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Spatial and temporal variations in source, diagenesis, and fate of organic matter in sediments of the Netravati River, India

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Abstract

Organic matter (OM) such as organic nitrogen plays a substantial role in the global biogeochemical cycling of bio-reactive components—amino acids (AA) in aquatic environments. Spatial and temporal variations in source, diagenesis, and fate of organic nitrogen such as AA in sediments of small tropical rivers and the role of oxbow/meandering loops under changing climatic conditions are poorly investigated. This study assessed the spatial and seasonal variations in OM composition, source, and diagenesis of a tropical small mountainous river—Netravati River, India, for 1 year. Water samples were determined for suspended particulate matter, and surface sediments were examined for bulk parameters, surface area (SA), and the L- and D-enantiomers of AA. The L- and D-enantiomers of AA displayed subtle seasonal variations in composition and depicted varying degrees of diagenesis. The concentration of D-enantiomer of AA was high and showed substantial contributions from bacteria, terrestrial source, and in situ production. The D-arginine was the most abundant D-enantiomer of AA in the study area, possibly due to extracellular secretion by bacterial species and adsorption onto sediments, and thus, it was protected from degradation. Degradation index was more negative at the oxbow and meandering loop stations during the dry season suggesting that local geomorphologic settings steer the diagenesis of OM within the river. A negative relationship between gamma-aminobutyric acid and organic carbon:surface area (OC:SA) ratio and a positive correlation between tyrosine and OC:SA ratio suggested accelerated loss of OM. Furthermore, the concentrations of most bulk parameters were higher in the lower reaches during monsoon and premonsoon seasons. Taken together, changes in seasons have an operational control in distinguishing the composition, source, and diagenesis of spatial OM distribution. Moreover, oxbows and river meandering loops influence the diagenetic processes in small tropical river systems.

KEYWORDS
amino acids, meandering loops, Netravati River, organic matter (OM), surface area (SA)

1 | INTRODUCTION

Organic matter (OM) plays a substantial role in the biogeochemical cycling of bio-reactive elements, especially carbon and nitrogen (Yan, Kim, Kim, Jeong, & Kim, 2015). The transport of OM as a nutrient under Anthropocene conditions has been altered considerably due to industrialization, urbanization, and expansion in agriculture to meet the demands of increasing population. Nitrogen (inorganic [nitrate, nitrite, ammonia, and nitrogen oxides] and organic forms) is considered as a vital nutrient in aquatic environments and is known to be a limiting factor for primary productivity (Conley et al., 2009; Elser et al., 2007). Organic nitrogen (ON) exists in different forms including monomers (amino acids and amino sugars), urea, and heterocyclic nitrogen-containing substances (Schnitzer & Schulten, 1998). Amino acids (AA) are bio-reactive components of OM, which exist ubiquitously in the environment originating from both marine and terrestrial source. They are used as indicators of bioavailability of nutrients from OM in marine environments (Benner, 2003; Davis, Kaiser, & Benner, 2009) and groundwater (Shen, Chapelle, Strom, & Benner, 2015) because they are one of the most readily mineralized forms of ON and account for the largest contribution of nitrogen mineralization rate. The ratio of protein AA to nonprotein AA is used as a diagenetic indicator of OM (Cowie & Hedges, 1994; Cowie, Hedges, & Calvert, 1992). Therefore, changes in composition and contents of AA in sediments and water provide a potential tool for studying the source and biogeochemical cycling of labile OM from rivers to the coastal seas and oceans (Ni, Wang, & Zhang, 2016; Tsukasaki & Tanoue, 2010).

The recent impacts of global climate change on rivers and estuarine systems have caused significant shifts in nutrients distribution and transport (Glibert et al., 2018; Sahu, Pati, & Panigrahy, 2018). However, such evidences are currently understood from large river systems such as the Amazon, Mississippi, Nile, Indus, Changjiang, and Huanghe (Bianchi & Allison, 2009; Hedges et al., 1994) and coastal and marginal seas (Anderson, Glibert, & Burkholder, 2002; Jessen et al., 2017). In such aquatic systems, major ecological problems such as shifts in the natural biogeochemical and nutrient cycles have caused increased occurrences of eutrophication in lakes (Yao et al., 2012), rivers and coastal ecosystems (Seitzinger et al., 2002), and harmful algae blooms, together with hypoxia in coastal and marginal seas (Anderson et al., 2002; Jessen et al., 2017). Unfortunately, large and small rivers experience variations in the natural biogeochemical and nutrient cycles (Degens, Kempe, & Richey, 1991). Transport of OM in small tropical rivers is likely to be more affected during periods of warmer climate due to their geological rock records (Latrubesse, Stevaux, & Sinha, 2005) and their sensitivity and vulnerability to even small changes (Syvitski, Cohen, Kettner, & Brakenridge, 2014). Thus, these rivers give rise to significant environmental and socio-economic problems. In addition, small tropical rivers have meandering loops and oxbows formations, which act as traps for sediments, providing favourable conditions for accumulation of suspended sediments such as clay, silt, and OM. These materials are usually transported as suspended load and deposited in sediments under low-energy settings (Bábek et al., 2008). Consequently, small tropical rivers provide ideal study settings to evaluate the shifts in bioavailability of OM and their linkage to changes in global cycles due to limited capacity and short residence time of water mass within the drainage basin and catchment area.

Limited studies have been conducted on the seasonal changes, composition, transport, and diagenesis of ON using AA in sediments of small tropical rivers under changing climatic conditions. Indeed, AA have been ignored in contemporary studies conducted in aquatic environments, with most available studies focusing on land use changes due to anthropogenic activities (Bao et al., 2013; Ni et al., 2016; Salas, Sujatha, Ratheesh Kumar, & Cheriyan, 2018). Moreover, the role of river meanders and oxbows in seasonal trapping of OM (AA) has not been explored in small tropical mountainous rivers. We hypothesized that geomorphological features such as river meanders and oxbow formation trap more degraded OM during the postmonsoon and premonsoon seasons, thus controlling the seasonal diagenetic processes of biochemical parameters in sediment and water of the Netravati River and its estuary in the south Indian state of Karnataka. Therefore, this study determined the spatial and seasonal variations in composition, transport, and diagenesis of OM in Netravati River, which is a tropical small mountainous river.

2 | MATERIALS AND METHODS

2.1 | Study area

Netravati River is a small mountainous river, which originates from the steep slopes of the Sahyadri ranges of the Western Ghats and discharges its water into the Arabian Sea, south of the New Mangalore Port. The river flows westwards for 148 km (Murthy, Madhyastha, Rao, & Chandrashekarappa, 1988) and has a basin surface area (SA) of 3,657 km^2 (Tripti et al., 2013). The river has two tributaries—the upstream part of Netravati River and the Kumaradhara River (Figure 1a). The Netravati River has meander loops and oxbows in the lower reaches caused by reduction in the slope/gradient through which the river channel flows forcing the water to flow slowly in meandering and zigzag paths (Kumar, Jayappa, & Deepika, 2010). The lower section of the river flows into an estuary located near Mangalore town along the southwest coast of India, which receives freshwater during south-west monsoon season (June to September) and is connected to the Arabian Sea throughout the year. During the monsoon season, the estuary is flooded by rainwater and becomes almost freshwater-dominated. During nonmonsoon/dry period (October to May), the estuarine region takes in seawater due to the reduction of freshwater discharge (Rajesh, Rajesh, & Reddy, 2014) and the tidal influence can be traced up to about 15 to 20 km inland due to the shallow and wide nature of the estuary mouth (Saravanan, Chowdhury, & Sivakumar, 2013). The average annual runoff and sediment load at the gauging site was 11.1×10^3 M m^3 and 1.2×10^6 ton, respectively (Dwarakish, Abdu Rahiman, & Natesan, 2009), and the mean annual river discharge was about 336 m^3/s (Higgins, Overeem, Roggers, & Kalina, 2018). Sediment yield of the Netravati River has

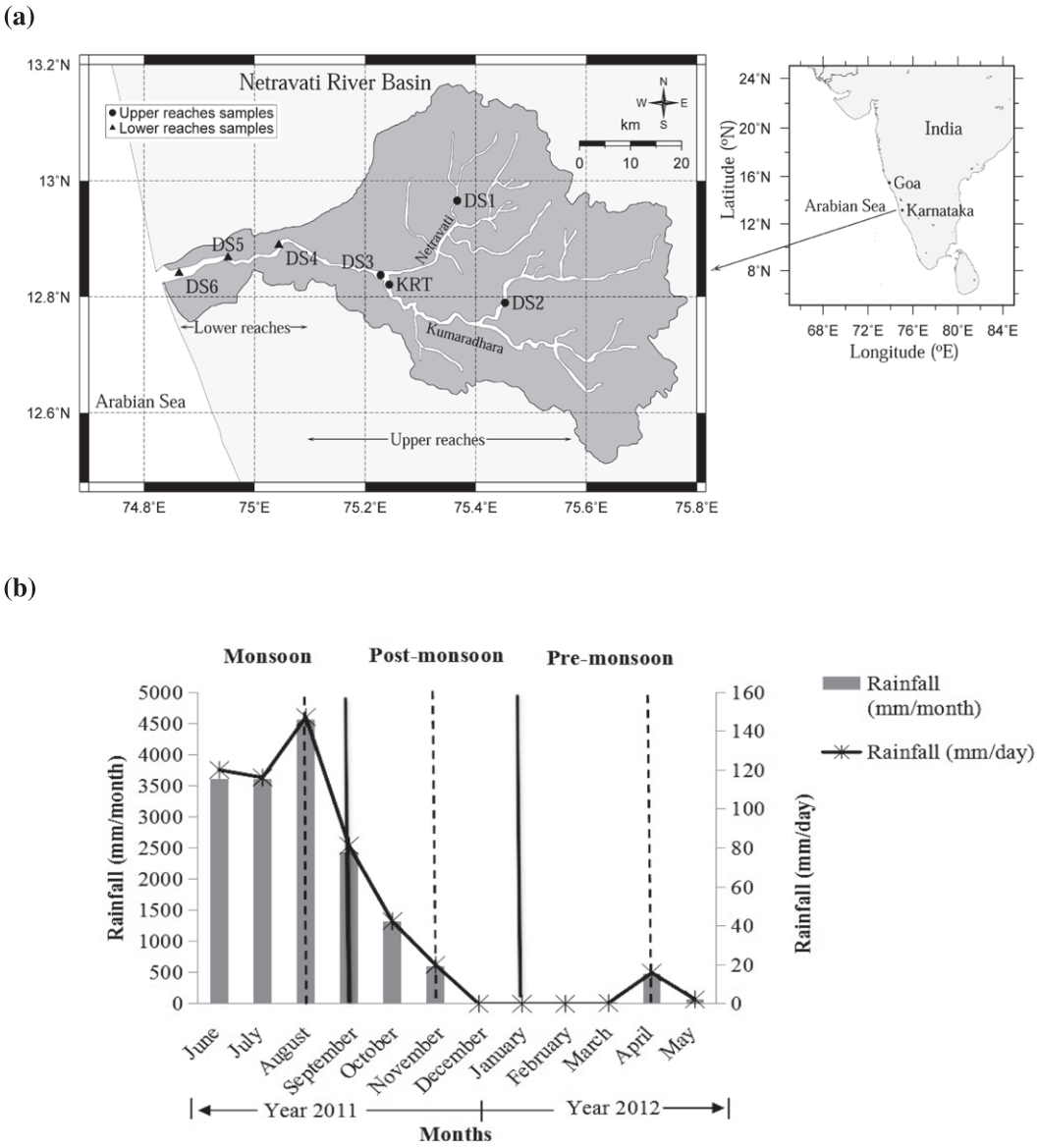

FIGURE 1 (a)The location of the sampling sites within the Netravati River basin (stations marked with circular symbol indicate upper reaches and triangular symbol indicate lower reaches). (b) Monthly and daily rainfall (in mm) during the year 2011-2012. (The two solid lines demarcate the change in season, and the three hyphened lines indicate the sampling month)

been projected to increase due to land use land cover (LULC) changes as a result of intensive agriculture and urbanization. The sediment yield due to LULC from 2000 to 2012 was about 658 ton/km^2 (Sinha & Eldho, 2018).

2.2 | Sampling sites and sample collection

The sampling stations Dharmasthala 1, 2, and 3 (hereafter abbreviated as DS1, DS2, and DS3), respectively, and Kumaradhara (KRT) were considered as the upper reaches or upstream, whereas stations Dharmasthala 4, 5, and 6 (abbreviated as DS4, DS5, and DS6, respectively) were in the lower reaches or the downstream region based on elevation (average meters above sea level). The stations located 100 m above sea level were classified as the upstream stations and below 100 m as the downstream region. Surface water and sediments samples were collected from the selected locations along the Netravati River during the South West Monsoon (SWM; August–September), postmonsoon (November–December), and premonsoon (April- May) between 2011 and 2012 (Figure 1b). Surface water samples from the river were collected by using clean buckets. Estuarine water samples were collected by using a 5-L Niskin water sampler (General Oceanic, USA) from a mechanized boat. Samples were preserved in an icebox and transported to the laboratory of the National Institute of Oceanography (NIO), Goa, India, for preliminary processing before shifting them to the State Key Laboratory of Estuarine and Coastal Research, Shanghai, China for further analyses.

Surface sediments were collected by using a Van Veen grab (15 × 15cm). After collection, the top layer of the sediments (0–2 cm) was

subsampled and transferred to clean zip lock polyethene bags and stored in an icebox. The samples were taken to the NIO laboratory where they were oven dried at 45 °C for 3 to 4 days. Part of the dried samples were finely ground using an agate mortar and pestle and used for bulk elemental and AA analyses.

2.3 | Hydrographic parameters

In situ measurements of temperature and salinity of the water samples were done by using a multiparameter probe (Inolab multi-720). The average precision for temperature and salinity measured by the probe was 0.01 °C and 0.01, respectively. Meteorological data were acquired from the India Meteorological Department website (http://www.imd.gov.in) (India Meteorological Department, 2011–2012).

2.4 | Suspended particulate matter

Water samples for the analysis of suspended particulate matter (SPM) were filtered through precombusted GF/F Whatman filters. The SPM was measured as the difference in weight after drying the filters at 40 °C for 48 hr.

2.5 | Elemental and stable carbon isotope analysis

Organic carbon (OC) content of sediments and its isotope $\delta^{13}C$ were measured by using the elemental analyser (Finnigan EA 1112) interfaced with continuous flow isotope ratio mass spectrometer (Finnigan Delta plus XP). Homogeneous ground sediments were directly treated with 1M HCl to remove inorganic carbon and then oven dried at 45 °C for 24 hr before the measurements of OC and its isotope ($\delta^{13}C$) were carried out. The analytical precision for carbon isotope $\delta^{13}C$ measurement in this study 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:

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

The total nitrogen (TN) content of sediments was measured without acid treatment by using the CHNOS Elemental analyser (Model: Vario EL III).

2.6 | Grain size analysis

The grain size of sediment samples was measured after removing the OM by using a Coulter laser granular meter (LS-100Q) as previously described by Pradhan, Wu, Shirodkar, Zhang, and Zhang (2014a). Briefly, 0.5 g of dry unground sediment was treated with 10% H_2O_2 to remove OM. Sediment grain sizes were expressed as a proportion of clay (<4 μm), silt (4–63 μm), and sand (>63 μm) with a measurement error of ≤1% in the entire dataset (Pradhan et al., 2014a).

2.7 | Specific SA analysis of sediments

Specific SA of sediments was measured by nitrogen adsorption using a five-point Brunauer–Emmett–Teller method (Keil, Montluçon, Prahl, & Hedges, 1994; Waterson & Canuel, 2008). The SA (m^2/g) was measured from oven-dried un-ground sediments after combustion at 350 °C for 12 hr to remove OM. The SA values obtained were used to calculate the OC and TN loadings as OC:SA ratio (OC: SA; mg C/m^2) and TN:SA ratio (TN:SA; mg N/m^2), respectively.

2.8 | Amino acid analysis

Approximately 100 to 150 mg of ground sediments were hydrolysed with HCl (16%, 20 mL) in precombusted glass ampoules sealed in a nitrogen environment and incubated at 110 °C for 24 hr in order to determine the total hydrolysable amino acids (THAA), according to Fitznar, Lobbes, and Kattner (1999) with minor modifications. Briefly, sediment samples were analysed using a Phenomenex™ Hyperclone column (5-μm particle diameter, BDS C18, 250-mm length, 4-mm inner diameter) with a guard column (4 × 2 mm). The mobile phases were (A) 125-mM sodium acetate with 2% methanol (pH 6.8, adjusted with acetic acid) and (B) 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 abbreviations Asx and Glx were used for the determined aspartic acid + asparagine and glutamic acid + glutamine, respectively, because the corresponding acids are formed via deamination during hydrolysis. The D- and L-enantiomers of the individual AA in the hydrolyzates were determined fluorometrically by using the high-performance liquid chromatography (HPLC) system (Agilent 1100 series). The relative standard deviation for the individual AA for triplicate analysis was <3.5% (Wu et al., 2007). The degradation index (DI) for the THAA samples was calculated according to Dauwe and Middelburg (1998).

2.9 | Statistical analyses

Results are presented as mean ± standard deviation (*SD*), and data were tested for normality using Shapiro–Wilk test and homogeneity of variance using Levene's test. The measured variables among the three seasons were analysed by using one-way analysis of variance (ANOVA) followed by Tukey's post hoc test for specific differences. The mean values for upper and lower reaches were compared by using independent *t* test. Pearson's correlation was used to show any association among different parameters measured both spatially and temporally during the study. All statistical analyses were performed using SPSS for windows version 20 (SPSS version 20, IBM, Armonk, NY, USA). Results with $p \leq .05$ were considered statistically significant for all statistical tests except for Pearson's correlations where both $p \leq .05$ and $p \leq .01$ were considered significant.

3 | RESULTS

3.1 | Spatial and temporal variations in rainfall and hydrographic parameters

The rainfall for the monsoon, postmonsoon, and premonsoon season were 3600 ± 870, 480 ± 620, and 140 ± 230 mm, respectively. Most of the rainfall occurred during June to September. The highest daily rainfall occurred during August (Figure 1b). The rainfall obtained during the Monsoon season was significantly higher compared with the postmonsoon and premonsoon seasons (p <.001), with no significant difference during the postmonsoon and premonsoon seasons. The water temperature varied from 25.7 ± 0.6 °C during the SWM to 31.6 ± 1.1 °C for the premonsoon season and was significantly higher during the premonsoon than the monsoon and postmonsoon (p <.001). Water temperature of the lower reaches was comparatively higher than the upper reaches; however, it was not significant different (p >.05; Table 1). Salinity was mostly zero during the monsoon and postmonsoon seasons, whereas during the premonsoon season the lower reaches displayed significant higher values than the upper reaches (p <.001).

3.2 | Distribution of bulk parameters and elemental compositions

The SPM loads of the river for the monsoon, postmonsoon, and premonsoon seasons were 18.5 ± 4.5 mg/L, 23.8 ± 22.6 mg/L, and 34.3 ± 33.4 mg/L, respectively. Higher SPM values were observed during the premonsoon season in the lower reaches (p <.001).

The OC values varied from 8.0 ± 2.0 mg/g to 31.5 ± 14.5 mg/g with the highest values obtained during the monsoon season and the lowest during the postmonsoon season in the lower reaches of the estuary (p <.001). The TN content varied from 0.7 ± 0.9 mg/g in the upper reaches during the premonsoon season to 2.4 ± 1.1 mg/g during the monsoon season for the lower reaches (Table 1). The C:N atomic values were higher in the upper (20.6 ± 9.2) and lower reaches (15.5 ± 2.2) during the monsoon. The C:N atomic ratio had no significant differences among the three seasons (p >.05). The $\delta^{13}C$ in sediments varied from -27.4 ± 0.2‰ to -25.6 ± 0.4‰ for the three seasons. The lowest (-28.4‰) and the highest (-24.8‰) values were observed during the monsoon and postmonsoon seasons, respectively. A narrow range of variation was observed in the $\delta^{13}C$ isotopic values for the monsoon and postmonsoon seasons between the upper and lower reaches (-26.2 ± 2.1‰ to -27.6 ± 0.8‰).

3.3 | Grain size and SA of bulk sediments

Silt fraction was the major component of sediments in the lower reaches for the monsoon and postmonsoon seasons, whereas the sand fraction was most abundant during the premonsoon season. Clay fraction was fairly less compared with silt and sand fractions (Table 1), and no significant differences were obtained (p >.05) among sediment fractions; nonetheless, they displayed different compositions temporally. The SA of bulk sediments ranged from 35.0 ± 12.9 m^2/g for the monsoon season in the lower reaches stations to 9.3 ± 6.9 m2/g for the premonsoon season in the upper reaches of the river. The average OC:SA ratio of the sediment varied from 0.97 ± 0.15 mg C/m^2 to 0.41

TABLE 1 The average concentrations (± standard deviations) of water and sediment bulk parameters of the Netravati River for the three seasons (monsoon, postmonsoon, and premonsoon)

Season	Monsoon		Post monsoon		Pre monsoon	
Region	Upper reaches	Lower reaches	Upper reaches	Lower reaches	Upper reaches	Lower reaches
Temperature (°C)	25.7 ± 0.6	26.8 ± 0.6	27.0 ± 1.5	29.2 ± 0.1	31.4 ± 1.2	31.6 ± 1.06
Salinity	0	0	0	0	0	25.2 ± 8.9
SPM (mg/L)	14.9 ± 1.0	22.2 ± 3.0	26.3 ± 28.3	18.8 ± 3.3	14.7 ± 12.4	47.3 ± 39.0
TOC (mg/g)	19.95 ± 17.9	31.5 ± 14.5	23.1 ± 12.7	8.0 ± 1.95	8.95 ± 11.9	8.05 ± 10.9
TN (mg/g)	1.5 ± 1.4	2.4 ± 1.1	1.7 ± 1.0	0.8 ± 0.2	0.7 ± 0.9	0.7 ± 0.9
$C:N_{atomic}$	20.6 ± 9.2	15.5 ± 2.2	16.6 ± 1.3	11.9 ± 0.7	14.0 ± 2.2	11.9 ± 3.1
$\delta^{13}C$ (‰)	-26.8 ± 1.6	-27.2 ± 1.2	-27.3 ± 0.8	-26.2 ± 2.1	-27.4 ± 0.2	-25.6 ± 0.4
Clay (%)	13.1 ± 9.0	17.7 ± 2.0	13.2 ± 4.1	17.7 ± 8.1	6.7 ± 7.31	13.3 ± 9.3
Silt (%)	39.1 ± 26.1	53.8 ± 12.1	39.2 ± 13.3	44.6 ± 22.8	16.6 ± 16.5	27.2 ± 18.8
Sand (%)	47.8 ± 35.2	28.5 ± 14.1	47.7 ± 17.3	37.7 ± 30.8	76.6 ± 23.8	59.5 ± 27.6
Surface area (SA; m2/g)	20.6 ± 15.5	35.0 ± 12.9	23.2 ± 10.9	26.3 ± 21.1	9.3 ± 6.9	15.4 ± 9.4
OC:SA (mg C/m2)	0.84 ± 0.26	0.9 ± 0.24	0.97 ± 0.15	0.41 ± 0.25	0.71 ± 0.54	0.48 ± 0.52
TN:SA (mg N/m2)	0.06 ± 0.03	0.07 ± 0.01	0.07 ± 0.01	0.04 ± 0.02	0.06 ± 0.04	0.04 ± 0.04
THAA (mg/g)	3.7 ± 3.4	4.9 ± 2.4	4.1 ± 2.4	1.2 ± 0.3	1.4 ± 1.5	2.2 ± 3.2
THAA-C (%)	5.3 ± 2.6	5.6 ± 1.9	6.2 ± 1.5	5.6 ± 0.2	7.8 ± 2.5	8.0 ± 2.6
THAA-N (%)	35.7 ± 7.3	32.5 ± 4.3	39.7 ± 9.8	26.4 ± 0.4	40.4 ± 10.5	37.8 ± 16.2

Abbreviations: SPM: suspended particulate matter; THAA: total hydrolysable amino acid; TOC: total organic carbon.

± 0.25 mg C/m^2 in the upper and lower reaches, respectively, for the postmonsoon season. The average TN:SA ratio varied from 0.07 ± 0.01 mg N/m^2 to 0.04 ± 0.02 mg N/m^2 during the postmonsoon season. The OC:SA and TN:SA ratios decreased from the upper to the lower reaches during the postmonsoon and premonsoon seasons (Table 1).

3.4 | Seasonal distribution of AA compositions

A total of 18 AA (L- and D-enantiomers) were detected from the sediments of the Netravati River. The THAA values varied from 1.2 ± 0.3 mg/g for the lower reaches during the postmonsoon season to 4.9 ± 2.4 mg/g for the lower reaches during the monsoon season. The contributions of THAA to OC (THAA-C%) and TN (THAA-N%) were between 2.3% to 10.3% and 26.1% to 56.4%, respectively. The proportion of nitrogen accounted for by AA (THAA-N%) was much higher than that of carbon and displayed lesser variation for the three seasons, with no significant differences (p >.05; Table 1). Protein AA were the most dominant forms accounting for 98 to 99 mol% of the THAA. Nonprotein AA accounted for 1 to 2 mol% of the THAA. The THAA were divided into different classes based on the presence and types of functional groups. Neutral AA (glycine, alanine, valine, isoleucine, and leucine) were the most abundant and accounted for about 55 to 62 mol% of the THAA for the three seasons. Acidic, hydroxylic, aromatic, and basic AA accounted for approximately 30 to 39, 17 to 21, 4 to 8, and 5 to 11 mol%, respectively, for the three seasons (Table 2). No significant spatial or temporal differences were observed for the AA groups (p >.05).

The molecular composition of THAA differed among the three seasons (Figure 2a) with relatively higher concentrations observed during the monsoon season than postmonsoon and premonsoon seasons (Table 1). The most abundant AA were glycine (16.4 ± 0.4 to 18.5 ± 2.7 mol%), aspartic acid (14.2 ± 1.0 to 16.5 ± 2.1 mol%), alanine (11.8 ± 0.2 to 13.2 ± 1.2 mol%), glutamic acid (11.1 ± 0.3 to 12.3 ± 0.8 mol%), serine (7.3 ± 0.4 to 8.7 ± 0.3 mol%), threonine (6.9 ± 0.4 to 8.0 ± 0.4 mol%), and valine (6.8 ± 0.7 to 7.7 ± 0.5 mol%). Higher proportions of aspartic acid, serine, threonine, tyrosine, and leucine were observed during the monsoon and postmonsoon seasons, but higher

TABLE 2 The average concentrations (± standard deviations) of sediment amino acids (individual and group) and diagenetic indices of Netravati River for the three seasons (monsoon, postmonsoon, and premonsoon)

Season	Monsoon		Post monsoon		Pre monsoon	
Region	Upper reaches	Lower reaches	Upper reaches	Lower reaches	Upper reaches	Lower reaches
Asx (mol %)	14.8 ± 0.3	15.2 ± 0.2	15.0 ± 0.4	16.5 ± 2.1	14.1 ± 0.2	14.2 ± 1.0
Glx (mol %)	11.3 ± 0.1	11.7 ± 0.3	11.1 ± 0.3	12.3 ± 0.8	11.1 ± 0.5	11.8 ± 0.2
Ser (mol %)	8.1 ± 0.7	8.5 ± 0.5	8.7 ± 0.3	7.3 ± 0.4	8.1 ± 1.2	7.3 ± 0.8
Thr (mol %)	7.8 ± 0.5	8.0 ± 0.4	7.5 ± 0.5	7.2 ± 0.1	6.9 ± 0.4	7.1 ± 0.5
Gly (mol %)	16.4 ± 0.4	16.8 ± 0.7	17.1 ± 0.2	17.4 ± 1.6	18.4 ± 2.7	16.2 ± 0.3
Arg (mol %)	4.9 ± 0.4	5.0 ± 0.2	5.0 ± 0.4	5.5 ± 0.4	5.5 ± 0.5	6.8 ± 2.1
Ala (mol %)	12.0 ± 0.2	12.2 ± 0.7	11.8 ± 0.2	12.2 ± 0.3	13.1 ± 1.2	11.7 ± 0.6
GABA (mol %)	0.8 ± 0.1	0.7 ± 0.1	0.6 ± 0.1	1.3 ± 0.7	1.0 ± 0.4	2.0 ± 1.9
Tyr (mol %)	2.1 ± 0.2	2.0 ± 0.4	1.9 ± 0.2	1.7 ± 0.9	1.7 ± 0.3	1.5 ± 0.8
Val (mol %)	7.0 ± 0.2	7.3 ± 0.5	7.2 ± 0.2	6.8 ± 0.7	7.7 ± 0.5	7.3 ± 0.8
Phen (mol %)	3.2 ± 0.3	3.4 ± 0.4	2.8 ± 0.1	2.5 ± 0.7	3.1 ± 0.3	2.7 ± 0.4
Ile (mol %)	4.2 ± 0.3	4.4 ± 0.5	4.4 ± 0.2	3.8 ± 0.8	4.4 ± 0.2	4.1 ± 0.6
Leu (mol %)	7.3 ± 0.2	7.2 ± 0.1	7.5 ± 0.2	5.9 ± 1.6	7.2 ± 0.2	7.2 ± 0.9
D-Asx (%)	6.8 ± 1.2	6.5 ± 0.8	7.1 ± 1.1	10.4 ± 3.2	7.2 ± 1.8	9.1 ± 2.2
D-Glx (%)	7.9 ± 0.8	7.5 ± 1.9	7.3 ± 0.7	10.9 ± 0.7	7.7 ± 1.2	10.6 ± 2.1
D-Ser (%)	6.6 ± 1.2	3.7 ± 1.2	4.6 ± 2.4	7.1 ± 1.5	5.3 ± 2.7	6.5 ± 4.3
D-Ala (%)	7.5 ± 1.5	7.0 ± 1.9	6.4 ± 0.5	10.2 ± 0.9	8.5 ± 2.3	9.2 ± 2.2
D-Arg (%)	30.4± 1.7	30.1 ± 4.4	27.6 ± 2.6	30.55 ± 8.0	28.2 ± 5.0	36.2 ± 15.6
DI	-0.02 ± 0.1	-0.3 ± 0.4	-0.1 ± 0.1	-0.4 ± 0.6	-0.4 ± 0.6	-0.2 ± 0.4
Tyr/Phen	0.7 ± 0.1	0.6 ± 0.1	0.7 ± 0.04	0.7 ± 0.2	0.6 ± 0.2	0.6 ± 0.3
DAA/(D+L)AA	5.6 ± 0.8	5.7 ± 1.0	5.3 ± 0.5	8.9 ± 4.0	6.2 ± 1.2	8.3 ± 3.8
Neutral (%)	56.7 ± 0.7	57.9 ± 3.3	58.0 ± 0.8	56.4 ± 0.9	60.3 ± 1.6	57.1 ± 2.7
Acidic (%)	31.7 ± 0.4	32.7 ± 0.6	31.5 ± 0.6	35.4 ± 4.5	31.3 ± 1.2	31.8 ± 1.5
Hydroxylic (%)	19.2 ± 0.2	20.0 ± 1.1	19.7 ± 0.6	17.8 ± 0.1	18.8 ± 1.9	17.6 ± 0.4
Aromatic (%)	6.3 ± 0.2	6.6 ± 1.0	5.8 ± 0.3	5.0 ± 1.8	6.0 ± 0.3	5.3 ± 1.3
Basic (%)	5.9 ± 0.5	6.0 ± 0.3	6.0 ± 0.5	6.8 ± 0.6	6.9 ± 0.8	8.4 ± 2.9

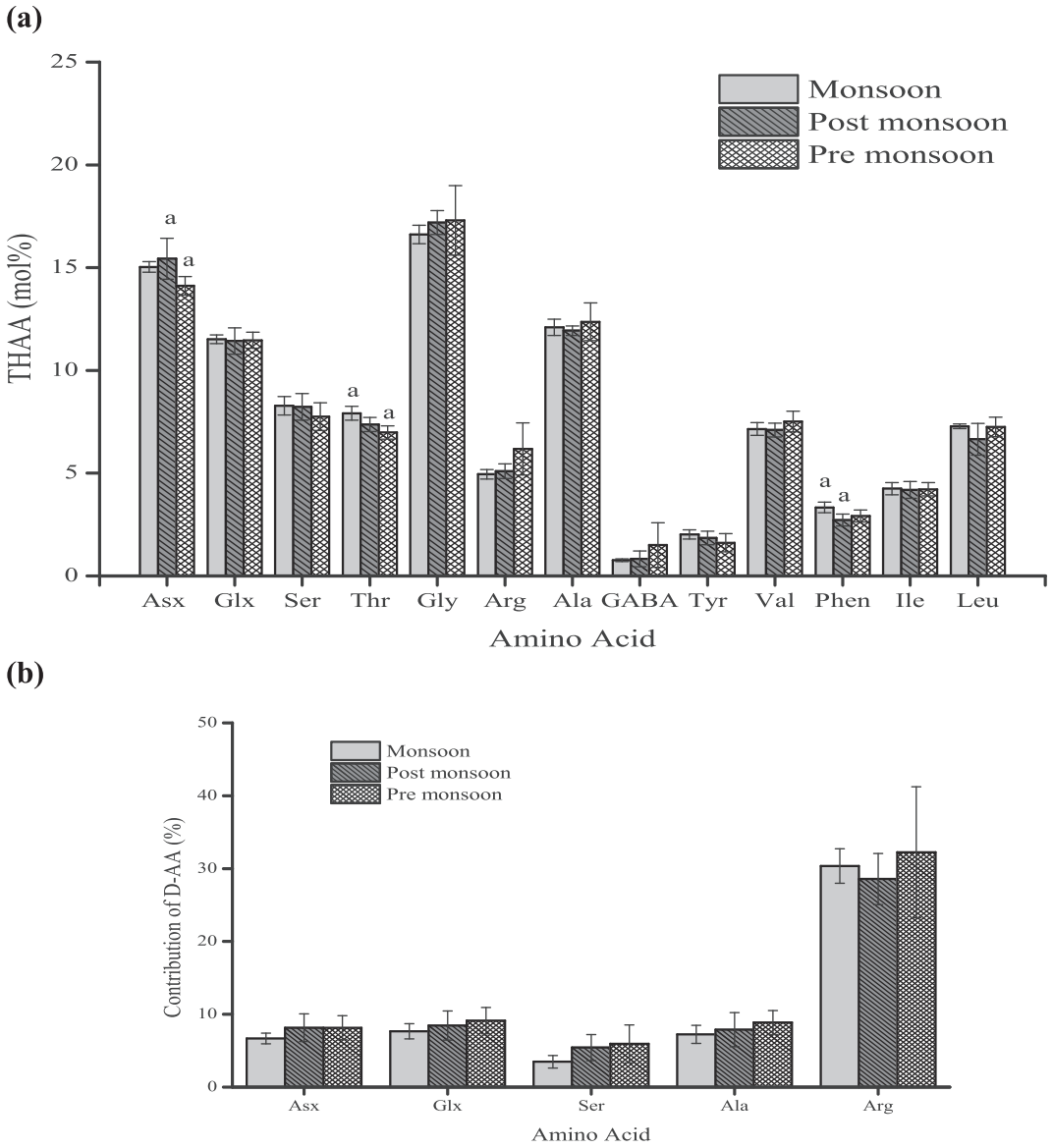

FIGURE 2 (a) The average individual amino acids (mol%) from sediments for the different seasons with confidence intervals (p <.05). Abbreviations: (Asx, aspartic acid + aspargine; Glx, glutamic acid + glutamine; Ser, serine; Thr, threonine; Gly, glycine; Arg, arginine; Ala, alanine; GABA, Gamma-aminobutyric acid; Tyr, tyrosine; Val, valine; Phe, phenylalanine; Ile, isoleucine; Leu, leucine). (b) Contribution of D-AA enantiomer in percentage of the individual amino acids in the sediment of the Netravati River for the three seasons with confidence intervals (p <.05). Abbreviations: (Asx, aspartic acid + aspargine; Glx, glutamic acid + glutamine; Ser, serine; Arg, arginine; Ala, alanine)

proportions of glutamic acid, glycine, arginine, gamma-aminobutyric acid (γ-aminobutyric acid; GABA), and valine were observed during the premonsoon season (Table 2 and Figure 2a). Aspartic acid and threonine varied significantly between the premonsoon and postmonsoon seasons, respectively (p <.05). Phenylalanine showed significant seasonal variation during the monsoon and postmonsoon seasons (p <.05). Only Glx showed significant differences spatially (p <.05).

Considerable amounts of D-enantiomers/D-AA namely aspartic acid, glutamic acid, serine, alanine, and arginine were found in all sediment samples and other D-AA were not present in reliable concentrations. The D-arginine values were the highest in proportion, accounting for more than 30% followed by D-aspartic acid (>7%), D-glutamic acid (>7%), D-alanine (>7%), and D-serine (>3%). Values obtained during the premonsoon season were higher than the monsoon and postmonsoon season (Figure 2b). Only D-Glx showed significant differences spatially (p <.05).

The DI values ranged between 0.22 and -1.06 with the lowest values obtained during the pre-monsoon season in the upper reaches at station DS-1. Positive DI values were observed at stations DS-2 (postmonsoon) and DS-5 (premonsoon). The tyrosine/phenylalanine (Tyr/Phen) ratio varied from 0.33 to 0.82 with the lowest and highest values observed during the premonsoon season. Higher Tyr/Phen ratios were observed during the postmonsoon season (Table 2). The DAA/(D+L)AA ratio varied from 4.7 to 12.5 with the highest values observed during the postmonsoon season (Table 2).

3.5 | Correlation among the measured parameters

The results on association among the measured parameters indicated contrasting relationships with some parameters depicting negative, and others showing positive correlations. The D/(D+L)AA ratio had a highly significant negative correlation with DI (r = -.930, p <.01) when stations DS-4 (monsoon) and DS-1 (premonsoon season) were not included. These stations had much lower DI values in relation to DAA/(D+L)AA ratio due to localized effects. Similarly, a negative correlation was detected between Tyr/Phen ratio and THAA (mg/g; r = -.577, p <.05) during the monsoon and postmonsoon seasons. The GABA was found to be negatively correlated with tyrosine, phenylalanine, aromatic AA, OC:SA, and TN:SA ratio (r = -.775, p <.01), (r = -.537, p <.05), (r = -.734, p <.01), (r = -.687, p <.01), and (r = -.636, p <.01), respectively.

A positive correlation was obtained between salinity and SPM (r =.622, p <.01). Also, OC displayed a positive correlation with TN (r =.992, p <.01) and THAA (r =.951, p <.01). Likewise, THAA normalized to sediment mass (THAA; mg/g) correlated positively with silt (r =.710, p <.01) and SA (r =.735, p < .01). A positive correlation was also obtained between Tyr/Phen ratio and THAA (mg/g; r =.843, p <.05) during the premonsoon season. Also, the THAA correlated positively with OC:SA and TN:SA ratios (r =.737 and r =.810, p <.01, respectively) and the D-alanine correlated positively with D-aspartic acid (r =.883, p <.01), D-glutamic acid (r =.901, p <.01), and D-serine (r =. 647, p <.05), respectively.

4 | DISCUSSION

4.1 | The effect of seasonal variations on water and sediment chemistry

The highest water temperatures were observed during the premonsoon season, which is attributed to the high intensity of solar radiation during this season coupled with high evaporation rates. During the monsoon season, lower water temperatures were observed due to the presence of cloud cover and reduction in solar radiation (Shruthi & Rajashekhar, 2014). Salinity data from this study were zero for two seasons with only higher values recorded during premonsoon, consistent with the previous results obtained by Rajesh et al. (2014). In this river, two extreme salinity conditions were observed, one during the monsoon season due to prevailing freshwater from rainfall and another during the premonsoon due to seawater intrusion, low rainfall, and increased solar radiation, causing high evaporation rates (Shruthi & Rajashekhar, 2014). The concentration of SPM observed in the Netravati River and estuarine system is similar to other Indian and European estuaries (Middelburg & Herman, 2007; Sarma et al., 2014). The SPM values ranging from 11.1 to 53.9 mg/L in the estuarine and coastal environments of Netravati and Gurpur River were also reported by Shankar and Manjunatha (1997), which could be attributed to resuspension of bottom sediments due to shallow depths, turbulent currents, and wind stress. The estuary is approximately 180 m wide, and the depth ranges from 2 to 4 m near the mouth to about 0.5 m near the head of the river. Higher values of SPM and sand content were observed in estuarine stations during premonsoon season as a result of tidal activity and reduced flow of freshwater, causing resuspension of finer particles and settled materials (Table 1).

Likewise the bulk parameters displayed variations in OC and TN contents, C:N ratios, $\delta^{13}C$, grain size, SA values, OC:SA, and TN:SA ratios indicating the influence of temporal variability in controlling the distribution of these parameters. The values observed are in similar ranges to other estuaries (Hedges & Keil, 1999; Salas et al., 2018). In contrast to the bulk parameters, the AA compositions did not show any differences for the three seasons (Table 2). The AA aspartic acid, threonine, and phenylalanine exhibited seasonal variations, suggesting changes in diagenesis. The L- and D-glutamic acid displayed spatial differences, indicating subtle effects of temporal and spatial variability controlling the dispersal patterns of AA. Similarly, the degradation indicators derived from AA composition also suggest the influence of temporal and spatial variability, thus indicating alterations of OM source and fate (Table 2).

4.2 | |Source of OM in small tropical rivers

We attribute the contributions of OM found in the river to three different sources based on the results of OC, C: N ratios, THAA-N%, THAA-C%, $\delta^{13}C$, and AAs. First, the OM originates from terrestrial plants and soils because our results indicated higher OC and C:N ratios during the monsoon season (Table 1) as well as higher proportion of THAA-N% than THAA-C% in the premonsoon. Terrestrial sources of OM are known to have higher C:N ratios of >20 typical of vascular land plants (Hedges & Oades, 1997). Another evidence for terrestrial plants as a source of OM in the present study comes from the $\delta^{13}C$ value, which is another important attribute used to differentiate OM sources. Terrestrial C_3 plants have more depleted $\delta^{13}C$ values closer to -25 to -28‰, and soil OM display values from -27.5 to -29.5‰ (Pasqual, Calafat, Lopez-Fernandez, & Pusceddu, 2015; Tesi et al., 2007). Terrestrial C_3 plants are dominant in the Netravati River basin and contribute to the possible source of OM, as reported by Pradhan, Wu, Shirodkar, Zhang, and Zhang (2014b). The values obtained are within the ranges for terrestrial and aquatic environments, which are between -25 and -30‰ in runoff originating from terrestrial source (Cifuentes et al., 1996; Wu, Zhang, Li, Wei, & Lu, 2003).

The second possible source of OM in the river is *in situ* production because the $\delta^{13}C$ values were more positive for the postmonsoon and premonsoon seasons than the monsoon season. The presence of a less depleted value (-25.6 ± 0.4‰) of $\delta^{13}C$ during the postmonsoon and premonsoon season suggests that *in situ* production is a more dominant source during this period. In addition to the $\delta^{13}C$ values, the C:N ratio indicates phytoplankton (C:N ratio = 6 to 10) as a source of OM suggesting subequal mixing of algal and terrestrial contributions to the lower reaches (Table 1; Meyers & Lallier-vergés, 1999; Meyers, 2002). The third possible source of OM in the studied river is contributions from bacteria and their remnants because all stations showed the presence of higher levels of D-AA during the monsoon and

postmonsoon in the upper reaches and in the lower reaches during the premonsoon season (Table 2). Bacteria and their remnants modify OM by transforming the AA, which is indicated by higher values of D-AA (Chen, Yang, Ji, Zhang, & Zhang, 2018; Fernandes, Garg, & Borole, 2014). Higher amount of D-arginine in the present study could be attributed to extracellular secretions by certain bacterial species (Alvarez, Aliashkevich, de Pedro, & Cava, 2017), suggesting their contribution to OM in the river.

Interestingly, the results revealed that the source of OM in the river were controlled by spatial and temporal variability in such a way that it was difficult to pinpoint a single source. For instance, the expected values for terrestrial OM (-27‰) were not obtained in the present study because of *in situ* production and contributions from other terrestrial source with little or no contributions from marine phytoplankton (~ -19 to -22‰). Furthermore, the expected $\delta^{13}C$ values from phytoplankton production (-18 to -22‰; Cifuentes et al., 1996; Wu et al., 2003) were also not obtained instead; less depleted values of -25.6 ± 0.4‰ were observed in the lower reaches of the river during the pre-monsoon season, suggesting a mixed source arising from *in situ* production, soil OM, and terrestrial source (Table 1). We also found that the spatial and temporal variability, particularly during the monsoon, had a profound influence on the source of OM. However, in the upper and lower reaches during the monsoon season, not much spatial variation in $\delta^{13}C$ was observed due to the combined effects of flushing, dilution, and contribution from terrestrial source (Figure 3). Thus, during the monsoon season, the river behaves like a pipe, which flushes the OM to the lower reaches where it mixes with other sources of OM derived from bacteria (C:N ratio 5 to 8) and *in situ* production due to higher amount of water discharge and sediment load because of seasonal rainfall (Figure 1b). Therefore, the OM within the sediments are subsequently transported and deposited into the adjacent sea. During the postmonsoon and premonsoon OM is trapped within the river and estuary due to reduced flow and water discharge.

In general, the results indicate variations in source of OM in the river depending on spatial and temporal variability. However, terrestrial source appear to contribute more to OM than other sources, an observation which calls for more research. The high yields of sediments due to LULC changes (Sinha & Eldho, 2018) and water discharge during the monsoon season observed in this river tend to dilute the OM source, highlighting the importance of site and season specific detailed investigations in small tropical rivers.

4.3 | Factors controlling diagenesis of OM in small tropical rivers

We identified physical and biochemical factors, which control the diagenesis of OM in the small tropical river, Netravati River, influenced by spatial and temporal variations. The first physical factor influencing diagenetic process of OM is grain size, which was indicated clearly by the OC:SA and TN:SA ratios. The OC:SA and TN:SA ratios decreased from the upper to the lower reaches during the postmonsoon and premonsoon seasons. The OC:SA and TN:SA ratios are used to express sedimentary OC and TN loadings, respectively, onto mineral

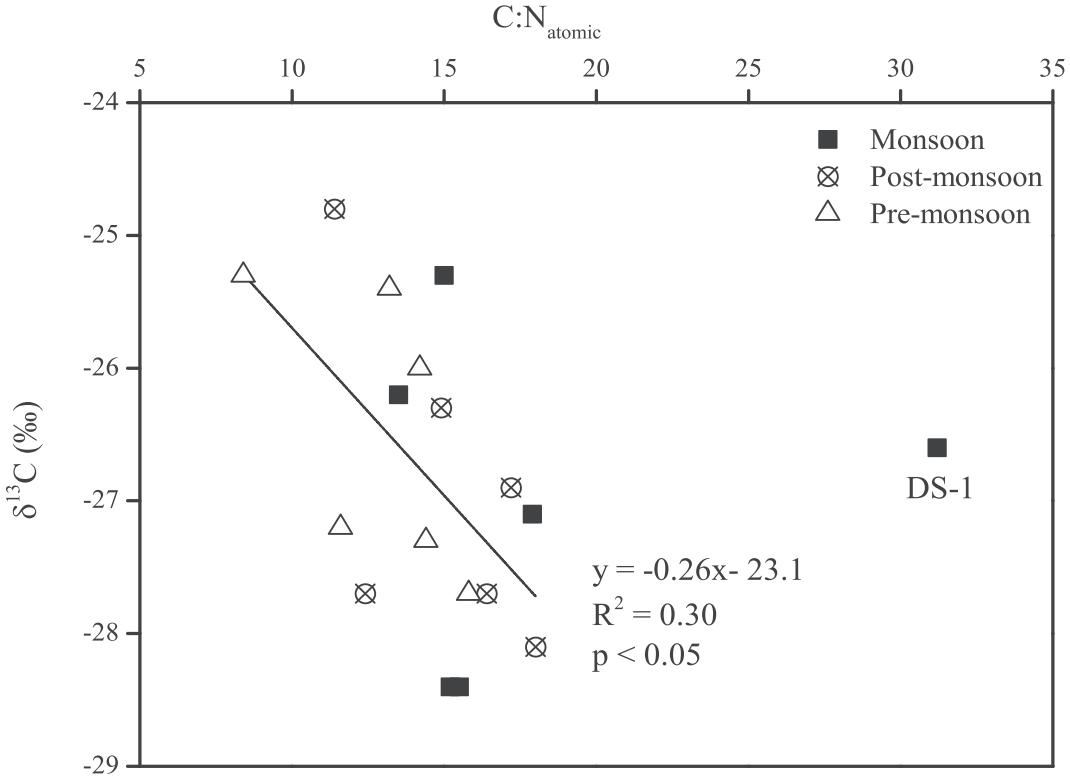

FIGURE 3 The relationship between $\delta^{13}C$ (‰) and C:N $_{atomic}$ ratio of sediments for the three seasons

grains. Therefore, the OM was protected from diagenesis. The OC:SA ratio to tyrosine showed an increasing trend (Figure 4), suggesting a positive influence of OC:SA on tyrosine degradation. These results imply that OC:SA ratio plays a decisive role in controlling the diagenesis of OM. The second physical factors affecting the diagenesis of OM are the natural processes such as flushing, dilution, erosion, leaching, and contribution from terrestrial source of OM. During high water discharge periods, the monsoon season causes relatively higher values of acidic AA compared with low discharge periods due to dilution, erosion effects, and leaching processes, which mobilize the older OM from newly formed soils (Jennerjahn et al., 2004). The third physical factor that controlled the diagenesis of OM was adsorption onto clay minerals between basic AA and clay on one hand and neutral AA and clay contents on the other hand (Figures 5a and 5b). It has been indicated that based on functional group compositions, aromatic and acidic AA are more labile, compared with neutral and basic AA such as arginine, which tend to be adsorbed onto clay minerals (Jennerjahn et al., 2008; Jennerjahn & Ittekkot, 1999). Therefore, along the river, basic AA and neutral AA are selectively preserved because of their association with clay fraction of the sediments, thus preventing them from diagenesis.

Another physical factor that controlled the diagenesis of OM in the river was geomorphological features such as oxbows and river meandering at stations DS4 and DS5 (Figures 5a and 5b). The oxbow formation and river meandering reduce the flow rates and increase the residence time of the water mass. In this way, the oxbow and meandering loops of the river behave as sinks during the postmonsoon and premonsoon seasons by trapping and accumulating older materials. Moreover, during the postmonsoon and premonsoon seasons, OM was more degraded (had lower DI) at DS4 and DS5 stations (Figure 6) compared with the other stations sampled during the same seasons, highlighting the role of oxbow and meandering loops in controlling OM digenesis. Further evidences of oxbow and meandering loops in controlling OM digenesis are provided by the higher GABA content and lower OC:SA ratios at the oxbow stations (Figure 7) coupled with moderate levels of SPM during the monsoon season. All these results indicate the role of oxbow and river meandering in trapping OM during the postmonsoon and premonsoon seasons.

We further identified bacterial decomposition as a biochemical factor responsible for diagenesis of OM in the river as evidenced by relatively more enriched basic AA during the premonsoon season, suggesting active bacteria decomposition process (Parsons & Tinsley, 1975). Furthermore, a higher DAA/(D+L)AA ratio indicated decrease in the content of labile OM resulting into relatively more degraded OM due to bacterial actions. The DAA/(D+L)AA ratio is used as an indicator of bacteria-modified OM. Thus, bacteria act as agents of decomposition by breaking down OM in small tropical rivers.

Generally, our results indicate that the diagenesis of OM is mainly controlled by physical factors coupled with biochemical factors, which are both governed by spatial and temporal variations.

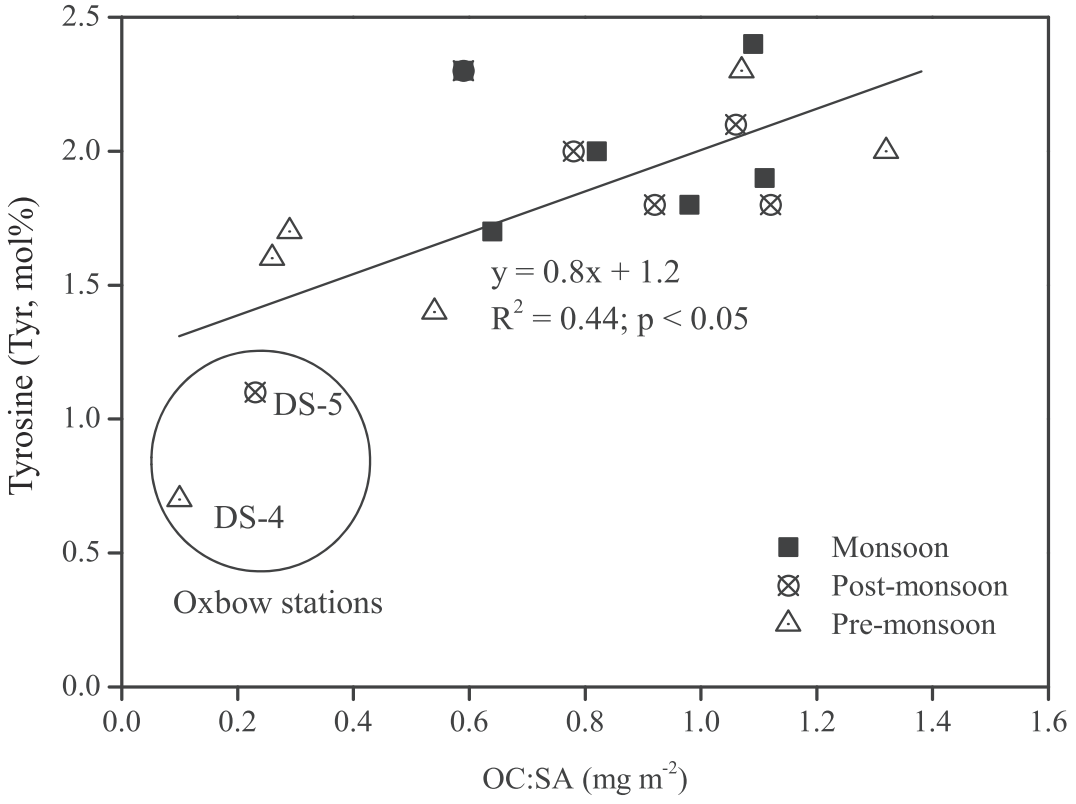

FIGURE 4 The relationship between tyrosine (Tyr, mol%) and organic carbon:surface area (OC:SA; mg/m^2) of sediments for the three seasons

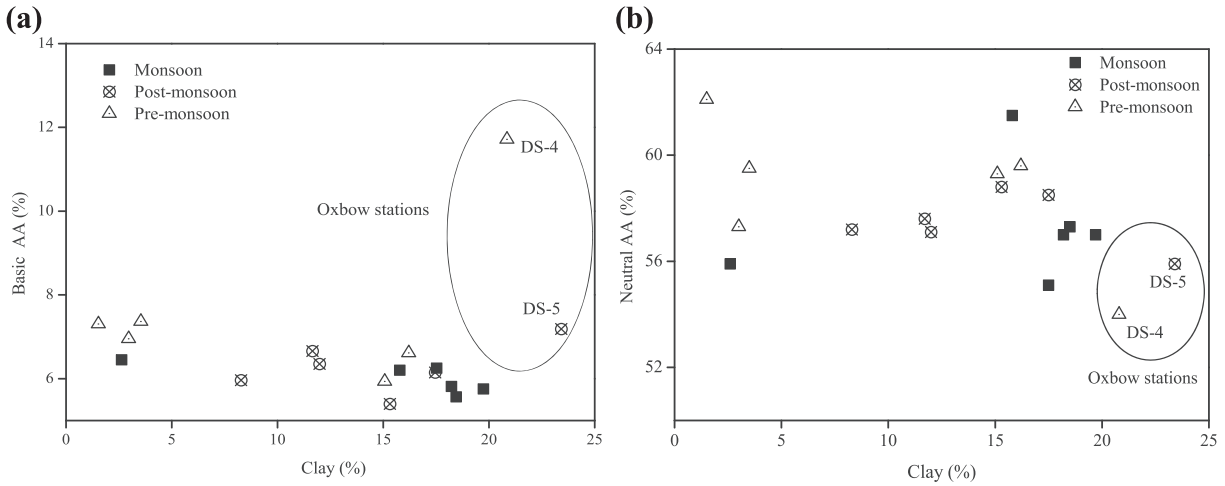

FIGURE 5 (a) The relationship between basic amino acids (%) and Clay fraction (%) of sediments for the three seasons. (b) The relationship between neutral amino acids (%) and clay fraction (%) of sediments for the three seasons

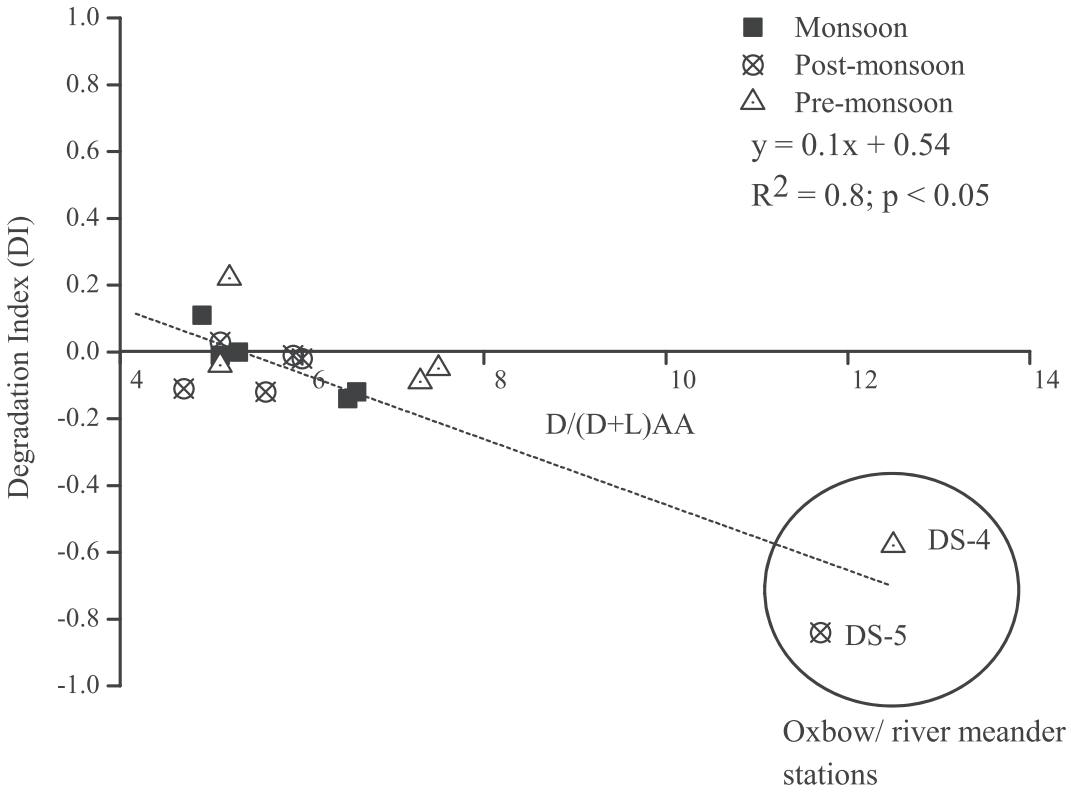

FIGURE 6 The relationship between degradation index and the ratio of D/(D+L)AA of sediments for the three seasons

However, we noted that complex processes were involved in the diagenesis of OM such as flushing times and hydrodynamics in the estuary and lower reaches, which produced OM with different diagenetic states, similar to previous results (Zhang, Wu, Jennerjahn, Ittekkot, & He, 2007). This is caused by hydrodynamic effects of freshwater discharge during SWM, water current, and tides during the postmonsoon and premonsoon seasons (Reddy, Hariharan, & Kurian, 1979). Consequently, suspended sediments in estuarine and nearshore environments undergo repeated cycles of erosion, transport, and deposition by ebb and flood tidal cycles before settling in the sediments (Nichols, 1986; Shankar & Manjunatha, 1997), resulting into OM with different diagenetic states.

4.4 | The fate of OM in the Netravati River

The OM studied in the river experienced different fate depending on spatial and temporal variability. Transport and trapping of OM, degradation, and utilization by bacteria as well as selective preservation

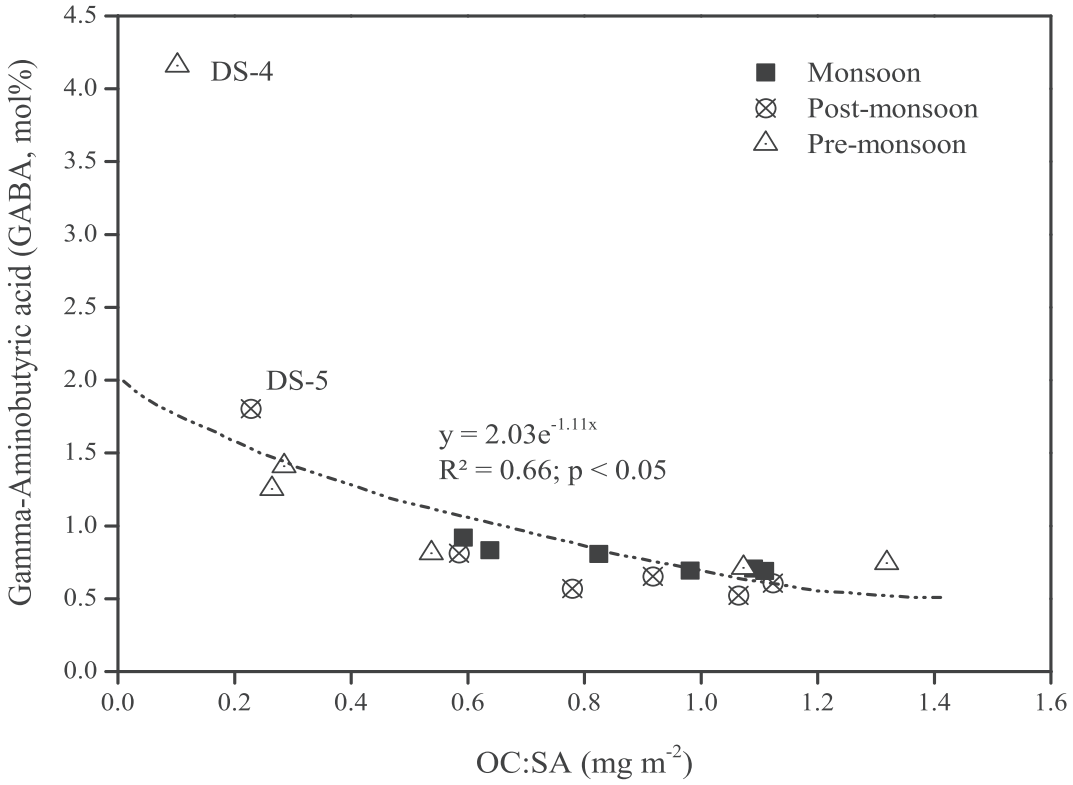

FIGURE 7 The correlation between gamma-aminobutyric acid (GABA, mol%) and organic carbon:surface area (OC:SA; mg/m^2) of sediments for the three seasons

were some of the possible fate of OM in Netravati River. The transport of OM as a fate led to temporal differences in THAA concentrations during the monsoon season due to increased water flow, which flushed out the older materials from the river. The THAA content of Netravati River was in the range of Wonoknomo River (0.8–3.9 mg/g), Brantas River (2.6–7.2 mg/g), and Porong Rivers (3.0-40 mg/g; Jennerjahn et al., 2004). Furthermore, the oxbow and river meandering stations (DS4 and DS5) had more negative DI values compared with neighbouring stations during the postmonsoon and premonsoon seasons (Figure 6), suggesting trapping of OM at the oxbow stations during reduced water flow conditions.

The highly significant negative correlation between D/(D+L)AA ratio and DI (Figure 6), the negative correlation between Tyr/Phen ratio and THAA (mg/g; Figure 8), and aromatic AA (%; Tables 1 and 2) provide evidences for bacteria degradation of OM. The Tyr/Phen ratio is an indirect indicator of degradation process (Gupta, Subramanian, & Ittekkot, 1997), which was more dominant during the monsoon and post-monsoon seasons. Contrary, low conditions of OM degradation process were evident during the pre-monsoon season due to the positive correlation between Tyr/Phen ratio and THAA (mg/g). A decrease in hydroxylic AA (serine and threonine) values was observed during the premonsoon season (Table 2), suggesting possible utilization of OM by heterotrophic organisms or diatoms, which are usually abundant during the postmonsoon and premonsoon seasons (Shruthi & Rajashekhar, 2014).

The higher glycine content found in the sediments of Netravati River (Figure 3a) indicates selective preservation. Glycine is a short chain amino acid, a cell wall constituent of diatoms, and has low nutritional value to heterotrophic organisms and is often associated with biogenic silica in diatoms cell walls and frustules (Dauwe & Middelburg, 1998; Ingalls, Lee, Wakeham, & Hedges, 2003); thus, it is preserved. Further evidence for selective utilization is provided by higher D-AA such as D-arginine, aspartic acid, and alanine. The D-AA are less accessible to bio-alteration than other AA present in bulk OM because they are embedded in the cell walls (Nagata, Fukuda, Koike, Kogure, & Kirchman, 1998; Tanoue, Nishiyama, Kamo, & Tsugita, 1995; Wu et al., 2007). In the present study, the most abundant D-AA was D-arginine, which accounted for more than 30% slightly higher than the results obtained by Wu et al. (2007), who reported D-arginine as the most abundant D-AA in the particulate OM of Yangtze River. Higher amount of D-arginine in the present study could be attributed to partial adsorption to mineral surfaces thereby protecting it from degradation (Hedges & Keil, 1999; Wu et al., 2007) and extracellular secretion by bacterial species (Alvarez et al., 2017) and thus accumulated over time. The higher amounts of aspartic acid and alanine in the sediments are attributed to the selective protection by mineral surface interactions (Hedges & Keil, 1999). Lastly, the higher concentration of GABA also provides evidence of selective preservation of OM. GABA is a biodegradation product of glutamic acid; it is more recalcitrant in nature and accumulates during bacterial degradation.

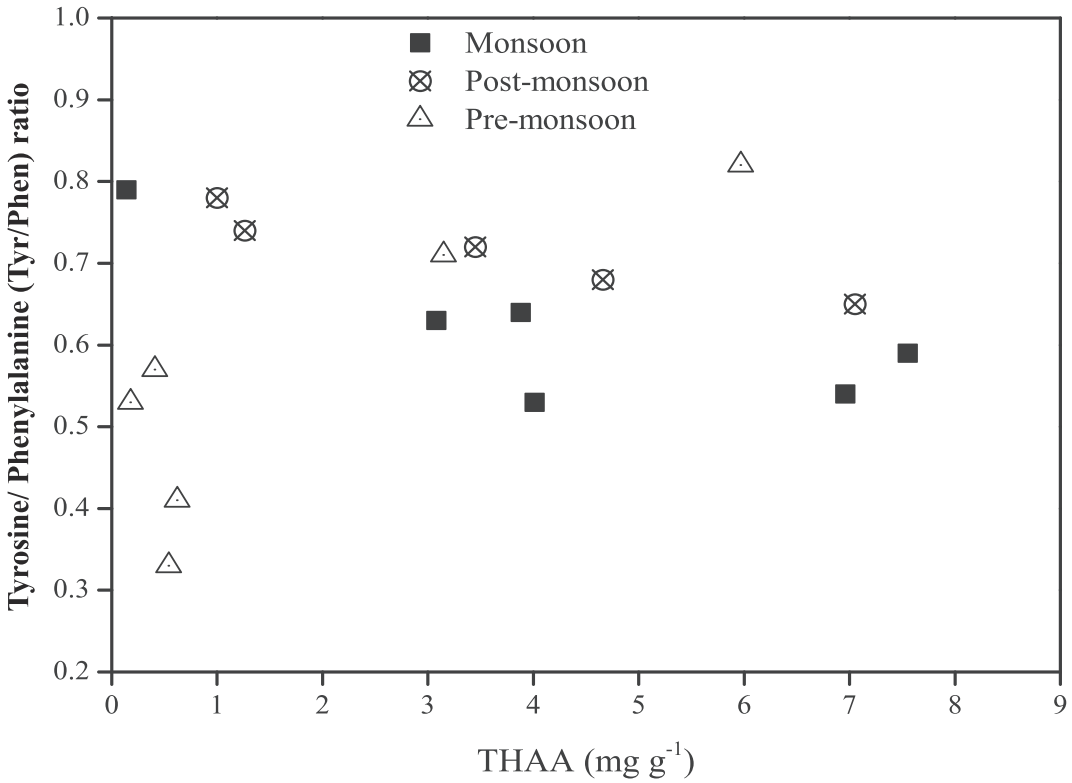

FIGURE 8 The relationship between tyrosine/phenylalanine (Tyr/Phen) ratio and THAA (mg/g) of sediments for the three seasons

In general, it is plausible to suggest that the OM in the sediments of small tropical rivers such as the Netravati River is subjected to transport and trapping, degradation and utilization by bacteria, and selective preservation, which depend on spatial and temporal variations.

5 | CONCLUSION

The OM transport from the upper reaches to the estuarine region and to the open seas or continental shelf is an important contributor to nutrient dynamics. This study revealed that seasonal changes, which are controlled by the monsoonal activity, have an operational role in discriminating source, transport, and diagenesis of OM. However, the effect of seasonal variations is less than the spatial influence. Shifts in monsoon intensity modify the bioavailability of ON, which in turn influences the nitrogen cycle in the coastal ecosystems. During the monsoon season, the river acts as a flushing pipe by dispersing the sediments and OM accumulated during the dry season. During the dry season, OM is trapped and held back within the river channel due to reduced water flow. Spatially, oxbows and meandering loops present in small tropical mountainous rivers behave as sinks by trapping and accumulating older materials during the dry season thereby providing ideal conditions for diagenetic processes. The OM of small tropical mountainous rivers thus experiences different fate such as transport and trapping, degradation and utilization by bacteria, and selective preservation depending spatial and temporal variations. In general, small tropical rivers experience enhanced or depressed monsoonal activity, which affect the spatial and temporal OM mineralization processes. Thus, in order to avoid aberrant interpretations of OM in small tropical mountainous rivers, a comprehensive evaluation of the source, transport, and diagenesis is essential.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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