysteine, glycine (Gly) and the D- and L-enantiomers for individual AA, [aspartic acid (Asp), glutamic acid (Glu), serine (Ser), alanine (Ala), arginine (Arg), threonine (Thr), (γ-)/gamma-Aminobutyric acid (GABA), valine (Val), phenylalanine (Phe), isoleucine (Ile) and leucine (Leu)] were detected. The samples for AA were analyzed by 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 × 3 mm). The mobile phases were: (A) 125 mM sodium acetate with 2% methanol (pH - 6.8, adjusted with acetic acid) and (B) high-performance liquid chromatography (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. The Glu and Asp are formed during hydrolysis by deamination process of glutamine (Gln) and asparagines (Asn), respectively. 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 individual AA in the standards and hydrolyzates were determined by using HPLC (Agilent 1100 series) fitted with an intelligent auto sampler for automatic derivatization and fluorescence detection (Wu et al., 2007). During the analyses, lysine and histidine were not detected due to method constraint and inaccessibility of the standards, respectively. Only the AA that were reproducibly quantified after derivatization are reported. The relative standard deviation for the individual AA for triplicate analysis was < 3.5% (Wu et al., 2007). We did not correct the sampled for the contribution of racemerized D-amino acid content during hydrolysis because its content is very small as compared to the naturally occurring D-amino acid reported by Dittmar et al. (2001). The AA based DI of the samples was calculated following the methods described by Dauwe and Middelburg (1998) and Dauwe et al. (1999). We did not quantify histidine in the present study and thus we assumed it's concentration was 0 mol%. We used the rest of the Dauwe dataset for calculating the DI of the sediment samples.

2.9. Statistical analyses

Data were tested for normality by using Shapiro–Wilk test and homogeneity of variance using Levene's test. The differences among the three seasons from the measured variables were analyzed by using one-way analysis of variance (ANOVA) followed by Tukey's *post hoc* test for specific differences. The mean values for riverine and estuarine regions were compared by using independent *t*-test. Pearson's correlation coefficient (*r*) was used to depict relationships among the measured parameters. Results with $p \leq 0.05$ were considered statistically significant for all statistical tests except for Pearson's correlations where both $p \leq 0.05$ and $p \leq 0.01$ were considered significant. The R-mode factor analysis (FA) with Varimax-normalized rotation by means of principal components extraction method was performed on selected variables of the data set (Kara, 2009). 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 conducted by using SPSS for Windows version 20 (IBM, Armonk, NY, USA).

Table 1
Concentrations of bulk parameters of water and surface sediment of Narmada River. (Abbreviations: total suspended matter/material – TSM; chlorophyll *a* – Chl *a*; total organic carbon – OC; total nitrogen – TN; carbon:nitrogen atomic ratio – $C:N_{atomic}$; organic carbon:surface area ratio – OC:SA; total nitrogen:surface area ratio – TN:SA).

	Distance from estuary (km)	Latitude	Longitude	Salinity	SPM	Chl *a*	Clay	Silt	Sand	OC	$\delta^{13}C$	TN	C:N $_{atomic}$	Surface area (SA)	OC:SA	TN:SA
		°E	°N		mg L^{-1}	mg m^{-3}	%	%	%	%	‰	%		$m^2 g^{-1}$	mg C m^{-2}	mg N m^{-2}
Monsoon																
NR-3	220	22.08	74.93	0.0	12.3	6.4	34.7	56.7	8.6	1.0	−21.1	0.14	8.1	33.9	0.28	0.04
NR-1	85	21.91	73.34	0.0	9.5	5.3	23.9	48.0	28.1	0.5	−21.3	0.04	13.0	21.7	0.22	0.02
NE-1	45	21.69	73.01	0.0	11.8	4.4	10.6	80.6	8.8	0.4	−15.7	0.04	11.4	20.4	0.17	0.02
NE-3	24	21.68	72.85	0.0	7.0	4.3	25.0	45.2	29.8	1.5	−23.3	0.06	31.2	21.6	0.70	0.03
NE-2	2	21.64	72.70	3.0	144.0	2.5	19.8	73.9	6.3	0.9	−15.1	0.08	11.9	44.5	0.19	0.02
Post-monsoon																
NR-1	85	21.91	73.34	0.0	3.0	5.7	24.4	51.8	23.8	0.8	−22.2	0.10	9.3	30.1	0.26	0.03
NE-1	45	21.69	73.01	0.0	2.5	4.8	10.0	77.0	13.0	0.6	−17.3	0.05	16.3	22.1	0.29	0.02
NE-3	24	21.68	72.85	4.2	1066.7	1.1	13.2	40.4	46.5	0.3	−18.5	0.03	13.2	16.1	0.20	0.02
NE-2	2	21.64	72.70	0.7	1252.5	1.3	19.7	65.9	14.3	0.6	−16.6	0.05	15.4	40.6	0.15	0.01
Pre-monsoon																
NR-1	85	21.91	73.34	0.0	3.8	3.1	28.4	64.5	7.1	1.2	−22.3	0.15	9.2	32.2	0.37	0.05
NE-1	45	21.69	73.01	0.0	292.0	2.1	8.6	74.6	16.8	0.4	−15.2	0.03	14.5	21.5	0.19	0.02
NE-3	24	21.68	72.85	8.0	711.7	1.2	14.9	65.9	19.2	0.4	−18.0	0.04	11.4	27.9	0.13	0.01
NE-2	2	21.64	72.70	1.4	141.3	2.1	7.2	72.6	20.2	0.4	−12.4	0.03	18.0	21.7	0.20	0.01

3. Results

3.1. Hydrographic, chlorophyll a and bulk sediment parameters

Low salinities values (< 10) were obtained in the Narmada River and its estuarine region (Table 1). Near zero salinity values were detected during the monsoon season. The SPM varied widely from 2.5 mg L^{-1} to 1252.5 mg L^{-1} (Table 1). The highest concentration of SPM was obtained at the estuarine stations NE-2 and NE-3 during the post- monsoon season with no significant differences between the seasons ($p > 0.05$). Chlorophyll *a* concentrations varied from 1.1 to 6.4 mg m^{-3} with significantly higher values in the riverine region compared to the estuarine region ($p < 0.05$). Sediments of the Narmada River were mainly composed of silt (> 40%; Table 1). The clay content was significantly higher in the riverine region compared to the estuarine region ($p < 0.05$). The sand content varied between 6.3% and 46.5% with the lowest values obtained at station NE-2 (monsoon season) and NR-1 (post-monsoon season), respectively (Table 1).

3.2. Bulk chemical parameters and surface area (SA)

The OC content varied from 0.4% to 1.5% with relatively higher values obtained during the monsoon season (Table 1). The TN content varied from 0.03% to 0.15% for the three seasons and was statistically not significant, both spatially and temporally ($p > 0.05$). The $C:N_{atomic}$ of sediments collected from the Narmada River and estuarine region for the monsoon, post- and pre-monsoon season varied from 8.1 to 31.2, 9.3 to 16.3 and 9.2 to 18.0, respectively. The $\delta^{13}C$ of OC in sediment varied from −23.3‰ to −15.1‰ during the monsoon season, from −22.3‰ to −12.4‰ during the post- and pre-monsoon seasons (Table 1). The $\delta^{13}C$ values of OC in sediments of the riverine stations were significantly more depleted than the estuarine stations ($p < 0.05$). The SA values varied from 16.1 to 44.5 $m^2 g^{-1}$ with the highest value observed at NE-3 and NE-2 stations during the post-monsoon and monsoon seasons, respectively. The OC:SA ratio of minerals particles ranged from 0.13 mg C m^{-2} at station NE-3 (pre-monsoon season) to 0.7 mg C m^{-2} at the same station (monsoon season; Table 1). The TN:SA ratio of minerals particles ranged from 0.01 to 0.05 mg N m^{-2}. Statistically, the OC:SA and TN:SA ratios were not significantly different, both spatially and temporally ($p > 0.05$).

3.3. Spatial and temporal distribution of THAA

A total of 18 AA (L- and D-enantiomers) were obtained from the sediments of the Narmada River. The highest concentration of THAA (2.2 mg g^{-1}) was observed at station NE-3 (monsoon season) and NR-1 (pre-monsoon season) (Table 2). The lowest concentration of about 0.2 mg g^{-1} was found at station NE-3 (post-monsoon season). The riverine stations had relatively higher content of THAA than the estuarine stations with an exception of station NE-3 (monsoon season), which displayed values similar to riverine stations. The contribution of THAA to OC (AA – C%) ranged from 3.7% to 8.2%, 2.7% to 7.3% and 2.1% to 6.6% for the monsoon, post- and pre-monsoon seasons, respectively. The contribution of THAA to TN (AA – N%) was low with most values below 30%, except stations NE-3 (63.7%) and NE-2 (30.6%; monsoon season; Table 2). Based on functional group classification, neutral AA (Gly, Ala, Val, Leu and Ile) were the most dominant followed by acidic (Asx and Glx; 29.3– to 39.6%) and hydroxylic (Ser and Thr; 13.1 to 19.2%) (Fig. 2, b). The percentage contribution of aromatic AA (Tyr and Phe) and basic (Arg) were almost the same and ranged from 4.2 to 8.0% (Table 2). Only hydroxylic AA (mol%) was statistically higher in the riverine stations compared to the estuarine stations ($p < 0.05$).

The molecular composition of THAA in the sediments collected from the riverine and estuarine regions were almost similar but the contribution from D-AA was different spatially (Fig. 2, b; Table 3). The most abundant AA in the riverine and estuarine regions were Asx, Gly, Ala, Glx, Thr, Ser and Val. High values of Arg (4.6 to 6.5 mol%) were obtained at all the stations. The non-protein AA (GABA) was lower in the riverine region (0.4 mol% to 0.7 mol%) compared to the estuarine region (0.8 mol% to 1.5 mol%) and its contribution was < 2 mol% (Table 3; Fig. 2, b). The riverine region had significantly higher Ser and lower GABA values compared to the estuarine region ($p < 0.05$). Only Gly and Tyr had higher values during the post- and pre-monsoon seasons than the monsoon season ($p < 0.05$). The Val and Leu had higher values during the pre-monsoon season compared to the monsoon season ($p < 0.05$).

The contributions of D-AA (Ala, Glx, Asx and Ser) were lower in the riverine region (5.1% to 12.4%) compared to the estuarine region (7.0% to 19.9%; $p < 0.05$). Similarly, the D/(D + L)AA values were statistically higher in the estuarine region compared to the riverine region ($p < 0.05$). The most abundant D-enantiomer was D-aspartic acid (D-Asx) in the riverine and estuarine region (Table 3; Fig. 2a, b).

Table 2
Bulk concentrations of amino acids in surface sediments of Narmada River. (Abbreviations: total hydrolyzable amino acids (THAA) concentration; yields of total amino acids (AA-C%; AA-N%); ratio of the D-enantiomers to D- + L-enantiomers of amino acids, D/(D + L)AA.

	THAA	AA-C%	AA-N%	D/(D + L)AA	Neutral	Acidic	Hydroxylic	Aromatic	Basic
	mg g^{-1}				%	%	%	%	%
Monsoon									
NR-3	2.2	8.2	25.8	5.7	51.3	35.4	19.2	5.7	5.5
NR-1	0.6	4.2	21.8	8.6	48.6	39.5	18.5	4.2	5.8
NE-1	0.4	3.7	16.9	9.8	48.9	39.6	17.4	4.5	6.2
NE-3	2.2	5.3	63.7	8.7	54.9	36.7	16.4	6.4	5.5
NE-2	1.5	6.4	30.6	9.7	75.2	32.4	13.1	5.7	7.7
Post monsoon									
NR-1	1.6	7.3	26.0	5.4	59.9	29.3	19.0	7.0	6.7
NE-1	0.5	3.0	18.6	9.0	60.3	31.7	16.1	7.3	5.7
NE-3	0.2	2.7	14.4	11.2	57.7	34.5	15.1	6.0	7.6
NE-2	0.6	3.3	20.0	11.0	58.6	33.1	16.4	6.1	8.0
Pre monsoon									
NR-1	2.2	6.6	23.6	7.6	61.5	30.0	18.2	6.1	6.8
NE-1	0.3	2.3	12.8	9.7	62.2	31.3	14.9	6.7	6.5
NE-3	0.4	3.6	16.1	10.2	61.5	30.6	15.8	6.8	7.4
NE-2	0.3	2.1	14.7	10.9	63.2	30.0	14.2	7.5	7.2

The DI values ranged from −0.66 to 0.40 (Table 3) indicating a wide range of degradation from fresh biomass (positive values) to moderately degraded OM (negative values). Low DI (negative) values were observed at all the stations during the monsoon season and high DI (positive) values for the pre-monsoon season (Table 3). Significant higher values of DI were detected during the pre-monsoon compared to the monsoon season ($p < 0.05$).

3.4. Principal component analysis and correlations among variables

The principal component analysis (PCA) was conducted on the data set taking into consideration physico-chemical, bulk and trace biomarker compositions as indicated in the supplementary data tables (Table S1). Principal components (PC) having Eigen-values > 1 were extracted. The components were rotated by using Varimax rotation, which led to the extraction of four components, which explained 85.8% of the total variance. The first component accounted for 29.3% of the total variance. The second, third and fourth components accounted for 23.1%, 16.8% and 16.7% of the total variation of the data set, respectively.

Correlations among the selected parameters are given in Table S2. A significant positive linear relationship was obtained between OC and clay on the one hand (%) ($r^2 = 0.70$; $p \leq 0.01$), and TN on the other hand ($r^2 = 0.66$; $p \leq 0.05$). The $\delta^{13}C$ values were positively correlated with silt (%) ($r^2 = 0.72$; $p \leq 0.01$) and D-Asx ($r^2 = 0.60$; $p \leq 0.05$). Similarly, a significant positive correlation was detected between SPM and basic AA ($r^2 = 0.73$; $p < 0.01$). Strong negative correlation was detected between acidic AA and aromatic AA ($r^2 = -0.84$; $p \leq 0.01$). Also, silt (%) correlated negatively with sand (%) ($r^2 = -0.77$; $p \leq 0.01$).

4. Discussion

4.1. The sources of OM to sediments of the Narmada River

Based on the variations in $\delta^{13}C$, higher values of $C:N_{atomic}$ ratio and AA and their enantiomers as well as low OC and TN contents, we attribute the sources of OM in sediments of the Narmada River to originate from terrigenous sources (C_3 and C_4plants and soils) and *in-situ* production. Higher values of $\delta^{13}C$ were observed in the estuarine region (approximately < −19‰; Table 1) compared to the riverine region. These results suggest a sizeable contribution of isotopically lighter OM (Fig. 3a, b) from terrigenous C_4 plants in the estuarine region and isotopically heavier C_3 plants (> −21‰; Table 1) in the riverine region. In the estuarine region the C_4 plant debris contributes substantial OM as evidenced by less depleted values of $\delta^{13}C$ in the sediments. The $\delta^{13}C$ values of C_4 plants such as salt resistant and desert vegetations range from −10‰ to −16‰ (Deines, 1980; Collister et al., 1994; Goñi et al., 2005a) and are found predominantly in arid and semi-arid environments. These conditions characterize the estuarine region of the Narmada River in the present study, whereby plants using the C_4 pathway are abundant in this region (Dahl et al., 2005). Also, the $\delta^{13}C$ values of commonly grown crops (*Saccharum* spp., *Sorghum* spp. and *Zea mays*) in the present study area have been reported to range between −11.5‰ and −12.8‰, which indicate contributions from C_4 plant (Pradhan et al., 2019). In addition, the values of $\delta^{13}C$ for algae ranges from −22‰ to −28‰ (Pradhan et al., 2019). The higher value of $\delta^{13}C$ (−22‰) was also obtained in our present study (Table 1), suggesting the contribution of OM from *in-situ* production.

On the other hand, the station NE-3 located in the estuarine region presented more depleted values of $\delta^{13}C$ and higher values of $C:N_{atomic}$ ratio (Table 1) during monsoon season, suggesting intense erosion of soils and degraded terrestrial plant materials. Most of the World Rivers are dominated by C_3 plants and their associated soil OM whose $\delta^{13}C$ values generally range between −28‰ and −26‰ (Wu et al., 2007). On the other hand, C_4 plants have $\delta^{13}C$ values between −15‰ and higher (Cifuentes et al., 1996). These results suggest that the OM of Narmada River is a mixture of C_3 plant debris, *in-situ* production and soil OM in the riverine region. In the estuarine region, the OM is derived from C_4 plants together with a mixture of sources from the riverine region.

Apart from the bulk geochemical parameters, further evidence of terrigenous source of OM in the Narmada River is provided by biomarkers such as AA, which have been used to determine the possible specific sources contributing to OM. Under shifting sedimentary and environmental conditions, sediments can act as potential source of AA and ON (Ni et al., 2016). Enhanced levels of Leu and Arg (pre-monsoon season) confirmed the addition of AA from *in-situ* production such as marine phytoplankton and zooplankton (Cowie and Hedges, 1992; Unger et al., 2005). The sediments of the Narmada River had a sizeable contribution from Gly (> 14 mol%). The AA Gly is often derived from diatoms (Keil et al., 2000), plants and soils in aquatic environments, suggesting contributions of OM from these sources. The accumulation of Gly in the sediments is ascribed to its close association to biogenic silica in diatom cell wall (Fernandes et al., 2014) and its low food value to micro- and macro-consumers as a result of its short chain length

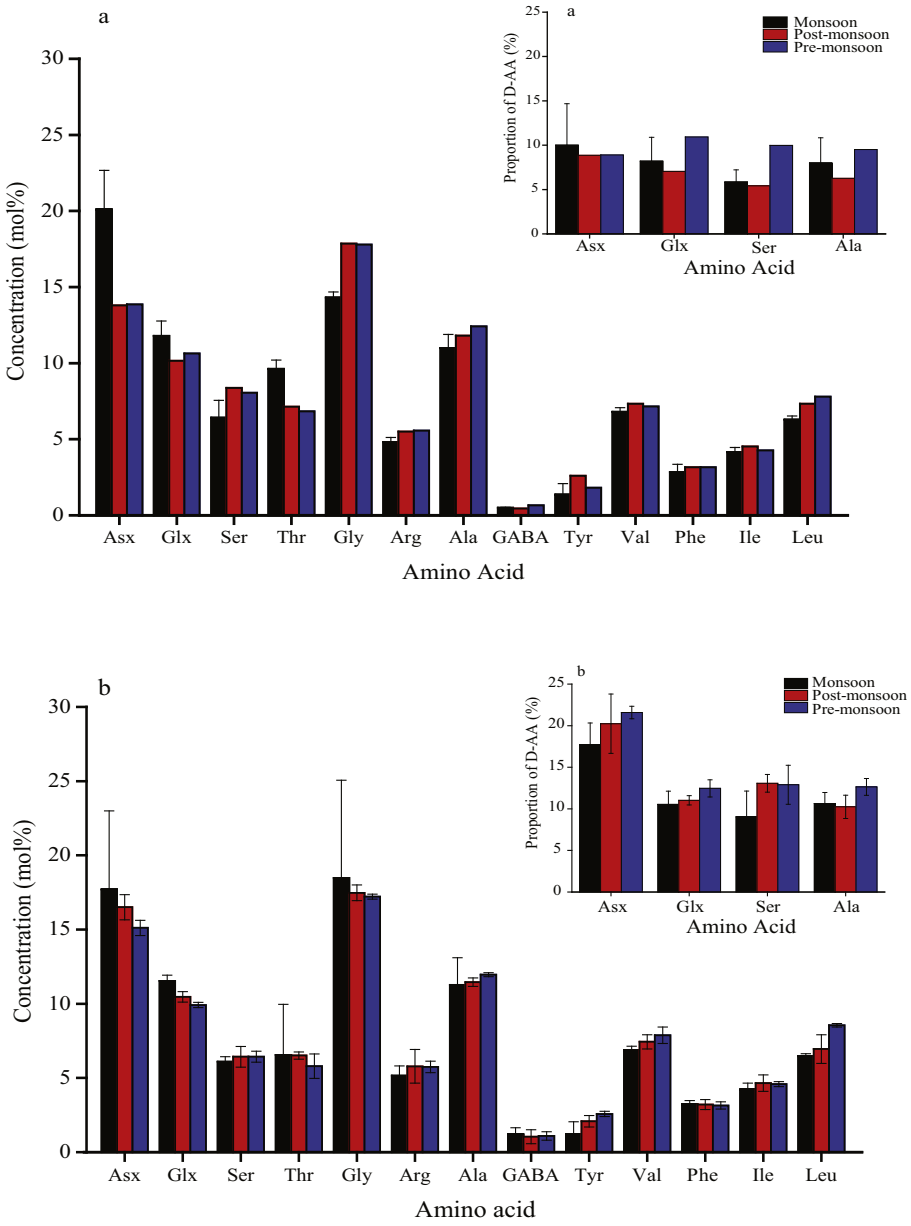

Fig. 2. a: Average mol percentage of individual amino acids (L- and D-enantiomer) of sediments from the riverine region for the different seasons with confidence interval. b: Average mol percentage of individual amino acids (L- and D-enantiomer) of sediments from the estuarine region for the different seasons with confidence interval ($p < 0.05$) (Asx, aspartic acid + asparagine; Glx, Glutamic acid + glutamine; Ser, serine; Thr, threonine; Gly, glycine; Arg, arginine; Ala, alanine; GABA, (γ-)/gamma-amino butyric acid; Tyr, tyrosine; Val, valine; Phe, phenylalanine; Ile, isoleucine; Leu, leucine).

(Dauwe and Middelburg, 1998). These attributes contribute to the accumulation of Gly in sediments leading to the higher detection in the present study.

Bacteria and their remnants are also contributors of the OM in the Narmada River due to higher Asx and Ala (> 10 mol%) in the estuarine region. It has been suggested that, cell wall materials derived from bacteria and their remnants associated sediments have an Ala signal (Mayer et al., 1995). The D-AA are a major component of bacterial cell wall (as peptidoglycan) and are not produced by algae or vascular plants (Wu et al., 2007; Chen et al., 2018). The D-AA are less accessible to biodegradation than the bulk OM (L-enantiomer) (Tanoue et al., 1996; Nagata et al., 1998), thus accumulate during diagenesis. The presence of considerable amounts D-Asx and D-Ala is a characteristic of soil humic substances and bacterioplankton, respectively (Dittmar and Kattner, 2003). Their detection and measurement during the present study indicate contributions from bacteria and their remnants to the OM reservoir. These values, together with the presence of D-AA in all the sediments sampled for the three seasons indicate substantial contribution from heterotrophic bacteria or OM that has been modified by bacteria (Table 3; Fig. 2a, b). Furthermore, the positive loadings of clay, OC and ON as well as the negative loading of D-Asx (Table S1, Fig. 4a) characterized the first component as OM associated with clay. In fact, our results showed significant positive correlation between D-Ala with the other measured D-AA, suggesting the presence of similar types of bacterial groups. All these results further indicate that there is a sizeable contribution of OM emanating from bacteria and their remnants to surface sediments of the Narmada River.

In general, the OM in surface sediments of the Narmada River originates from a mixture of C_3 and C_4 plant debris and soil, *in-situ* production, bacteria and their remnants. However, we noticed the sources of OM to be region specific (C_4 plants material in the estuarine region and C_3 plant material in the riverine region) coupled with mixed

Table 3
Concentration of amino acids (L- and D-enantiomer) and diagenetic index (DI) from surface sediments of Narmada River. (Abbreviations: Asx, aspartic acid + asparagine; Glx, glutamic acid + glutamine; Ser, serine; Thr, threonine; Gly, glycine; Arg, arginine; Ala, alanine; GABA, Gamma-aminobutyric acid; Tyr, tyrosine; Val, valine; Phe, phenylalanine; Ile, isoleucine; Leu, leucine; D-Asx, D-aspartic acid + D-asparagine; D-Glx, D-glutamic acid + D-glutamine; D-Ser, D-serine; D-Ala, D-alanine; DI, degradation index).

	Asx	Glx	Ser	Thr	Gly	Arg	Ala	GABA	Tyr	Val	Phe	Ile	Leu	D-Asx	D-Glx	D-Ser	D-Ala	DI (Dauwe)
	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%	%	%	%	%	
Monsoon																		
NR-3	18.8	11.3	7.0	9.3	14.5	4.7	11.4	0.5	1.7	6.9	3.1	4.3	6.4	7.6	6.8	5.1	6.5	−0.34
NR-1	21.4	12.3	5.8	9.9	14.1	5.0	10.5	0.5	1.0	6.7	2.6	4.0	6.2	12.4	9.6	6.5	9.4	−0.66
NE-1	21.8	11.9	5.8	9.0	14.1	5.3	10.1	0.8	0.8	7.0	3.0	4.1	6.3	15.9	7.9	12.0	10.3	−0.55
NE-3	18.7	11.5	6.0	7.5	16.2	4.5	10.6	1.4	2.1	7.1	3.2	4.7	6.6	16.2	8.2	7.4	8.3	−0.03
NE-2	12.6	11.2	6.4	3.2	25.1	5.7	13.1	1.5	0.7	6.6	3.5	3.9	6.5	11.7	10.6	7.0	10.5	−0.15
Post monsoon																		
NR-1	13.8	10.1	8.4	7.1	17.9	5.5	11.8	0.4	2.6	7.3	3.2	4.5	7.3	8.9	7.0	5.4	6.3	0.13
NE-1	15.9	10.2	6.9	6.3	17.3	4.6	11.2	0.6	2.5	7.9	3.5	5.2	7.9	19.9	9.2	13.9	8.0	0.40
NE-3	17.3	10.8	5.7	6.6	17.1	6.2	11.7	1.3	2.0	7.4	3.0	4.4	6.5	18.8	10.0	12.1	10.5	−0.20
NE-2	16.3	10.4	6.6	6.7	18.0	6.5	11.5	1.3	1.8	7.0	3.1	4.3	6.5	16.6	10.6	12.8	10.3	−0.22
Pre monsoon																		
NR-1	13.9	10.6	8.1	6.8	17.8	5.6	12.4	0.7	1.8	7.2	3.2	4.3	7.8	8.9	10.9	10.0	9.5	0.03
NE-1	15.6	10.0	6.1	6.1	17.3	5.4	12.0	0.8	2.5	7.8	3.0	4.8	8.6	18.5	9.9	12.0	10.7	0.27
NE-3	15.0	10.0	6.6	6.3	17.3	6.0	11.8	1.1	2.5	7.4	3.0	4.5	8.4	18.3	10.9	11.0	12.0	0.21
NE-2	14.8	9.7	6.7	5.0	17.0	5.9	12.0	1.3	2.8	8.4	3.4	4.5	8.6	19.7	11.8	15.0	12.5	0.39

sources (*in-situ* production, soil and bacteria) within the study region. For example, we observed limited overlap between the sources of OM in the riverine and estuarine samples (Fig. 3a, b), indicating substantial contribution from soil and plankton to both regions, while mainly C_4 plants signatures acted as source of OM in estuarine and C_3 plant signatures in the riverine region. Moreover, terrigenous OM was mainly observed during the monsoon season, while *in-situ* production occurred mainly during the post and pre-monsoons (Table 1) and bacteria were the predominant source of OM for all the seasons (Fig. 2a, b). Also, a significant linear relationship existed between TOC and TN suggesting that TN was predominantly from organic sources (Gupta and Kawahata, 2000). An overlap in the sources of OM was observed at all the sampling stations indicating contributions from terrigenous and aquatic sources, *in-situ* production (river and marine phytoplankton) and bacteria and their remnants.

4.2. Diagenetic characteristics of sedimentary OM of the Narmada River

The AA-C%, AA-N%, THAA, D/(D + L)AA ratio and DI have been used as indicators of diagenetic status of OM (Wu et al., 2007; Salas et al., 2018). Both AA-C% and AA-N% showed a decreasing trend from riverine to estuarine stations. At most of the stations, the AA-N% ranged from 12.8 to –30.6% except for station NE-3, which displayed a higher value (63.7% monsoon season; Table 2). These values are in same ranges as those obtained from other regions (Wu et al., 2007; Menzel et al., 2013). The mol% composition of THAA (Fig. 2a, b) provides primary information on the degree of degradation of OM (Ittekkot, 1988; Keil et al., 2000; Ingalls et al., 2003). Higher concentration of THAA indicates higher bioavailability of OM, while a decline in the concentration indicates preferential utilization of labile OM. The values of THAA and AA-N% obtained in our study indicate moderate diagenesis of OM. Usually AA-N% values > 50% are obtained from living organisms and tree leaves, which subsequently decrease during diagenesis (Cowie and Hedges, 1994).

Likewise, sediments of the Narmada River were rich in Gly and Asx (Table 3). Enrichment of these AA is an indicator of the degradation process occurring within the sediments. Gly is a known cell wall constituent, with a simple stable structure (Dauwe and Middelburg, 1998). The Gly (mol%) of plant material such as leaves ranges from 10.0 mol% to 17.66 mol% (Menzel et al., 2013). Furthermore, Gly values of 13.7 mol% in phytoplankton, 14.4 mol% in SPM and 17.7–19.7 mol% in sinking particles and surface sediments were reported by Gupta et al. (1997). These values are mostly similar to those obtained in the present study except a few (Table 3). Therefore, the enrichment of Gly in the sediments in the present study may be attributed to its close association with biogenic silica in diatom cell wall and frustules thereby protecting

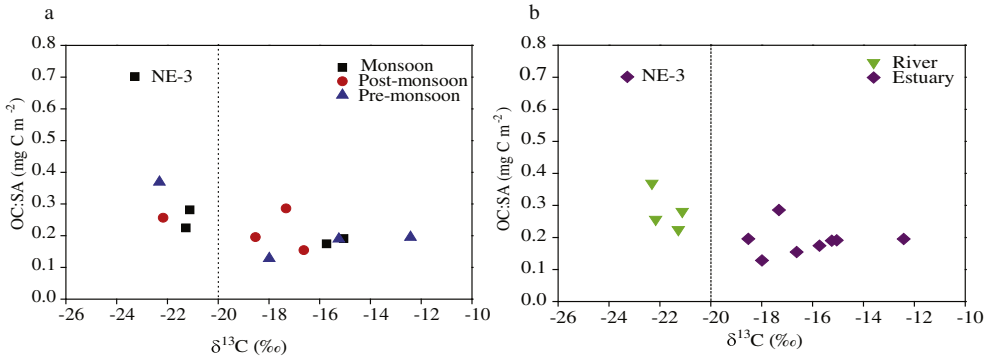

Fig. 3. a, b: Temporal and spatial distributions of OC: SA (mg C m^{-2}) and δ^{13}C (‰) of sediments along the river (the station labeled NE-3 was located within Narmada estuary).

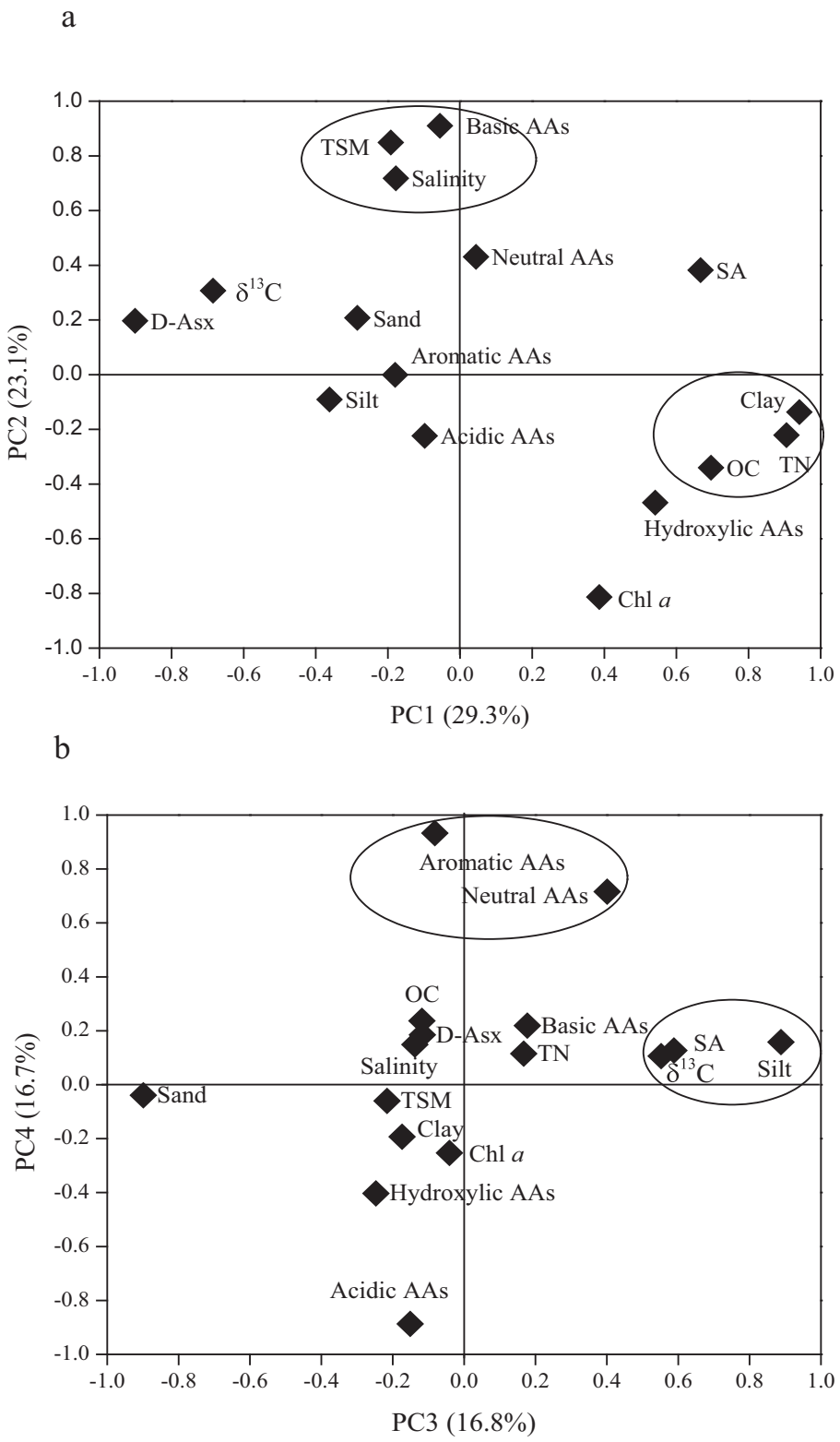

Fig. 4. a, b: Varimax rotated principal component (PC1) and PC2 loadings; PC3 and PC4 loadings.

it from degradation (Lee et al., 2000; Ingalls et al., 2003). Alternatively, its enrichment may be attributed to steric interference, selective diagenesis of biomass (OM) from plant detritus, phytoplankton and sinking particles.

The presence of Ala in considerable amounts (> 10 mol%) indicates the presence of partially degraded OM in the river (Dauwe et al., 1999). Lower and higher D/(D + L)AA ratios in the riverine and estuarine regions, indicate the presence of more degraded OM and the role of heterotrophic bacteria in transforming OM within the riverine and estuarine regions, respectively. The D-Ala (%) and GABA showed a fairly linear relationship during the pre-monsoon season (Fig. 5a) and in the riverine region (Fig. 5b), confirming the role of bacteria in degrading OM. Some of the estuarine stations did not follow the linear relationship, suggesting the presence of additional sources of GABA during the

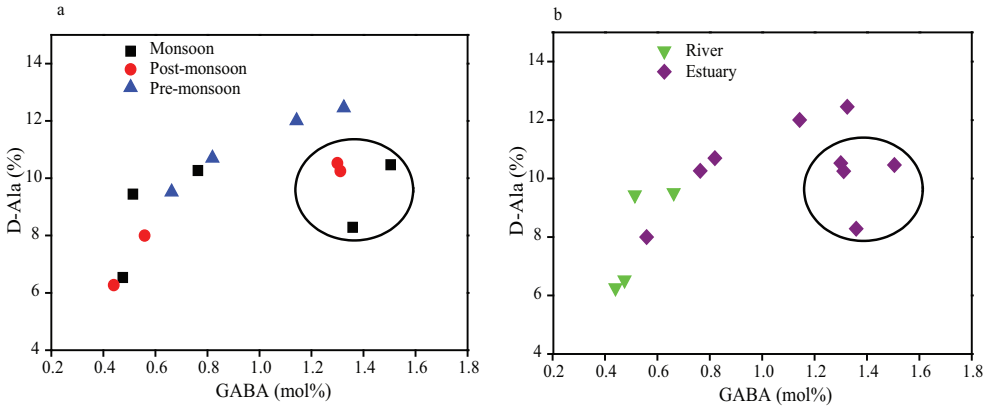

Fig. 5. a, b: Seasonal and region wise relationship between D-Ala (%) and GABA (mol%) of sediments.

monsoon and post-monsoon seasons. More likely, the additional content of GABA originates from plants, which are known to synthesize it under environmental stress conditions such as heat, salt and flooded soil (Kinnersley and Turano, 2000; Menzel et al., 2013). Bacteria, phyto- and zooplankton and vascular plants, usually contain < 1 mol% of GABA as a byproduct of metabolic activity of Glx (Cowie and Hedges, 1992).

We further measured the diagenetic status of the sediments by using the DI. The DI of sediments from the Narmada River was relatively fresher during the pre-monsoon season (positive values) and more degraded (negative values) during the monsoon season due to selective diagenesis and transport of relatively older OM. The DI values for all the samples measured in the present study were near zero and are comparable with other coastal and estuarine sediments (Lomstein et al., 2006; Fernandes et al., 2014; Salas et al., 2018). We attribute the diagenesis of OM in the river to extreme climatic conditions such as elevated temperatures and low rainfall during the various seasons in the Narmada basin (Fig. 1b). Erosive activities, chemical weathering and biological breakdown of OM are enhanced at higher temperatures.

Also, the fourth extracted principal component showed strong positive loadings of aromatic AA and neutral AA and negative loading of acidic AA, this factor can be termed as the freshness factor (Table S1; Fig. 4b). Thus, the AA-C%, AA-N%, D/(D + L)AA ratios and DI were useful as indicators for depicting ontogenetic changes in sediments of the Narmada River. Hence, under variable climatic conditions, the diagenetic status of OM will play a decisive role in the biogeochemical cycles of OM within riverine and estuarine sediments.

4.3. Factors controlling the distribution of sedimentary OM

Physical and geochemical factors played a decisive role in the distribution of sedimentary OM of the Narmada River. Sediment load and SPM are controlled by physical factors like rainfall, size of the catchment area, relief, basin geology and soil characteristics and impact of reservoirs/dams. Rainfall has been commonly understood to have a predominant influence on river water flow and sediment discharge. Sediments collected during different seasons and sampling locations exhibited fluctuations in textural characteristics, which was dependent on river discharge between the riverine and estuarine regions. Water discharge in the Narmada River is mostly confined to the monsoon season (Fig. 1b) and is directly dependent upon rainfall in the catchment area as the region experiences extreme conditions. The volume of water discharged and sediment load of a river basin is a function of the size of the catchment area. Larger catchment areas receive more rainfall and tend to retain the surface runoff for a considerable time depending on velocity of the flow, fluxes, relief and gradient of the stream channel. The amount of runoff and velocity accelerate erosion of weak rock substrates (Dadson et al., 2003) and soils with thick vegetation producing organic acids, which affect the OM distribution. Therefore, the large drainage area of the Narmada River (98.8×10^3 km^2) and the relatively high amounts of rainfall during the monsoon season (Fig. 1b) might be controlling the distribution of OM within the river and estuary.

We also observed that the turbidity maximum zone (TMZ) (as inferred from the SPM data) shifted from the station NE-2 (monsoon and post-monsoon season), which is located towards the mouth of the estuary to station NE-3 (pre-monsoon, Table 1) within the estuary. This suggests more re-suspension and turbulence of OM due to tidal influence at this station together with reduced freshwater inputs during the post- and pre-monsoon seasons as a result of extreme climatic conditions compared to the monsoon season. Furthermore, the second and third extracted components displayed strong positive loadings of salinity, SPM, silt and SA (Fig. 4a, b) suggesting the influence of tides and sorting effects, we termed them as tidal factor and hydrodynamic sorting factors, respectively. Denudation of catchment has led to the occurrence of high silt contents in the river and runoff waters (Bhaumik et al., 2017). The presence of steep gradients in the upper and lower parts of the basin is responsible for the high SPM concentrations in the lower reaches as seen in Table 1. All these physical factors further control the distribution of OM in the Narmada River.

Furthermore, the lower OC:SA ratios (organic loading) observed in the estuarine region suggests a net loss of OM in this region except at station NE-3 (monsoon season), which behaves differently, indicating that it is strongly influenced by terrestrial OM eroded during the monsoon season (Fig. 6a, b, c, d). Most of the OC:SA ratio values were < 0.4 mg C m^{-2} and are below the range of 0.5–1.1 mg C m^{-2} measured along continental margins (Nuwer and Keil, 2005) for river and marine sediments (OC:SA = 0.5 to 1.0; Hedges and Keil, 1995; Keil et al., 1997; Mayer, 1999; Goñi et al., 2005b). The downward shift in OC:SA ratio (Fig. 6b, d) denotes a net loss of OM from the estuarine region due to selective diagenesis. It is known that, changes in mineral grain size alter the OC:SA ratio, which consequently affect the adsorption processes of OM (Keil et al., 1994). Moreover, the OC:SA ratio also affects diagenesis of degradation resistant of OM, which takes place on mineral surfaces (Mayer, 1994). Therefore, when OM from sediments is selectively degraded by microorganisms (Mayer, 1999), the OC:SA decreases, indicating net loss. However, when the OM is preserved due to adsorption onto fine mineral grains, the OC:SA ratio increases.

Changes in grain size distribution often reflect changes in the hydraulic environments (Williams and Block, 2015). Usually, the presence of low energy settings in the riverine region facilitates the deposition of sediments. In the estuarine region, we observed lower clay content and higher silt content (Fig. 6a, b, c, d) due to relatively higher energy resulting from tides. Similarly, the TN:SA ratios were lower than those observed in other river sediments (Mayer et al., 1998). Like previous

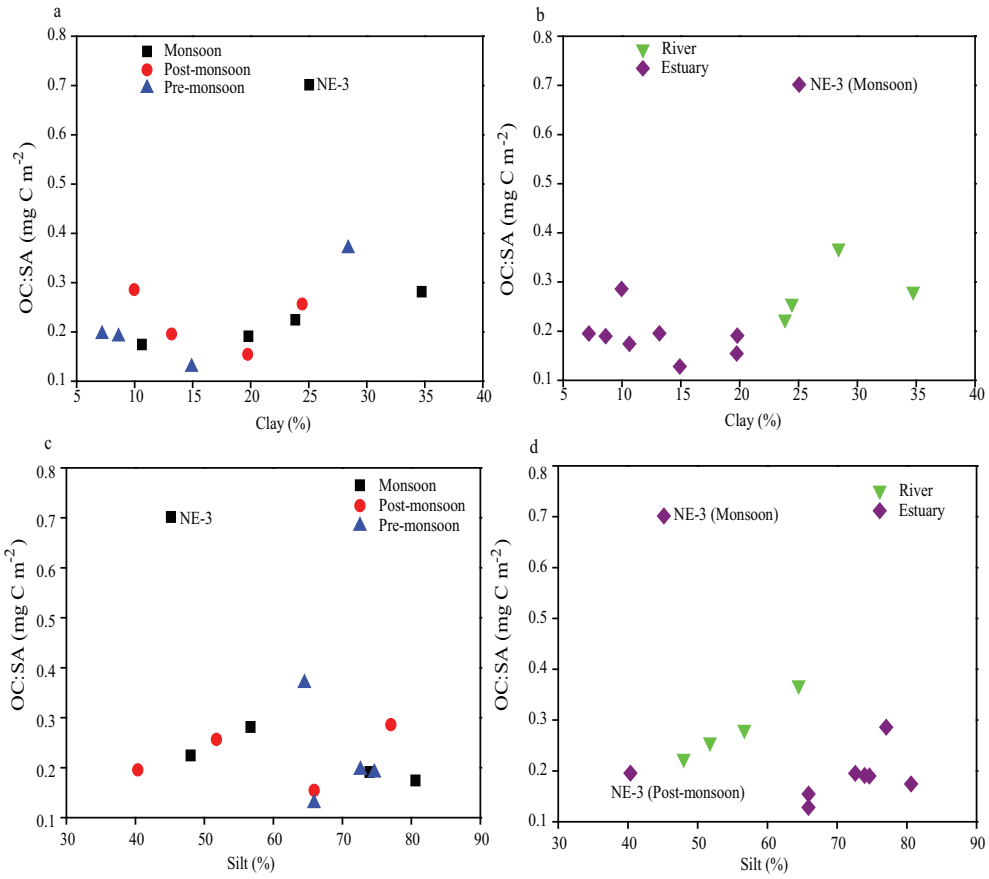

Fig. 6. a, b, c, d: OC:SA (mg C m^{-2}) with Clay (%) and Silt (%) displaying temporal and spatial variability (the station labeled NE-3 was located within Narmada estuary).

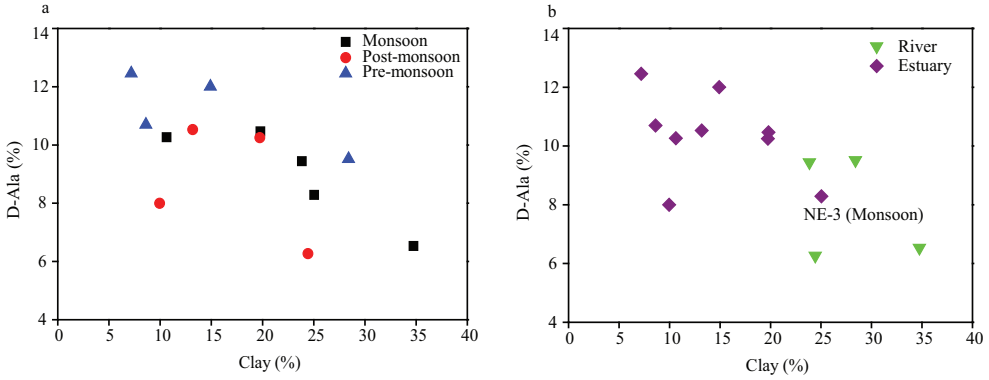

Fig. 7. a, b: Relationship between D-Ala (%) and Clay (%) temporal and spatial distributions in sediment (the station labeled NE-3 was a located within Narmada estuary).

studies, we observed a positive relationship between OC and clay content (Mayer, 1994; Hedges and Keil, 1995; Li et al., 2014), indicating that the finer fractions have an important role in controlling the bulk OC content associated with sediments. One would also expect a positive relationship between clay particles and D-AA due to attachment of microbes to finer particles, but our results showed negative correlation between the D-Ala (%) and clay (%) seasonally and spatially (Fig. 7a, b). This might be due to the influence of tides and turbulence in the Narmada River. Under the influence of enhanced tidal activity, lighter particles (clay) undergo repeated cycles of re-suspension and mobilization leading to a decoupling effect thereby exposing the OM to re-working and degradation, which lead to negative correlation. Furthermore, fine grain sediments (clay + silt) have higher SA (Table 1), carry a net negative charge and can therefore adsorb more NH_4^+ than coarse sediments (Meyers, 1997; Chen et al., 2018). The association between OM and fine-sized sediment particles (clay, silt) with higher SA suggests that, OM loadings are controlled by the mineral SA available for adsorption processes (Keil et al., 1994).

Another important factor controlling the distribution of OM in the Narmada River is the water residence time. The residence time of the waters of Narmada River varies between 2and 54.61 days (Sharma and Naik, 1996). During the monsoon season the river experiences flood like conditions whereby the accumulated OM are transported from the upper regions to the estuarine region. However, during the dry seasons the flow of the water is reduced considerably due to low rainfall and water management practices along the course of the river. This period

provides sufficient time for labile OM to undergo selective and preferential diagenesis. Thus, under hydrodynamically stable conditions the suspended load transported by the river settles under gravity within the river. Contrary, during turbulent conditions the sediment particles remain suspended in the water and are transported to the estuarine region. Lastly, anthropogenic activities such as agriculture and dam construction also control the OM distribution in rivers, but studies detailing their effects are scarce in the Narmada River. Damming of the river channel as was observed in the Narmada River does not only restrict the water flow but also traps mobilized sediments and OM, thereby reducing its inputs to the estuaries, coasts and shelf regions. Thus, physical (rainfall, tidal activity, residence time) and geochemical (adsorption) factors were responsible for controlling the spatial and temporal distribution of OM in the surface sediments of the Narmada River.

5. Conclusion

The sources, degradation and factors affecting the distribution of OM from the surface sediments of the Narmada River were investigated in this study. The values of OC, $\delta^{13}C$, TN, $C:N_{atomic}$ and AA indicated that, the OM of most sediments were derived from detrital plant matter (terrestrial and *in-situ* production) and soils in addition to bacteria and their remnants. Terrestrial C_3 plants and C_4 plant detritus were the main sources of OM in the riverine region and the estuarine region, respectively. Temporally, heterotrophic bacteria and their remnants contributed to OM sources. Lower values of AA-C%, AA-N%, indicated the presence of OM that has undergone selective diagenesis. Relatively fresher OM was observed during the pre-monsoon season as compared to the monsoon season. Physical (rainfall, tidal activity, residence time) together with geochemical (mineral surface adsorption processes) and biological (allochthonous and autochthonous sources and diagenetic processes) factors exert decisive role in controlling the distribution and transport of OM within the Narmada River. Thus, tropical rivers and their estuaries, which experience dynamic temporal variations due to extreme seasonality of the monsoons are vital in the interpretation of benthic nutrient budgets in coastal seas and continental margins.

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Author contributions

DF, WY and JZ conceived and designed the experiments. UKP and PVS collected the samples and provided logistics support. DF and UKP performed the experiments. DF and SML analyzed the data. DF, WY, SML and PVS wrote and corrected the manuscript. All authors approved the final version of the manuscript for submission.

Declaration of competing interest

The authors declare that no competing interests exist.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmarsys.2019.103239.

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