

Sources and distribution of organic matter in thirty five tropical estuaries along the west coast of India- a preliminary assessment

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Abstract

Studies characterizing the sources of organic matter (OM) to the west coast of India (WCI) and its continental shelf are limited. This study examined sedimentary OM in 35 estuaries along the WCI using molecular biomarkers (lignin phenol), elemental ratio (C/N), and stable carbon isotope ($\delta^{13}\text{C}$) values. Multivariate statistical techniques, such as cluster analysis, identified similar sedimentary chemical properties among the estuaries and their distribution patterns highlight the strong control of geographical province on sedimentary OM composition from south to north along the WCI. Results of an end-member mixing model reveal that terrigenous sources (C_3 plants, C_4 plants, and soil) contribute ~80% of estuarine OM, with the remaining 20% derived from marine sources (marine plankton and estuarine macrophytes). In the estuaries of large rivers, such as the Narmada and Sabarmati rivers, C_4 plant and soil OM were found to be the dominant contributors of OM, which is likely the result of an abundance of C_4 vegetation and agriculture in their catchment areas.

High OC (organic carbon content) of sediments (0.5–5%) from the WCI estuaries indicates that large amounts of OM are present in the sediments. The sources of OM (plant and soil) shift substantially throughout the study area, corresponding to changes in land use patterns along the Western Ghats. Sediments with low nitrogen contents (C/N >15–20) and degraded lignin ($(\text{Ad}/\text{Al})_V=0.4\text{--}0.6$ and $\text{DHBA}/V=0.16\text{--}0.34$) were observed in all estuaries, indicating humification and/or degradation of OM originating from terrestrial plants (bio-degradation) and soil (de-mineralization). The collective results of this study illustrate the benefits of using biomarkers (lignin phenols) along with C/N and $\delta^{13}\text{C}$ values for evaluating land use changes and the impacts of land use changes on aquatic ecosystems.

Keywords: Organic matter; Sediments; Carbon isotopes; Biomarkers; India, west coast

1. Introduction

The decomposition and eventual burial of organic matter (OM) in estuarine and coastal regions plays an important constraint on atmospheric CO₂ levels (Liu et al., 2010; Mackenzie, 1981). The autochthonous and allochthonous organic carbon (OC) are subjected to various physical, chemical, and biological processes in estuaries before their eventual burial to sediments and become part of the sedimentary record. A substantial fraction of the sedimentary OM in estuaries is derived from terrestrial sources that include vascular plants and soil, and contains signals of both natural and anthropogenic processes that have acted to modify its composition. Plant and soil OM undergo primary degradation processes driven by bacterial and/or fungal action, which alters their molecular composition before their input into riverine and estuarine systems (Otto and Simpson, 2006; Feng et al., 2008; Kuzyakov, 2010; Thevenot et al., 2010). Furthermore, the OM degradation also occurs along the river continuum due to microbial composition, which fuels gross respiration and CO₂ out gassing (Mayorga et al., 2005). Studies indicated that about 40% of the vascular plant-derived OC in Amazon basin is sequestered by the terrestrial biosphere undergoes degradation within soils, 55% is degraded along the river continuum, and only less than 5% is delivered to the ocean (e.g. Ward et al., 2013). Changes in land use, including deforestation and managed agro-ecosystem development, can increase the supply of soil-derived OM such that it becomes a major component of terrestrial OM stored in aquatic sediments (Farella et al., 2001). Constraining the sources of OM in estuarine sediments, and understanding the factors and processes that control OM distributions, are important for our further understanding of OM biogeochemical cycling and the fate of terrigenous OM in marine systems (Hu et al., 2006).

The concentration and isotopic composition of organic carbon (OC and $\delta^{13}\text{C}$ respectively) and C/N ratio are widely used tracers to quantify the sources and pathways of OM in estuarine sediments (Canuel et al., 1995; Graham et al., 2001; Hu et al., 2006; Thornton and McManus, 1994 and references therein). The relative abundances molecular components of lignin, a biopolymer uniquely synthesized by terrestrial vascular plants, in sediments indicate the presence of various plant-derived OM contributions (Hedges and Mann, 1979). The advantage of using lignin phenols, unlike proxies such as C/N or $\delta^{13}\text{C}$, is that it can be used to unambiguously determine the terrestrial sources of OM in estuarine and coastal environments (Bianchi et al., 2002, 2011; Goñi et al., 1998). The compositional ratios of lignin phenols and their monomers (e.g., cinnamyl (C), vanillyl (V) and syringyl (S) acid to aldehyde ratio (Ad/Al)) are used to quantify the nature of plant tissues and extent of degradation (e.g. Hedges et al., 1984; Dittmar and Lara, 2001; Otto and Simpson, 2006). Therefore, lignin phenols are useful for identifying terrestrial sources of OM, but hardly "unambiguously." C/V, S/V, Ad/Al ratios are useful for identifying general trends, but there is still a great amount of ambiguity on what the actual OM

sources. These signals are further complicated by selective degradation of specific phenols (e.g. [Dittmar and Lara, 2001](#)).

In this paper, we present our results on the characterization of OM sources to the estuaries of 35 small and large rivers along the west coast of India (WCI), between 12°N and 24°N, comprising of ~100 rivers flowing across the WCI originating from the Western Ghats draining to the Arabian Sea. The anthropogenic impacts in the watersheds of these rivers have significantly altered the OC flow to the estuaries ([Menon and Bawa, 1998](#); [Panigrahy et al., 2010](#); [Roy and Srivastava, 2012](#)). This study aims to (i) investigate the distribution of sedimentary OM in estuaries along the WCI, (ii) elucidate the sources of OM to estuarine sediments, and (iii) to understand the impact of land use changes on the composition and distribution of estuarine OM. Results from the present investigation will serve not only as a baseline data set for future researchers to quantify the anthropogenic impact on carbon flow to the Arabian Sea, but also as a model study for tropical regions in the world.

2. Materials and Methods

2.1 Study area

The WCI stretches from Cape Comorin (8°N) in the south to Kuchchh (22°N) in the north. The Narmada (watershed area: $\sim 10^5$ km²) and Tapti ($\sim 10^4$ km²) are the two major rivers in this region along with numerous small rivers (watershed area: $\leq 10^3$ km²), flowing into the eastern Arabian Sea. The range of length to elevation ratio (L/H) of WCI rivers varies from 0.07–1.24 (average = 0.36 ± 0.15). The catchment of small rivers in the central and south WCI are steeper (i.e. lower L/H) compared to the large rivers in the north. The sediment load of the 35 rivers included in this study is $\sim 7 \times 10^{12}$ g yr⁻¹, 73% of the total supplied by westward flowing rivers on the Indian subcontinent (which has a load of 9×10^{12} g yr⁻¹, excluding the Indus; [CWC, 2012](#)). Information on land use patterns within individual river catchments is sparse for this region. Broadly, river basins between 12°N and 16°N have dense forest cover upstream and mangroves in the estuarine region, whereas agriculture and degraded forests dominate estuaries above 16°N ([FSI, 2011](#); [Figure 1](#)). Annual rainfall varies from 600 to >5000mm ([www.nih.ernet.in](#); [CWC, 2012](#)) and generally decreases from south to north. Soils along the WCI is mainly derived from Deccan Trap basalts between Tapti ($\sim 21^\circ\text{N}$) and Mormugao (15.5°N) and Precambrian gneisses and schist from lower Mormugao to Cape Comorin ([Nair et al., 1982](#)). The rate of soil erosion in the Deccan Traps is slightly greater ($20 \text{ mg ha}^{-1}\text{yr}^{-1}$) than that in the Precambrian/lateritic region ($10\text{--}15 \text{ mg ha}^{-1}\text{yr}^{-1}$; [Singh et al., 1992](#)).

2.2 Land use pattern distribution

Quantifying the land use practices over each estuarine system is a major challenge, as little information exists on individual river systems. In this study we made a preliminary assessment by classifying our study area into 14 segments according to the geographical terrains present within four coastal provinces (see Figure 1). The percentage of dense forest, C₃, and C₄ agricultural areas were computed for each segment based on the data obtained from India state of forest report (FSI, 2011). Small river catchments generally represent 90%–100% of a segment area, whereas for large rivers only land use in the estuarine region was considered. Because the upstream section of large rivers are heavily dammed, while downstream is dominated by intense agriculture practice (FSI, 2011).

2.3 Sample collection

A variety of plant samples at the bank of estuarine regions (mangroves) and the Western Ghats (higher plants including agricultural plants) along with non-agriculture species such as aquatic submerged grasses were collected. Plant parts including leaves, woods, and flowers were segregated for individual lignin-biomarker analysis. Surface soil samples were collected (avoiding fresh plant roots and disturbed soil) from 3 different land use regimes: non-agricultural (forest/mountain), agricultural (from a freshly ploughed agriculture field), and mining (dredged mine tailings). Sediments were collected from middle of the estuary by boat using a Van-Veen grab (15×15cm) during neap tide (average tidal height: 1–1.5m). Sampling was undertaken in 2008 and 2009 during the early post monsoon season (October), as >90% fluvial material enters the estuary. Also there was no flood event evidenced during this two year in any of the watersheds (CWC, 2012). Two to five sediment samples were collected from each estuary depending on the length of the estuarine zone that varies from 10 to 45 km in different rivers. All the samples (plant, soil and sediment) were oven-dried at 45°C to complete dryness and homogenized before isotope and lignin phenol analysis.

2.4 Analytical Methods

About 10 mg of sediment and soil samples were treated with 1 M HCl to remove inorganic carbon prior to $\delta^{13}\text{C}$ and OC (OC refers to total sedimentary organic carbon throughout this paper). The weight percent of total nitrogen (TN) was analyzed without acid treatment. The concentration of OC and TN (relative precision, $\pm 5\%$) were measured in elemental analyzer (CHNOS; Vario EL III). Stable carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) were measured using an elemental analyzer interfaced with an isotope ratio mass spectrometer (EA-IRMS Delta plus/XP, Finnigan MAT co.). The analytical precision for $\delta^{13}\text{C}$ was $\pm 0.1\%$. Results are expressed as per mil (‰) deviation relative to the Vienna–Pee Dee Belemnite (V-PDB) standard and as defined below.

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

Lignin phenols were extracted using cupric oxide (CuO) oxidation technique (Hedges and Ertel, 1982). Briefly, ~50–500 mg (depending on the OC content so as to have ~5 mg OC) of powdered samples were weighed, placed in O₂ free Teflon-lined vessels, and digested in a microwave (CEM MARS5) at 150°C for 90 minutes (Goñi and Montgomery, 2000). A known amount of Ethylvanillin standard was then added and later used to check recovery. The recovery rate of Ethylvanillin was found to be 90±2% during this study. Samples were acidified to pH < 2 and phenolic monomers were extracted into 99:1 (volume ratio) ethyl acetate/petroleum ether, dried, and stored at -20°C until further analysis. Samples were analyzed as trimethylsilyl derivatives of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS)(99:1) by Agilent 6890N gas chromatography (DB-1 column, FID). The lignin phenol concentration was quantified with calibration curves based on commercial standards (Sigma–Aldrich). The concentration of lignin phenols V (vanillin, acetovanillone and vanillic acid), S (syringaldehyde, acetosyringone, syringic acid), and C (*p*-coumeric acid, and ferulic acid), along with other phenols such as *p*-hydroxybenzenes (*p*-hydroxyacetophenone, *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde) and benzoic acid (3,5-dihydroxy benzoic acid), were quantified. The mean analytical precision of lignin parameters used in this study was ≤10%.

2.5 Statistical Analysis

The statistical significance (95% confidence interval) of differences in lignin phenol, δ¹³C, C/N, TN and OC observed between samples was tested using standard t-test and one-way analysis of variance (ANOVA). Komogorov-Smirnov test was carried to check the normality in the data. The results were significant (*p*≤0.05) indicating non-normal nature of data. Therefore the data were normalized through z-scale transformation in order to avoid wide differences in data dimensionality (Ross, 1988). Principal component analysis (PCA) was performed on the elemental, isotopic and lignin phenol data. CuO oxidation products were normalized to OC (mg/100 mg OC), and all variables were mean centered before PCA. Cluster analysis was performed to explore the relationship between different estuaries. Pearson's correlation coefficient was used to test the correlation between land use and geochemical parameters, and two-tailed *p* values were calculated. All analyses were performed using SPSS.10 for Windows (Inc., USA).

3. Results

3.1 Elemental and isotopic properties

Based on the cluster analysis of their sedimentary properties (OC, TN, δ¹³C, and lignin phenols), the estuaries were classified into three different groups (north (16.02–23.11°N), central (13.45–15.80°N)

and south (12.83–14.86°N)) and the data are presented in [Table 1](#). The clustering pattern of these chemical parameters is closely linked to the geographical location of the estuaries with the exception of sediments in the Chapora, Damanganga, Shastri, Kali, Karle, and Kharda estuaries ([Figure 2](#)). The range of OC was much larger in the southern group estuaries (0.3–6.4%, mean: $2.3 \pm 0.6\%$) compared to central (0.5–4.9%, mean: $2.0 \pm 0.9\%$) and northern group (0.1–2.2%, mean: $0.6 \pm 0.3\%$). The range of TN was identical for the southern group estuaries (0–0.29%, mean: $0.12 \pm 0.03\%$) and central (0.03–0.29%, mean: $0.15 \pm 0.04\%$) compared to northern group estuaries (0.01–0.1%, mean: $0.04 \pm 0.0\%$). The range of C/N values was much larger in the northern group estuaries (0.01–56.8, mean: 18.7 ± 6.9) compared to central (0.1–26.5, mean: 15.3 ± 3.4) and southern group (9.3–31.1, mean: 19.8 ± 4.1). The range of $\delta^{13}\text{C}$ was lower in the southern group estuaries (-29.2 to -23.2‰, mean: $-26.3 \pm 0.8\%$) compared to central (-28.2 to -23.1‰, mean: $-25.9 \pm 0.9\%$) and northern group (-27.0 to -16.6‰, mean: $-22.9 \pm 0.9\%$).

The $\delta^{13}\text{C}$ values of botanical samples provide evidence that both C_3 and C_4 plants exist in the study area. Soil samples exhibit a wide range of $\delta^{13}\text{C}$ (-19‰ to 27‰), which varied with the proportion of C_3 to C_4 plants in overlying vegetation. Agricultural soils showed higher $\delta^{13}\text{C}$ values than non-agriculture soils ([Table 1](#)), and the average C/N ratio varied significantly among plant, soil and macrophyte samples ($p \leq 0.05$; ANOVA). The estuaries of large rivers such as the Sabarmati, Narmada, and Tapti, located within the northern group, contain less OC (mean: $0.45 \pm 0.2\%$) and TN (mean: $0.03 \pm 0.01\%$) than the small estuaries of the central and southern groups. The sediment in estuaries located south of 16°N is rich in OC (~1% to >2%) compared to that deposited farther north ([Figure 3](#)). Estuaries below 16°N exhibit lower sedimentary $\delta^{13}\text{C}$ than those above this latitude ([Figure 3](#)). High $\delta^{13}\text{C}$ values recorded in the sediments of the Sabarmati (-17.2‰) and Narmada (-16.6‰) estuaries are distinctly different from those observed in the other estuaries. The distribution of sedimentary C/N displays a non-uniform pattern among all estuaries ([Figure 3](#)).

3.2 Lignin phenol yield and compositional ratios

The range of mass normalized yield (Σ_8 in mg/g dry wt.) of eight lignin phenols (S+V+C) was much larger in the southern group estuaries (0.2–4.9, mean: 1.7 ± 0.5) compared to central (0.2–1.3, mean: 0.7 ± 0.3) and northern group (0.01–0.3, mean: 0.11 ± 0.1). The OC normalized yield (Λ_8 in mg/100mg OC) of eight lignin phenols (S+V+C) was larger in the southern group estuaries (2.0–12.6, mean: 6.7 ± 2.8) compared to central (0.6–15, mean: 4.2 ± 1.7) and northern group (0.01–6.5, mean: 1.6 ± 1.0). The range of C/V ratio varied from 0.2–0.3 (mean: 0.3 ± 0.1) in southern group estuaries than in central (0.01–0.4, mean: 0.2 ± 0.1) and northern group (0.01–0.9, mean: 0.2 ± 0.1). The range of S/V ratio in southern group estuaries (0.1–3.5, mean: 1.5 ± 0.5) was higher compared to central (0.4–2.2,

mean: 1.0 ± 0.3) and northern group ($0.1\text{--}1.9$, mean: 0.9 ± 0.2). The range of vanillic acid to vanillin ratio $[(Ad/Al)_V]$ was higher in northern group estuaries ($0.3\text{--}1.6$, mean: 0.7 ± 0.2) than central ($0.2\text{--}0.8$, mean: 0.4 ± 0.1) and southern ($0.3\text{--}0.7$, mean: 0.5 ± 0.1). The range of total P (*p*-hydroxybenzenes) to sum of V and S ratio ($P/(V+S)$) was higher in northern group estuaries ($0.1\text{--}2.8$, mean: 0.4 ± 0.2) than central ($0.1\text{--}0.4$, mean: 0.2 ± 0.1) and southern ($0.1\text{--}0.6$, mean: 0.2 ± 0.2). The range of Pn (*p*-hydroxyacetophenone) to total P ratio (Pn/P) was higher in southern group estuaries ($0.01\text{--}0.5$, mean: 0.1 ± 0.1) than northern ($0.01\text{--}0.4$, mean: 0.1 ± 0.1) and central group ($0.1\text{--}0.2$, mean: $0.1 \pm nd$). The range of benzoic acid to total V ratio ($DHBA/V$) was higher in northern group estuaries ($0.01\text{--}1.9$, mean: 0.3 ± 0.2) than central ($0.01\text{--}0.6$, mean: 0.1 ± 0.2) and southern group ($0.01\text{--}0.4$, mean: 0.2 ± 0.1). The Λ_8 , Σ_8 and the compositional ratios of lignin and non-lignin phenols in different plant tissues, macrophytes, soils, and sediments are presented in [Table 2](#). Mean values of Λ_8 and Σ_8 in tissues were lowest in flowers and increased through grass and leaf material to highest values in wood. Similarly in the soils, the mean values of Λ_8 and Σ_8 increased in the order of mining soil < non-agriculture soil < agricultural soil. The C/V and S/V ratios of the plant tissues analyzed reflect their angiosperm origin. The C/V and S/V ratios were lower in non-agriculture soil than in agriculture soil due to a lower abundance of woody angiosperm tissue in the former as C phenols are mainly sourced from non-woody tissues.

Distribution of Σ_8 and Λ_8 values in sediments suggest that in most estuaries below $16^\circ N$ have higher values than that in the estuaries above $16^\circ N$ ([Figure 3](#)). The high values of $(Ad/Al)_V$ and $DHBA/V$ were observed in plant tissue (leaves), soil, and estuarine sediments ([Table 2](#)). Both the $P/(V+S)$ and Pn/P were higher in plants than soil due to the high lignin content of plants and the presence of degraded lignin phenols in the soil. The relative abundance of lignin ($S+V+C$) and non-lignin phenols (P and DHBA) was similar in all estuarine sediments, with $DHBA < P < (S+V+C)$. The abundance of lignin phenols was higher ($82 \pm 5\%$) in central and southern group estuaries than in the northern ($71\% \pm 15\%$), with the exception of the Sabarmati estuary where the abundance of non-lignin phenol (P) was higher ($53 \pm 2\%$) ([Figure 4](#)).

3.3 Principal Component Analysis (PCA)

PCA was performed to gain an overview of the factors controlling the composition of OM in estuarine sediments, and the results indicate that two factors can explain $\sim 85\%$ of the total variance ([Figure 5](#)). The clustering of non-lignin products (*p*-hydroxybenzoic acid and *p*-hydroxybenzaldehyde) with OC and TN, as well as salinity with $\delta^{13}C$, together highlight that elemental properties and isotope ratios are influenced due to mixed contribution from terrestrial and marine OM sources. OC, TN and all lignin phenols clustered in the upper right quadrant suggesting that vascular plant matter dominates sedimentary OM. DHBA may have both terrestrial (soil; [Houel et al., 2006](#)) and marine (brown macro

algae; Goñi and Hedges, 1995) origins. The association of DHBA with lignin phenols (Figure 5) observed in this study suggests that DHBA is contributed predominantly from terrigenous sources (Zou et al., 2008). This is consistent with a positive correlation (Pearson's $r=0.80$; $p\leq 0.001$; $n=112$ (data not shown)) between DHBA and *p*-coumeric acid, which is produced by leaf tissues and also between DHBA/V and C/V (Pearson's $r=0.85$; $p\leq 0.001$; $n=112$), observed in this study.

3.4 Quantification of OM sources

The elemental, isotopic and molecular limits of sediments varied within the compositional limits of various OM sources from terrestrial (soil, C₃ and C₄ plants) and marine (macrophytes/plankton) environment, suggesting their potential contribution to the OM mixture in sediment (Figure 6a and b). Therefore a four end-member mixing model was used to quantify the amount of OM contributed by different sources.

$$f_{C3} + f_{C4} + f_{Soil} + f_{Mar} = 1 \quad [2]$$

$$f(N/C)_{C3} + f(N/C)_{C4} + f(N/C)_{Soil} + f(N/C)_{Mar} = (N/C)_{sample} \quad [3]$$

$$f(\delta^{13}C)_{C3} + f(\delta^{13}C)_{C4} + f(\delta^{13}C)_{Soil} + f(\delta^{13}C)_{Mar} = (\delta^{13}C)_{sample} \quad [4]$$

$$f(\Lambda_8)_{C3} + f(\Lambda_8)_{C4} + f(\Lambda_8)_{Soil} + f(\Lambda_8)_{Mar} = (\Lambda_8)_{sample} \quad [5]$$

Where f_{C3} , f_{C4} , f_{Soil} and f_{Mar} are the fractions of OM derived from C₃ plants, C₄ plants, soil (non-agriculture) and marine plankton, respectively. The end-member values of $\delta^{13}C$, N/C ratios, and Λ_8 for C₃, C₄, soil and marine plankton are given in footnote of Table 1. The individual percentages were normalized to 100% of their sum in order to achieve mass balance (Gordon and Goñi, 2003). The sensitivity of the mixing model was examined by altering the isotopic and lignin phenol composition of end-members. Absolute errors for end-members are estimated to be ~ 10% for C₃ plants, 6% for C₄ plants, 12% for soil and 18% for marine OM sources. The model results suggest that terrigenous OM sources (C₃ plants, C₄ plants, and soil) contribute ~80±13% to the total sedimentary OM of all the estuaries, whereas marine sources contribute only ~20±10%. In most of the southern group estuaries, non-agriculture soil with lower $\delta^{13}C$ serves as the second most abundant OM source, after C₃ plants, whereas in the central and northern groups soil OM is dominant (Figure 6c).

3.5 Land use property variability across WCI

The land use pattern such as percentage of dense forest, C₃, and C₄ agricultural areas indicated that forest and C₃ agriculture is dominant across small river basins and decreases northward along the

WCI (Figure 7). The estuaries lies within a segment showed distinct elemental, isotopic and molecular properties, therefore the average values for a particular segment is calculated and are presented in supplementary Table A. The interaction between land use parameters such as ratio of forest to agriculture area in each segment and their relationship with average sedimentary properties of that segment is discussed in later section.

4. Discussion

4.1 Composition and origin of OM in WCI estuaries

The estuarine sediment compositions obtained in present study were clustered depending upon the latitude, and is attributed to variations in climate and geomorphology. The estuaries Chapora, Damanganga, Shastri, Kali, Karle, and Kharda display abnormal clustering patterns, being associated with various groups irrespective of latitude is due to similarities in rainfall and L/H with the group it is associated (Figure 2). Northern group estuaries have a mean L/H of 0.4 and mean annual rainfall of 2423 mm, therefore experience semi-arid climatic conditions. This is in contrast to the central (mean L/H=0.24) and southern group estuaries (mean L/H=0.14), where wet climate conditions and higher rainfall (central: ~3100 mm and southern: ~3400 mm; <http://nih.ernet.in>) prevail in the river catchment. A higher terrigenous sediment supply occurs within the south and central group estuaries due to higher rainfall as steep terrain coupled with high rainfall, contributes to the high erodibility of the catchment (CWC, 2012; Singh et al., 1992). Also this is consistent with higher concentrations of OC and lignin phenol in central and south estuaries (Figure 3).

Lower $\delta^{13}\text{C}$ and higher Λ_8 in estuarine sediments deposited below 16°N (i.e. central and southern group estuaries; Figure 3) are consistent with the dominance of terrestrial OM sources (C_3 plants and soil). Conversely, higher $\delta^{13}\text{C}$ and lower Λ_8 in sediments above 16°N (i.e. northern group) suggests OM composition is influenced to a variable extent by both terrestrial and marine (phytoplankton/ algae/ macrophyte) sources. Terrestrial OM is likely to be a mixture of C_3 ($\delta^{13}\text{C} = -29 \pm 1\text{‰}$) and C_4 ($\delta^{13}\text{C} = -13.1 \pm 0.9\text{‰}$) plant debris, which produce similar $\delta^{13}\text{C}$ as estuarine macrophytes ($-20 \pm 0.2\text{‰}$) and soil ($-23.1 \pm 1.4\text{‰}$) measured in this study (Table 1). Degradation of algal sedimentary OM is unlikely have an effect on the $\delta^{13}\text{C}$ signature (Cifuentes, 1991), while the lignin concentration/composition can be controlled by hydrodynamic sorting in estuarine environment (Bianchi et al., 2007). Furthermore, the biological alteration such as attack of fungi alters the lignin compositional ratio $[(\text{Ad}/\text{Al})_v]$ which can be enhanced by the sorption processes (Hedges et al., 1988; Hernes et al., 2007). Such conditions likely prevailed in northern group estuaries as revealed from higher $\delta^{13}\text{C}$, lower Λ_8 and higher $(\text{Ad}/\text{Al})_v$ in these samples. The higher sedimentary $\delta^{13}\text{C}$ in the estuaries of large rivers

are due to the prevalent C₄ vegetation in the catchment. The non-linear variation of C/N ratios in the estuarine sediments is likely to be caused by changes in OM sources because the plants and macrophytes have distinct C/N ratios in this study, with higher C/N in former due to nitrogen free biomolecules such as lignin (Hedges et al., 1986).

Higher Λ_8 and Σ_8 in the southern and central group estuaries tells us that there is more terrestrially derived carbon is present. Furthermore the range of S/V and C/V ratios indicated the dominance of angiosperm plant tissues from mixed sources (leaves and grasses) (Hedges and Mann, 1979; Table 2). Leaf litter from higher plants and mangrove abundant in lignin phenols, are supplied to estuarine sediments either during littering or by mixing with soils (Prasad and Ramanathan, 2010). The latter process is dominant in the studied region because higher plant litter production has been documented in Western Ghats (Sundarapandian and Swamy, 1999). Also, high lignin content in southern and central group estuaries (Figure 4) tells us that there is a high amount of vascular plant relative to other OM sources (e.g. aquatic and marine algae). The fungal abundance play a major role in degradation and storage of OM in plants and soil (e.g. Averill et al., 2014). Degradation of lignin in soils is certainly an important process, but it has also been shown that lignin is significantly degraded in the aquatic environment after export from soils into rivers (e.g. Ward et al., 2013). The monsoonal system like WCI, the abundant fungi degrade terrestrial vegetation and soil substrata and further exported to estuarine regions by rainfall and riverine runoff, consumes the estuarine vegetation (mangroves) (Manoharachary et al., 2005). This process have resulted high ratios of P/(V+S) and (Ad/Al)_v in plant, soil and estuarine sediment samples, which together point to the diagenesis of terrestrial OM prior to its incorporation into estuarine sediments. Sediments from the northern group estuaries have higher P/(V+S) than the southern and central groups indicating that more degraded lignin is present in the former as process such as lignin diagenesis eliminates V and S phenols without influencing P (Dittmar and Lara, 2001). Low Pn/P across the estuary suggest that a fraction of non-lignin (autochthonous) OM is contained in all sampled sediments. Higher values of DHBA/V (>0) in all estuarine sediments indicate the presence of matured soil OM and humification (Farella et al., 2001; Louchouart et al. 1999). The presence of kelp and brown algae represents an alternative explanation (Goñi and Hedges, 1995); however, the correlation between *p*-coumeric acid and DHBA, as well as between DHBA/V and C/V, suggests that soil humification is the more likely explanation, as is consistent with the land use changes along the WCI (Panigrahy et al., 2010). In the Sabarmati River estuary, extremely higher DHBA/V (1.38±0.5) is associated with higher P/(V+S) and lower Pn/P, indicating that the OM source is predominantly derived from macrophytes and soils. Among the P phenols, only Pn is originated from lignin and higher P/(V+S) can be a result of lignin diagenesis (Benner et al., 1990; Dittmar and Lara, 2001). This is in contrast to the small estuaries where higher

lignin phenols indicated dominant plants and soil OM. In this study, variation of soil and plant OM and its correspondence to latitude and land use change highlight the linkage between them along the WCI. As revealed from the PCA results, the association of non-lignin products with elemental properties, as well as salinity with $\delta^{13}\text{C}$ (Figure 5), indicate the mixing of OM from marine sources. However the proportions of mixing from marine sources have further variability among the different groups of estuary, depending upon the potential contributions from different terrestrial OM sources.

As indicated by the end-member mixing model results, soil serves as primary abundant OM source in sediments from central and northern group estuaries which can be attributed to the accelerated soil erosion in the Deccan Traps (Singh et al., 1992) that cover the majority of the central and northern river catchments. The sediments from south group estuaries are dominated by OM sourced from plant due to the combined effect of littering in the Western Ghats as well as soil erosion. The Narmada and Sabarmati estuaries contain mainly C_4 plant and soil derived OM because of the intense impact of C_4 agriculture (Kurian et al., 2013). Terrestrial OM from C_3 and C_4 plant detritus is dominant (57%) in the near shore and coastal sediments of the Bay of Bengal (Krishna et al., 2013), which contain 47% of marine OM. However along the WCI, lower proportion of marine OM ($\leq 30\%$) occurs in the estuarine sediments of small and large rivers due to the type of land use (i.e. forest and agriculture) and soil erosion.

4.2 Land use and terrigenous OM composition

Positive and negative correlations between the ratio of forest/agricultural land and average Λ_8 ($r=0.79$; $p\leq 0.001$) and average $\delta^{13}\text{C}$ (Pearson's $r=-0.73$; $p\leq 0.001$), respectively (Table 3; Figure 8), found in this study is consistent with larger plant OM input from the forested regions. However, this is not consistent with the extent of deforestation along the Western Ghats (Menon and Bawa, 1998). We suggest that in this case abundant plant OM is sourced from plant litter contained in soil mobilized by erosion. This explanation is further attested to by the positive correlation between DHBA yield, *p*-coumeric acid ($r=0.78$; $p\leq 0.001$), and the forest/agriculture ratio (Figure 8) because *p*-coumeric acid is a vital component of lignin phenol in leaf litter (Prasad and Ramanathan, 2010). The forest/agriculture ratio is negatively correlated with $\delta^{13}\text{C}$ and this is attributed to intense remineralization of OM during agricultural activities, causing the preferential loss of ^{12}C , thus driving $\delta^{13}\text{C}$ toward higher values (Holtvoeth et al., 2005). A similar correlation has been observed in other tropical river basins (Amazon), where decreasing forest cover has caused sedimentary $\delta^{13}\text{C}$ values to increase (Bird et al., 1992). A positive correlation between the forest/agriculture ratio and DHBA yield in estuarine sediments reflects the importance of soil OM, rich in minerals (Houel et al., 2006), derived from the Western Ghats. The lower DHBA/V reported for mining soils in this study is limited to specific mines and is not

representative of mineral soils. We suggest that the mineral richness of soil preferentially controls the DHBA yield of soil OM during erosion in this region, as the forest/agriculture ratio did not show a significant correlation with DHBA/V ($r=-0.23$; $p \geq 0.05$; [Table 3](#)).

4.3 Potential fate of terrigenous OM

Soil OM represents a considerable fraction of estuarine sediments in the WCI. The lignin phenol concentration and compositional ratio of the 35 WCI estuaries studied here indicate that a considerable fraction of soil OM is present in sediments. After export from soils, the lignin undergoes further degradation in the estuarine environment (e.g., [Ward et al., 2013](#)). The trapped OM has the potential to be transported to the coastal environment during tidal exchange or flood events. The origin of sedimentary OM deposited on the continental shelf of the Arabian Sea has previously been something of a paradox, with one group suggested that the shelf sediments contained high concentrations of labile biological OM during the summer and winter monsoon seasons ([Madhupratap et al., 1996](#)) while the other group reported far less labile sedimentary OM ([Jacob et al., 2008](#)). The extent of degradation of OM in the estuaries has bearing on the remineralization of OM in the shelf and slope regions of the Arabian Sea. The present study can be compared to sources and sinks of OM in other river-dominated margin systems.

In the Gulf of Mexico, which is located at similar latitude to the WCI, sedimentary OM is derived from plants and soil. There, plant material tends to be deposited in the estuary and delta, while soil OM is transported farther offshore ([Gordon and Goñi, 2003](#)). Similarly, in the tropical continental margins of West Africa, a significant proportion of soil OM is present in deep marine sediments supplied by the Congo River (e.g. [Holtvoeth et al., 2005](#)). The soil OM in the WCI estuaries is humified and degraded in the terrestrial environment as a result of changing land use practices, which we suggest has resulted in the preservation of OM in the marine environment of Arabian Sea.

5. Conclusion

Based on changes in elemental, isotopic and molecular properties of sediment in 35 estuaries along the WCI, we draw the following conclusions:

- (i) Estuaries clustered into three major groups based on the sedimentary chemical properties (OC, TN, $\delta^{13}\text{C}$, CuO oxidation products), and followed latitudinal pattern due to the geomorphology and climate of their riverine catchments;
- (ii) End member mixing model result showed terrigenous OM sources (C_3 plants, C_4 plants, and soil) contribute $80 \pm 13\%$ to the total sedimentary OM in WCI estuaries, while marine sources (plankton/macrophyte) contribute only $20 \pm 10\%$;

- (iii) Soil was found to be the second most abundant source of OM, after C₃ plants, in most southern group estuaries, but was the primary source in the central and northern groups. The estuaries of large rivers, such as the Narmada and Sabarmati, contained predominantly C₄ plant and soil OM, which is suggested to result from intense C₄ agriculture; and
- (iv) Lignin phenol concentrations and compositional ratios indicate that estuarine sedimentary OM is dominated by non-woody angiosperm vegetation that has been degraded by fungal action prior to deposition. The source of terrigenous OM in estuarine sediments is influenced by land use changes in the adjacent environment, which alters lignin phenol ratios and $\delta^{13}\text{C}$ by oxidative degradation and humification.

Due to accelerated land-use changes and human-induced climatic changes (temperature and amount and frequency of precipitation) in the Indian sub-continent, there will be likely significant changes in the concentration and composition of OC to the estuaries which could affect its mineralization process. This study will serve as the baseline for future studies in the WCI as well as a model study for other tropical regions in the world.

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Legends to figures

Figure 1: Study area map: the Western continental margin of India (WCI). Left: positions of small and large rivers flowing through two contrast geological provenance such as Deccan traps (grey highlighted) and Precambrian gneisses and schist (un-highlighted; Kurian et al., 2013). Right: Land use characteristics and sampling locations (Source: NRSC, ISRO (RS&GIS) India).

Figure 2: Dendrogram resulted from hierarchical cluster analysis. Association of estuaries in a particular cluster represents their similar sedimentary chemical properties.

Figure 3: Spatial distribution of mean values of bulk properties and lignin phenols in the estuarine sediment of WCI.

Figure 4: Relative abundance of CuO oxidation products. The abundance of lignin ($\Lambda_8 = S+V+C$) and non-lignin phenols (P and DHBA) in estuarine sediments arranged according to their clustering pattern. Also the relative abundance of lignin and non lignin phenols in leaf (L), flower (F), wood (W), grass (G), macrophyte (M) and soils (S) collected from the WCI estuaries.

Figure 5: Principal components diagram of variables merged with samples. Variables and their proximities are highlighted and the inset is an enlargement of the box highlighted in grey color. PC1 and PC2 represent the principal components.

Figure 6: End-member mixing plot of different group estuaries showing different compositional signatures of estuarine sediment along the WCI when plotted with their limits of (a) Λ_8 and $\delta^{13}C$ (b) N/C and $\delta^{13}C$. (c) Quantified proportion of end-member contribution to the estuarine sediments of different estuaries based on mixing model results.

Figure 7: Distribution of Land use properties (forest and C_3 and C_4 agriculture areas) in the 14 coastal districts along WCI.

Figure 8: Relationship between sedimentary parameters and land use properties. p value is the level of significance resulted from Pearson's correlation analysis. Error bar indicated the standard deviations over mean values of parameters found in the estuarine sediments within a particular segment.

Legends to tables

Table 1: Panel A: Bulk compositional parameters in plants, soil and macrophyte from the WCI. **Panel B:** Elemental and isotopic properties of sediments from WCI estuaries. Salinity in Practical Salinity Scale (PSS), values are presented in the format of average \pm standard deviation and number in the parenthesis indicates sample size.

Table 2: Panel A: Lignin phenols and ratios in plants, soil and macrophyte from the WCI. **Panel B:** Sedimentary lignin phenols and ratios in estuary groups. Abbreviations: leaf (L), flower (F), wood (W), grass (G), macrophyte (M) and soil (S). Values are presented in the format of average \pm standard deviation and number in the parenthesis indicates sample number.

Table 3: Pearson's correlation matrix for land use parameters bulk compositional parameters, lignin phenols and their ratios. Abbreviations: ratio of forest: agriculture (F/A); percentage of forest area (FA); percentages of agriculture area (AG) and *p*-coumeric acid (PCD). Bold numbers are significant at 99.9% ($p \leq 0.001$) and italic underlined numbers are significant at 95% confidence level ($p \leq 0.05$).

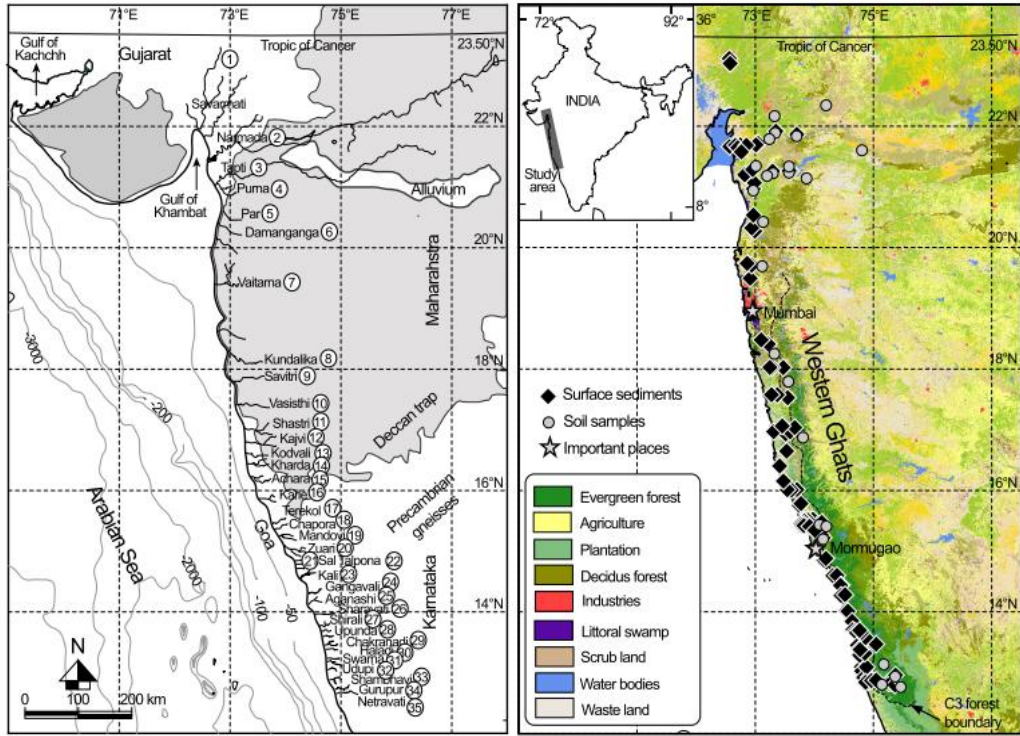


Figure 1

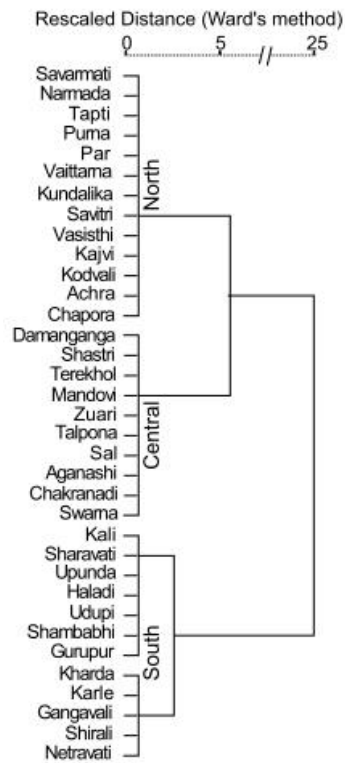


Figure 2

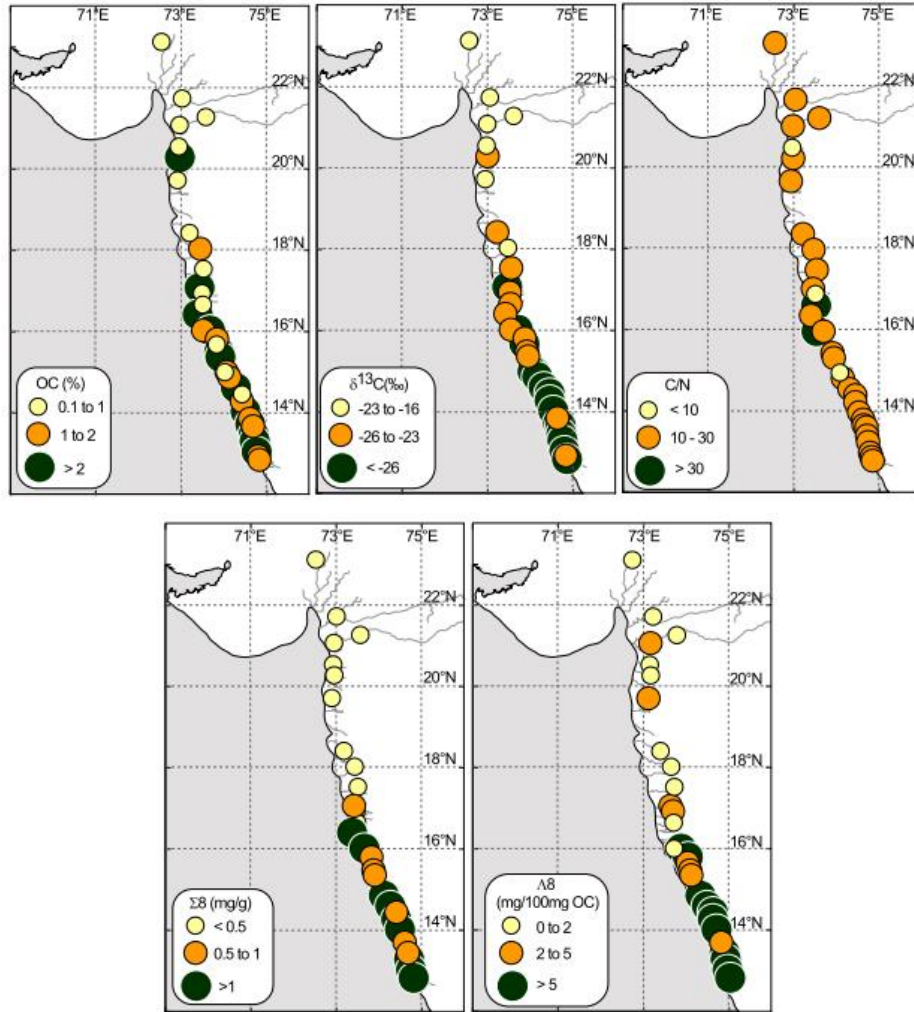


Figure 3

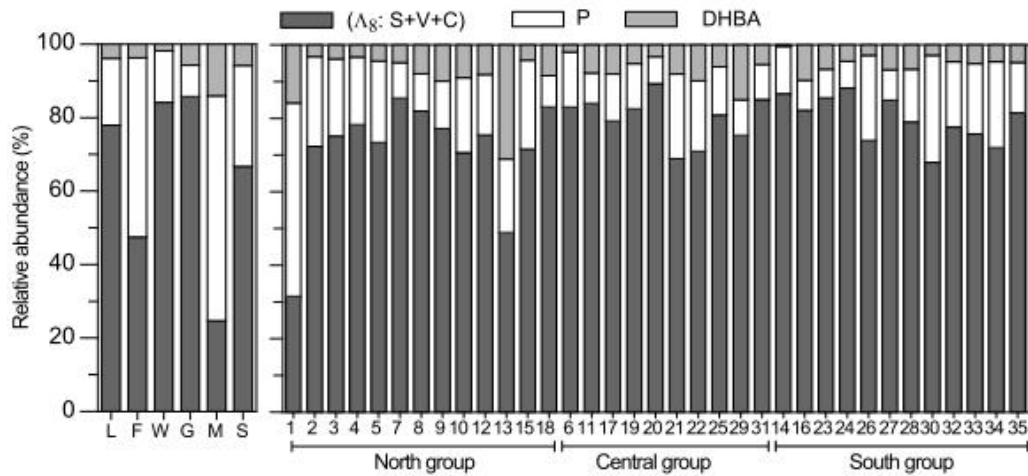


Figure 4

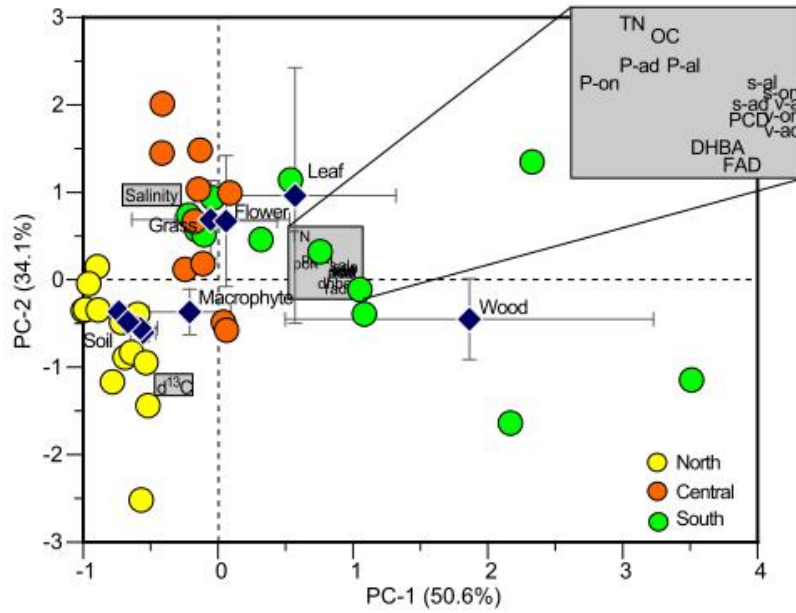


Figure 5

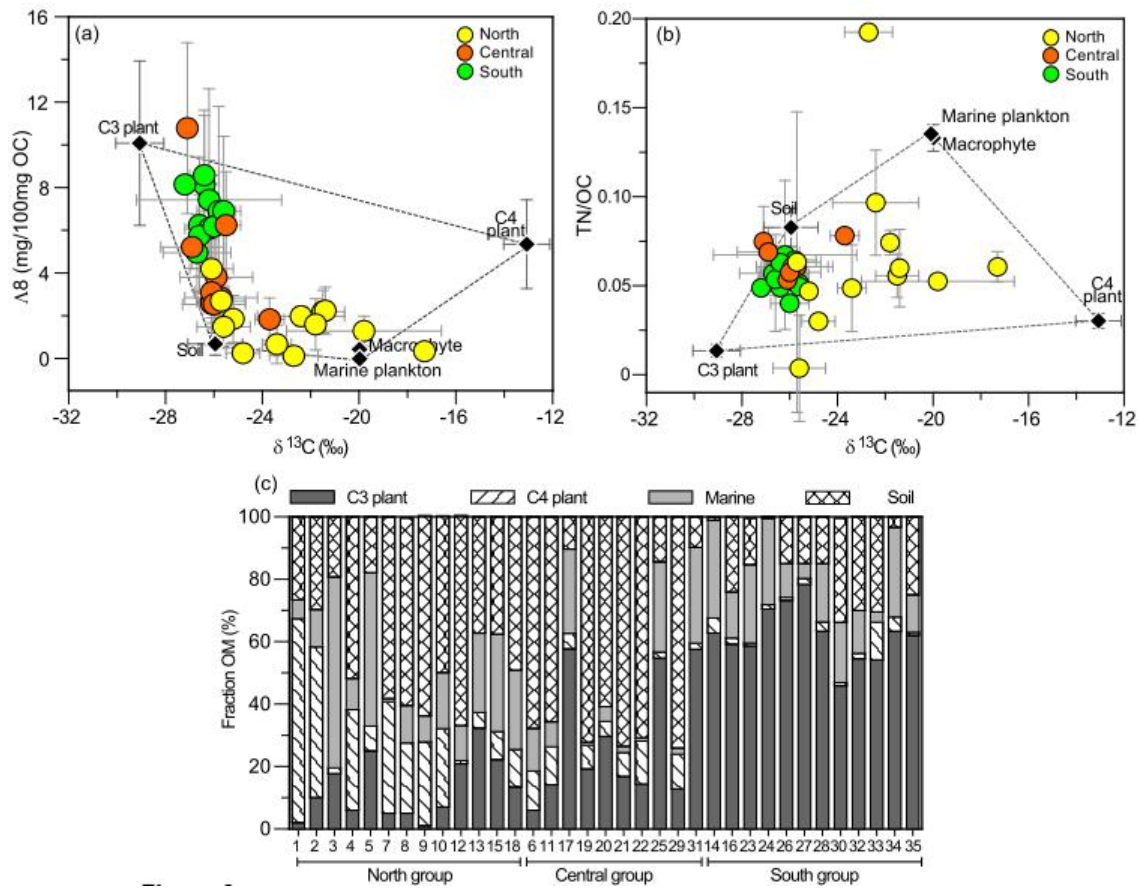


Figure 6

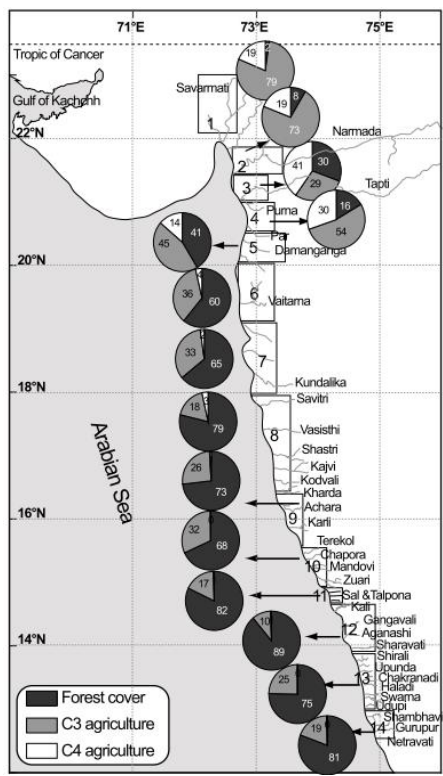


Figure 7

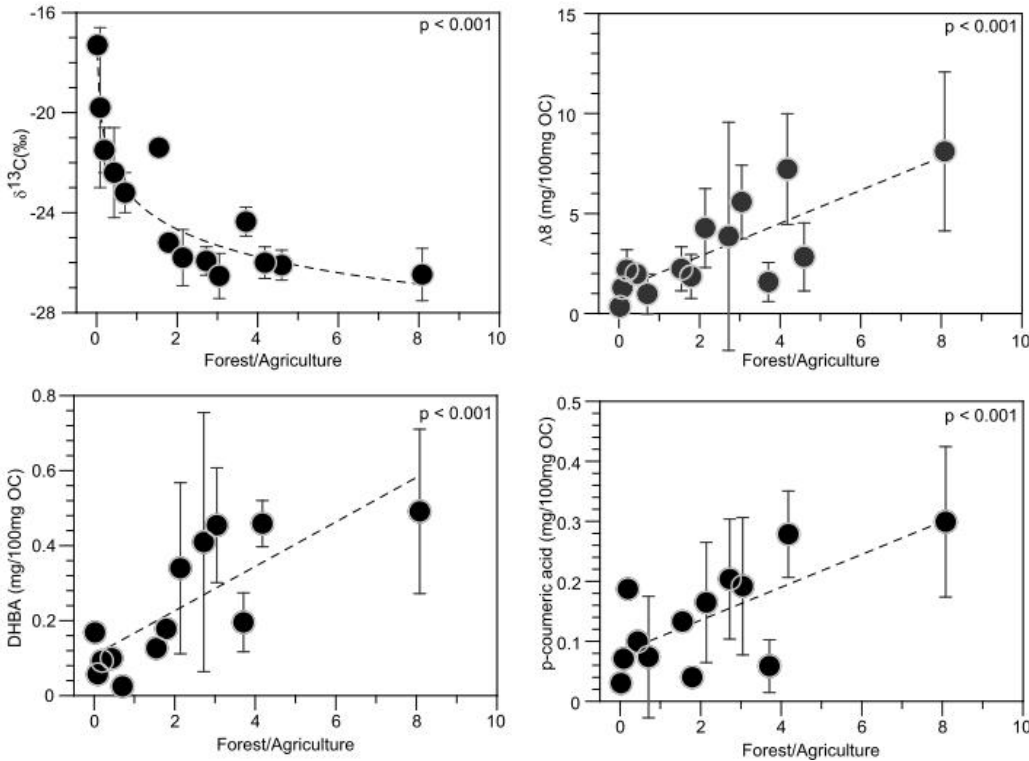


Figure 8

Table 1**Panel A**

Type	Description	$\delta^{13}\text{C}$ (‰)	OC (%)	TN (%)	C/N
C₃ plants	Higher (3)	-29.1±1.0	35.7±4.5	0.5±0.1	77.1±20.5
	Agriculture (7)	-29.2±0.6	31.2±1.0	2.0±0.3	16.3±2.6
	Mangroves (10)	-28.7±1.3	35.7±4.0	2.5±1.2	17.2±7.8
	C₃ plant mean	-29.0±1.0	34.2±3.2	1.6±0.5	36.9±10.3
C₄ plants	Agriculture (5)	-12.0±0.6	33.7±1.3	1.0±0.1	33.7±5.1
	Non-agriculture (4)	-14.2±1.3	25.8±1.0	2.4±0.1	10.8±0.3
	C₄ plant mean	-13.1±0.9	29.8±1.1	1.7±0.1	22.3±2.7
Soils	Non-agriculture (23)	-25.9±1.1	0.5±0.4	0.04±0.03	12.3±2
	Agriculture (14)	-20.5±1.5	1.0±0.2	0.07±0.02	13.5±3.2
	Mining (7)	-22.8±1.5	0.1±0.02	0.01±0	16.1±4
	Soil mean	-23.1±1.4	0.5±0.2	0.04±0.02	14±3.1
Macrophyte	Macrophytes (2)	-20.0±0.2	17±0.9	2.3±0	7.5±0.4

Soil: N/C=0.08±0.01; $\delta^{13}\text{C}$ =-25.9±1.1‰ and $\Lambda_8 = 0.7±0.5$ mg/100 mg OC (see Table 2)

C₃ plants: N/C=0.01±0.004; $\delta^{13}\text{C} = -29.1±1.0$ ‰ and $\Lambda_8 = 10.1±3.8$ mg/100mgOC (see Table 2)

C₄ plants: N/C=0.03±0.004; $\delta^{13}\text{C} = -13.1±0.9$ ‰ and $\Lambda_8 = 5.3±2.1$ mg/100mgOC (see Table 2)

Marine plankton: N/C=0.13±0.007 (Calvert et al., 1995); $\delta^{13}\text{C} = -20±0.2$ ‰ (Fontugne and Duplessy, 1986) and $\Lambda_8 = 0$ (Gordon and Goni, 2003)

Panel B

Name	Longitude (°E)	Latitude (°N)	Salinity (PSS)	$\delta^{13}\text{C}$ (‰)	OC (%)	TN (%)	C/N
Sabarmati (n=2)	72.56	23.11	5.9 ± 3.8	-17.3 ± 0.1	0.21 ± 0.01	0.01 ± 0	16.5 ± 3
Narmada (n=4)	73.04	21.72	15.9 ± 7.5	-19.8 ± 3.2	0.46 ± 0.3	0.02 ± 0.01	19.1 ± 21
Tapti (n=5)	73.60	21.26	24.1 ± 5.4	-22.4 ± 1.8	0.69 ± 0.3	0.07 ± 0.02	10.3 ± 8
Purna (n=3)	72.98	21.06	15.9 ± 5.5	-21.5 ± 0.9	0.66 ± 0.3	0.03 ± 0.01	19.1 ± 6.9
Par (n=2)	72.96	20.53	8.7 ± 0.9	-22.7 ± 1.0	0.33 ± 0.2	0.06 ± 0	5.2 ± 4.2
Vaitarna (n=3)	72.93	19.71	9.7 ± 0.5	-21.4 ± 0.1	0.75 ± 0.1	0.05 ± 0.02	16.0 ± 6.8
Kundalika (n=3)	73.22	18.41	10.5 ± 2.1	-25.2 ± 0.1	0.79 ± 0.1	0.04 ± 0	21.3 ± 2
Savitri (n=3)	73.47	18.02	11.9 ± 5.8	-21.8 ± 0	1.15 ± 0	0.09 ± 0.01	13.5 ± 1.2
Vasisthi (n=3)	73.54	17.53	19.5 ± 0.4	-23.4 ± 0.6	0.43 ± 0	0.02 ± 0.01	20.6 ± 2.2

Kajvi (n=3)	73.51	16.93	15.6 ± 0.9	-25.7 ± 1.0	0.23 ± 0.1	0.04 ± 0.02	6.6 ± 10.5
Kodvali (n=3)	73.52	16.65	15.7 ± 1.5	-24.8 ± 0.7	0.52 ± 0.1	0.02 ± 0	33.3 ± 3.5
Achara (n=3)	73.54	16.02	17.6 ± 3.1	-25.6 ± 1.1	1.19 ± 1.0	0.03 ± 0.02	43.0 ± 13.8
Chapora (n=2)	73.85	15.67	12.2 ± 7	-26.1 ± 0.9	0.52 ± 0.2	na	na
North group	–	–	14.1 ± 3.4	-22.9 ± 0.9	0.61 ± 0.3	0.04 ± 0.01	18.7 ± 6.9
D.Ganga (n=3)	72.99	20.27	13.5 ± 2.9	-23.7 ± 0.6	2.57 ± 0.5	0.20 ± 0.01	12.8 ± 1.9
Shastri (n=3)	73.45	17.06	22 ± 2.3	-26.1 ± 0.6	3.41 ± 0.2	0.18 ± 0.01	18.8 ± 2.5
Terekhol (n=2)	73.86	15.80	13.6 ± 2.1	-25.5 ± 0.6	1.07 ± 0.6	na	na
Mandovi (n=5)	73.91	15.48	20.4 ± 0.4	-25.7 ± 1.5	2.10 ± 1.1	0.12 ± 0.06	17.0 ± 1.3
Zuari (n=5)	73.94	15.36	15.2 ± 2.3	-25.9 ± 1.5	2.30 ± 0.7	0.14 ± 0.03	16.8 ± 1.6
Talpona (n=2)	74.08	15.00	34 ± 0.9	-26.1 ± 0.5	1.70 ± 1.2	0.19 ± 0	9.0 ± 3.5
Sal (n=2)	74.04	14.99	33.8 ± 0.7	-26.1 ± 0.7	0.72 ± 0.2	na	na
Aganashini (n=3)	74.45	14.45	11.1 ± 9.8	-27.1 ± 0.0	0.93 ± 0.3	0.07 ± 0.01	14.2 ± 2.4
Chakra(n=3)	74.64	13.71	26.2 ± 2.3	-26.0 ± 1.3	2.64 ± 1.5	0.15 ± 0.08	18.0 ± 3.7
Swarna (n=3)	74.72	13.45	26.8 ± 0.9	-26.9 ± 1.3	2.77 ± 2.1	0.17 ± 0.12	16.0 ± 10.5
Central group	–	–	21.7 ± 2.5	-25.9 ± 0.9	2.0 ± 0.9	0.15 ± 0.04	15.3 ± 3.4
Kharda (n=3)	73.41	16.41	16.8 ± 5.5	-25.6 ± 0.4	5.71 ± 0.2	0.29 ± 0	19.5 ± 0.6
Karle (n=3)	73.70	16.02	8.6 ± 0.5	-26.6 ± 0.2	2.22 ± 1.6	0.09 ± 0.03	25.2 ± 1.7
Kali (n=2)	74.15	14.86	24.7 ± 5	-26.2 ± 1.0	1.86 ± 0.1	0.11 ± 0.04	17.6 ± 6.6
Gangavali (n=3)	74.31	14.60	15.9 ± 8.4	-26.4 ± 0.2	2.15 ± 0.1	0.11 ± 0.02	20.3 ± 3.5
Sharavati (n=3)	74.44	14.28	26.5 ± 1.3	-26.2 ± 3.0	1.09 ± 0.8	0.05 ± 0.02	20.8 ± 5.1
Shirali (n=4)	74.53	14.02	12.5 ± 7.5	-27.2 ± 0.3	3.89 ± 2.5	0.18 ± 0.11	21.2 ± 2
Upunda (n=4)	74.63	13.85	24.2 ± 4.6	-25.8 ± 0.9	1.35 ± 0.2	0.09 ± 0.01	15.5 ± 4
Haladi (n=4)	74.71	13.66	26 ± 3.1	-26.7 ± 1.4	1.14 ± 0.3	0.06 ± 0.01	17.6 ± 5.8
Udupi (n=5)	74.75	13.30	15.6 ± 7.4	-26.6 ± 0.2	2.38 ± 0.1	0.13 ± 0.03	18.6 ± 3.9
Shamvavi(n=3)	74.79	13.03	28.1 ± 3.6	-26.0 ± 0.8	2.18 ± 0.3	0.09 ± 0.02	24.7 ± 2.2
Gurupur (n=3)	74.83	12.93	22.7 ± 0.2	-25.6 ± 0.5	1.92 ± 0.6	0.10 ± 0.03	20.2 ± 10.9
Netravati (n=5)	74.85	12.83	14.8 ± 6.9	-26.4 ± 0.6	1.99 ± 0.1	0.13 ± 0.01	15.9 ± 2.7
South group	–	–	19.7 ± 4.5	-26.3 ± 0.8	2.3 ± 0.6	0.12 ± 0.03	19.8 ± 4.1

Table 2

Panel A

Category	Name	Σ_8	Λ_8	C/V	S/V	(Ad/Al) _v	P/(V+S)	Pn/P	DHBA/V
		(mg/g dry wt.)	(mg/100mg OC)						
L (n=20)	Higher	25.8 ±19	6.9 ±4.4	0.2 ±0.1	1.1 ±0.6	0.4 ±0.2	0.2 ±0.2	0.4 ±0.2	0.1±nd
	Agriculture	25.3 ±17.8	7.6 ±5.2	0.6 ±0.4	0.8 ±0.2	0.7±0.4	0.3±0.2	0.2±0.1	0.1±0.1
	Mangroves	15.7±7.1	4.2±1.9	0.8±0.4	1.3±0.6	0.5±0.1	0.5 ±0.3	0.2 ±0.1	0.3±0.2
	Leaf mean	22.2±15	6.3±3.8	0.6±0.3	1.0±0.5	0.5±0.2	0.3±0.2	0.2±0.1	0.2±0.1
F (n=5)	Higher	8.3 ±3.1	3.3 ±1.4	0.3 ±0.2	1.0 ±0.9	0.4 ±0.2	1.5 ±1.3	0.2 ±0.3	0.1±0.2
W (n=7)	Higher	29.1±16	6.6±1.0	0.1±0.07	1.8±0.6	0.3±0.1	0.2 ±0.2	0.1±0.1	0.1±0.1
G (n=3)	Non-Agr.	13.7±5	5.3±2.1	0.2±0.3	1.3±1.8	2.9±3.5	0.1±nd	0.2±0.2	0.1±nd
M (n=3)	Macrophyte non-	0.7±0.3	0.3±0.2	0.4±0.2	1.0 ±0.5	0.9±0.9	4.2±3.8	0.03±0.02	2.4±3.1
S(n=40)	agriculture	0.04±0.05	0.68±0.52	0.28±0.1	0.61±0.37	0.68±0.27	0.56±0.4	0.11±0.06	0.15±0.08
	Agriculture	0.16±0.08	1.56±0.67	0.49±0.2	0.98±0.24	0.47±0.12	0.31±0.21	0.13±0.06	0.14±0.11
	Mining	0.01±0.002	0.82±0.29	0.11±0.04	0.48±0.46	0.30±0.13	1.02±0.53	0.09±0.1	0.08±0.05
	Soil mean	0.07±0.04	1.02±0.49	0.29±0.11	0.69±0.36	0.48±0.17	0.63±0.39	0.11±	0.12±0.09

Panel B

Name	Σ_8 (mg/g dry wt.)	Λ_8 (mg/10 0mg OC)						
		C/V	S/V	(Ad/Al) _v	P/(V+S)	Pn/P	DHBA/V	
Sabarmati (n=2)	0.01±nd	0.3±0.1	0.5±0.4	1.3±0.6	0.8±0.2	2.1±0.7	0.04±nd	1.38±0.5
Narmada (n=4)	0.1±0.1	1.3±0.7	0.2±0.1	0.7±nd	0.8±0.2	0.4±0.2	0.09±0.1	0.10±0.1
Tapti (n=5)	0.2±nd	2.0±0.5	0.2±0.1	0.8±nd	0.3±nd	0.3±0.2	0.07±0.1	0.10±0.1
Purna (n=3)	0.1±nd	2.2±1.0	0.4±0.1	1.0± nd	0.4±nd	0.3±0.2	0.09±nd	0.11±nd
Par (n=2)	0.004±nd	0.1±nd	0.1±nd	0.2±0.1	0.5±0.2	0.4± nd	0.29±0.1	0.07± 0.2
Vaitarna (n=3)	0.2±0.1	2.2±1.1	0.3±nd	1.2±0.3	0.6±0.2	0.1± nd	0.17±nd	0.14±nd
Kundalika (n=3)	0.1±0.2	1.9±1.1	0.1±0.1	0.9±0.1	0.5±0.1	0.2±0.1	0.18±nd	0.19±nd
Savitri (n=3)	0.2±0.1	1.6±1.2	0.1±nd	0.8±0.1	0.5±0.1	0.2±0.1	0.21±nd	0.25±0.1
Vasisthi (n=3)	0.03±nd	0.7±0.9	0.2±0.1	0.9±nd	0.7±0.1	0.4±0.5	0.13±nd	0.26±0.1
Kajvi (n=3)	0.1±nd	2.7±1.5	0.3±0.1	1.1±0.2	0.4±0.1	0.3±0.2	0.19±0.1	0.25±0.1
Kodvali (n=3)	0.1±0.1	0.2±0.1	0.2±0.1	0.6±0.3	1.3±0.3	0.5±0.2	0.10±nd	0.10±nd
Achara (n=3)	0.03±nd	1.5±1	0.2±nd	0.8±0.1	1.2±0.4	0.4±0.2	0.14±0.1	0.12±0.1
Chapora (n=2)	0.2±0.1	4.2±2.3	0.4±nd	1.3±0.2	0.5±nd	0.2±0.1	0.22±nd	0.27±0.1
North group	0.11±0.12	1.6±1.0	0.2±0.1	0.9±0.2	0.7±0.2	0.4±0.2	0.1±0.1	0.3±0.2
D.Ganga (n=3)	0.5±nd	1.8±1.0	0.2±nd	0.6±0.1	0.3±nd	0.2±0.1	0.10±nd	0.04±nd
Shastri (n=3)	0.9±nd	2.7±1.2	0.1±nd	0.9±0.3	0.4±0.1	0.1±0.1	0.23±nd	0.18± nd
Terekhol (n=2)	0.7±0.2	6.2±2.5	0.3±0.1	1.3±nd	0.5±0.1	0.2±0.2	0.18±nd	0.26±nd
Mandovi (n=5)	0.8±0.5	2.8±1	0.1±0.1	0.9±0.4	0.3±0.1	0.2±0.1	0.13±nd	0.03±nd
Zuari (n=5)	0.8±0.4	3.8±2.1	0.1±nd	0.8±0.1	0.4±0.1	0.1±0.1	0.13±nd	0.01±nd
Talpona (n=2)	0.6±0.4	2.6±0.9	0.1±0.1	1.0±0.3	0.3±0.1	0.2±0.1	0.15±nd	0.02±nd
Sal (n=2)	0.6±0.3	3.1±2.5	0.1±nd	0.6±0.1	0.4±0.1	0.1±0.1	0.13±nd	0.01±nd
Aganashini (n=3)	0.7±0.2	11±4	0.3±0.1	1.3±0.9	0.4±0.1	0.2±0.2	0.13±nd	0.19±nd

Chakra(n=3)	0.7±0.2	2.5±1.1	0.2±nd	0.9±0.2	0.7±0.1	0.2±0.1	0.16±nd	0.41±0.2
Swarna (n=3)	0.9±0.4	5.2±1	0.2±nd	1.3±nd	0.5±0.1	0.1±0.1	0.12±nd	0.15±nd
Central group	0.7±0.3	4.2±1.7	0.2±0.1	1.0±0.3	0.4±0.1	0.2±0.1	0.1±nd	0.1±0.2
Kharda (n=3)	2.4±nd	4.6±1.3	0.3±nd	1.7±1.6	0.4±0.1	0.3±0.2	0.41±0.1	0.14±0.1
Karle (n=3)	2.1±0.5	6.2±3.2	0.3±0.1	1.1±0.1	0.4±0.1	0.1±0.1	0.23±0.1	0.28±0.1
Kali (n=2)	1.2±0.3	6.1±3.2	0.3±nd	1.2±0.2	0.6±0.1	0.1±0.1	0.18±nd	0.20±0.1
Gangavali (n=3)	1.8±0.6	8.1±3.5	0.2±nd	1.4±0.2	0.4±nd	0.1±0.1	0.13±nd	0.13±nd
Sharavati (n=3)	1.1±0.9	7.4±5.2	0.3±0.1	2.3±1.2	0.6±0.1	0.3±0.2	0.04±nd	0.15±nd
Shirali (n=4)	3.4±1.5	8.1±0.3	0.3±0.1	1.2±0.1	0.5±0.1	0.1±0.4	0.15±nd	0.20±0.1
Upunda (n=4)	0.9±0.6	6.9±4.9	0.3±0.1	2.0±0.9	0.5±0.1	0.4±0.2	0.03±nd	0.15±nd
Haladi (n=4)	1.3±0.3	5±1.8	0.2±nd	1.2±0.1	0.4±0.1	0.3±0.2	0.06±nd	0.20±nd
Udupi (n=5)	1.4±0.4	5.7±1.9	0.2±nd	1.4±0.1	0.4±0.1	0.3±0.2	0.08±nd	0.16±nd
Shamvavi(n=3)	1.4±0.4	6.2±2.0	0.2±nd	1.5±0.1	0.5±0.1	0.3±0.2	0.07±nd	0.18±0.1
Gurupur (n=3)	1.4±0.6	6.9±3.5	0.2±nd	1.8±0.5	0.5±0.2	0.3±0.1	0.08±nd	0.20±nd
Netravati (n=5)	1.6±0.5	8.6±2.8	0.2±nd	1.4±0.3	0.4±0.1	0.2±0.1	0.09±nd	0.15±nd
South group	1.7±0.5	6.7±2.8	0.3±0.1	1.5±0.5	0.5±0.1	0.2±0.2	0.1±0.1	0.2±0.1

Table 3

Parameters (unit)	FC	AG	F/A	OC	TN	$\delta^{13}\text{C}$	C/N	Σ_8	Λ_8	C/V	S/V	(Ad/Al) _v	P/(V+S)	Pn/P	DHBA/V	DHBA	PCD	Salinity
FC (%)	1.00																	
AG (%)	-1.00	1.00																
F/A	0.83	0.83	1.00															
OC (%)	0.67	0.67	0.47	1.00														
TN (%)	0.68	0.68	0.50	0.72	1.00													
$\delta^{13}\text{C}$ (‰)	-0.91	0.91	0.73	0.75	-0.76	1.00												
C/N	0.17	0.17	0.12	0.44	-0.19	0.17	1.00											
Σ_8 (mg/g dry wt.)	0.69	0.69	0.67	0.90	0.61	0.73	0.44	1.00										
Λ_8 (mg/100mg OC)	0.68	0.68	0.79	0.63	0.43	0.71	0.29	0.86	1.00									
C/V	-0.45	0.45	0.18	0.22	-0.53	0.57	0.32	-0.08	-0.06	1.00								
S/V	0.39	0.39	0.55	0.35	-0.01	0.25	0.49	0.65	0.75	0.50	1.00							
(Ad/Al) _v	-0.30	0.30	0.19	0.12	-0.52	0.49	0.53	-0.13	-0.30	0.46	0.12	1.00						
P/V+S	-0.59	0.59	0.36	0.39	-0.46	0.69	0.01	-0.30	-0.38	0.67	0.16	0.51	1.00					
Pn/P	0.44	0.44	0.05	0.50	0.33	0.43	0.39	0.17	-0.02	-0.37	-0.22	0.04	-0.54	1.00				
DHBA/V DHBA (mg/100mg OC)	-0.44	0.44	0.23	0.30	-0.43	0.58	0.09	-0.19	-0.26	0.67	0.30	0.52	0.98	-0.50	1.00			
PCD (mg/100mg OC)	0.60	0.60	0.71	0.62	0.58	0.63	0.18	0.83	0.92	-0.03	0.67	-0.42	-0.40	0.00	-0.33	0.78	1.00	
Salinity (PSS)	0.37	0.37	0.46	0.23	0.56	0.50	-0.26	0.34	0.39	-0.33	0.00	-0.58	-0.48	-0.23	-0.51	0.38	0.53	1.00
Rainfall	0.89	0.89	0.60	0.69	0.58	0.83	0.26	0.70	0.66	-0.49	0.42	-0.26	-0.53	0.40	-0.39	0.71	0.53	0.25