

## Carbon isotopic and biochemical fingerprints of sedimentary organic matter in lower Narmada and Tapi, north-west coast of India

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### Abstract

Sources of organic matter (OM) in lower Narmada and Tapi river-estuaries were examined using organic carbon to nitrogen ratio ( $C_{org}/N$ ), stable carbon isotope ratio ( $\delta^{13}C_{org}$ ) and lignin phenol biomarkers. The signature of lower  $C_{org}$  (av. 0.50%) and higher  $\delta^{13}C_{org}$  (av. -20.3‰) in Narmada and, higher  $C_{org}$  (av. 0.85%) and lower  $\delta^{13}C_{org}$  (av. -22.8‰) in Tapi highlight the difference in OM characteristics of both systems, nevertheless they flow adjacent to each other. The OM in Tapi was predominated by fresh plant tissues, as indicated by higher  $\Lambda_8 = 1.2-3.2$  mg/100mg  $C_{org}$ , lower  $Ad/Al_v = 0.22-0.46$  and lower LPVI = 17-23. The plant OM present in the sediments of Narmada was previously degraded and mixed with soil. The OM contribution from algae was restricted to estuarine stations in both the rivers, which was ~50% in Narmada and ~35% in Tapi. The contribution of OM from fresh vascular plant was higher (20% to 63%) in Tapi than Narmada (2% to 35%). This study illustrated the benefits of using lignin phenols along with  $C_{org}/N$  and  $\delta^{13}C_{org}$  to identify the potential OM sources in two large river-estuary systems of India, which highlighted the complex interaction of natural and anthropogenic processes acted on the terrestrial OM compositions.

**Keywords:** Carbon isotope; lignin phenol; organic carbon; sediment; Narmada; Tapi

## 1. Introduction

Organic matter (OM) transported through river-estuary systems has potential implication towards global carbon cycle. The OM composition across the river-estuary continuum is critically influenced by local and global ecological perturbations<sup>1-2</sup>. The OM is primarily sourced from autochthonous (algae/plankton) and allochthonous (soil and plants) materials, filtered through the water column due to the action of various physicochemical and biological processes and eventually buried into sediments of river-estuary systems. The composition of OM plays an important role in the sustenance of benthic food web and ecology along the river-estuary systems. In tropical river-estuaries, the compositions of OM significantly influence the processes of microbial decomposition and mineralization, which lead to CO<sub>2</sub> out-gassing and nutrient re-generation, respectively<sup>3-5</sup>. The river borne OM also take part in pelagic and benthic carbon cycling, which thereby significantly influence the surface ocean productivity<sup>6-7</sup>. Therefore, knowledge on the OM composition across river-estuary continuum is essential for better understanding of role of the river borne terrigenous OM in marine carbon cycle.

Both natural and anthropogenic processes influence the OM composition across river-estuary systems in tropical region. Precipitation variability (excess and/or less rainfall) is the natural process that largely corresponds to hydrologic modification of river-estuary systems in tropics, which cause enhancement of diagenetically altered OM<sup>8-9</sup>. Similarly, anthropogenic processes such as dam construction, deforestation, excessive agriculture etc. cause input of increased amounts of algal OM and/or soil OM, which influence the OM cycling in river-estuary ecosystems<sup>10</sup>. In order to better identify the OM composition and their sources in sediment mixture, which will help in delineation of natural and anthropogenic processes, the organic geochemical tools such as C<sub>org</sub>/N (organic carbon to total nitrogen ratio) and  $\delta^{13}\text{C}_{\text{org}}$  (stable isotopic ratio of organic carbon) are widely used for numerous river-estuary systems<sup>11</sup>. Additional use of biomarker alongside of C<sub>org</sub>/N and  $\delta^{13}\text{C}_{\text{org}}$  provides relatively unambiguous information about complexities in mixed OM sources.

Biomarker such as lignin phenols are uniquely synthesized by terrestrial vascular plant and have complex molecular biopolymer characteristics that helps in better characterization of OM generated from terrestrial vascular plants and present in suspended particulate matter as well as sediments in river-estuary systems<sup>12-15</sup> and ocean<sup>16-17</sup>. The characterization of sedimentary OM in river-estuary systems of tropical Indian continental margins have previously been sparsely reported<sup>4,7,18-23</sup>. In this study, we attempt to understand the sedimentary OM composition across the lower reaches of two major river systems; Narmada and Tapi (north-west coast of India) by using

multiple geochemical proxies ( $C_{org}/N$ ,  $\delta^{13}C_{org}$  and lignin phenols). The Narmada and Tapi river basins are largest among the rivers of western peninsular India, also significantly contributes to the total amounts of fluvial sediment and carbon draining into the Arabian Sea from Indian subcontinent<sup>7 & 20</sup>. To date, there remains a considerable uncertainty in our understanding of the OM compositions in Narmada and Tapi river-estuary systems. Through this study, we aimed to provide useful background information by considering the fact that the river basins would inevitably be developed in future due to growing population, also the biogeochemical processes across these basins will be influenced by anthropogenic processes. Specific objectives of this study are to (i) determine the sources and distribution of sedimentary OM in the lower Narmada and Tapi river-estuaries; and (ii) understand the processes that control OM compositions in Narmada and Tapi.

## 2. Materials and Methods

### 2.1 Study area description

The catchments of Narmada ( $0.09 \times 10^6 \text{ km}^2$ ) and Tapi ( $0.06 \times 10^6 \text{ km}^2$ ) drain into the Gulf of Khambhat, across the north-east Arabian Sea (Figure 1). Rainfall over these river basins occurs mainly during south-west monsoon (SWM) i.e. from June to September of a year. The net delivery of sediment from both Narmada and Tapi river systems to the Arabian Sea is  $\sim 95 \times 10^6 \text{ t yr}^{-1}$ , which equals to  $\sim 30\%$  of total sediment supply by all the monsoonal rivers of India (excluding Indus, Ganges–Brahmaputra rivers)<sup>24</sup>. In order to safeguard the flood-prone deltaic region and to supply water during drought and/or non-monsoon period, two large dams: Sardar Sarovar and Ballabhsagar have been built on the mainstems of Narmada and Tapi, respectively (Figure 1). Present study was carried out along the lower reaches of these river-estuary systems i.e. after the Sardar Sarovar in Narmada and Ballabhsagar in Tapi. The mean annual rainfall across lower Narmada is relatively less ( $916 \pm 131 \text{ mm}$ ) as compared to that in lower Tapi ( $1335 \pm 211 \text{ mm}$ ). The land-use-land-cover along the lower reaches of both the systems is dominated by deciduous forest, agriculture and urbanized areas. Bahruchon Narmada and Surat on Tapi are the two urbanized cities with population densities 238 and 1440 inhabitants  $\text{km}^{-2}$ , respectively<sup>25</sup>. Lower rainfall and dam building across both the river systems have caused significant reduction in sediment load during the last decade<sup>24</sup>.

### 2.2 Sampling and analysis

Sediment samples were collected during August–September 2010 (SWM), using a Van–Veen grab ( $15 \text{ cm} \times 15 \text{ cm}$ ), from six locations (N1–N6) on Narmada and four locations (T1–T4) on Tapi river-estuary systems (Figure 1). Carbon end-members such as leaves and woods of dominant higher plants; *Tectonagrandis* (V1), agriculture plants; *Saccharum spp.* (V2), *Sorghum spp.* (V3), *Zea*

*mays* (V4), *Gossypium spp.* (V5), *Oryza sativa* (V6), river algae; *Anabaena ambigua* (V7), submerged aquatic grass; *Mayacaceae* (V8) and *Alismataceae* (V9) were picked from their litters along the river-estuary systems. Similarly, soils categorized as mountainous soils (S1-S3), agriculture soils (S4-S9) and river bank soils (S10-S12) were collected across both the river systems (Figure 1). The samples were immediately stored at 4°C, which were then freeze dried and homogeneously grinded using an agate mortar prior to the bulk chemical analyses in laboratory.

Contents of C<sub>org</sub> and TN (organic carbon and total nitrogen, respectively) were measured with an Elemental Analyzer (Vario ELIII; Elementar Co. Germany). The measurement for δ<sup>13</sup>C<sub>org</sub> in sample was carried out using an elemental analyzer (Finnigan EA 1112) interfaced with continuous flow isotope ratio mass spectrometer (Finnigan Delta plus XP IRMS; Thermo Fisher Scientific, USA) at State key Laboratory of Estuarine and Coastal Research, China. Prior to the analysis of C<sub>org</sub> and δ<sup>13</sup>C<sub>org</sub>, 1M concentrated hydrochloric acid (HCl) was added into the samples in order to remove inorganic carbon present in the samples. The samples were then oven-dried at 45°C prior to the measurement. TN was measured directly on untreated sample. The relative precision for C<sub>org</sub> and TN measurement was ±5% in this study, which was calculated by repetitive measurement of a specific sample. The analytical precision for δ<sup>13</sup>C<sub>org</sub> measurement was ± 0.1‰ and the results are expressed as per mil (‰) deviation relative to the Vienna–Pee Dee Belemnite (V-PDB) standard, which was calculated as follows;

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

Lignin phenols were extracted from sediment matrices using microwave assisted cupric oxide (CuO) digestion technique<sup>26</sup>. About 50–500 mg (depending on the C<sub>org</sub> content so as to have ~5 mg OC) of powdered samples were placed in acid-washed Teflon vessels, then added with copper (II) oxide powder, ferrous ammonium sulfate (Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>) and 8M NaOH. The vessels were Nitrogen-purged and put in a Microwave Accelerated Reaction System (MARS5; CEM) at 150°C for 90 minutes at pressure ranging between 55 and 70 PSI. A known amount of Ethylvanillin was then added and later used to check recovery. The recovery rate of Ethylvanillin was found 95±2% during this study. Samples were acidified to pH < 2 and phenolic monomers were extracted into 99:1 (V/V) ethyl acetate/petroleum ether, later analyzed as trimethylsilyl derivatives of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS)(99:1) by a gas chromatography (Agilent 6890N–FID). The lignin phenol concentration was quantified with calibration curves based on commercial standards (Sigma–Aldrich) and mean analytical precision of lignin parameters were ≤ 10%<sup>27&22</sup>. Total of eleven extracted phenol monomers were categorized

intofive groups viz. syringyl (S), vanillyl (V), cinnamyl (C), p-hydroxyl (P) and 3,5-dihydroxy benzoic acid (DHBA). The lignin phenol monomers and their use as potential indicators of different plant OM and diagenetic processes are presented in Table 1. The total lignin phenol is equals to sum of syringyl phenols mainly the particulars of angiosperm plant [S = syringaldehyde (Sl) + acetosyringone (Sn) + syringic acid (Sd)], vanillyl phenols, which are present in all terrestrial plants, [V = vanillin (Vl) + acetovanillon (Vn) + vanillic acid (Vd)] and cinnamyl phenols, which corresponds to non-woody tissues [C = p-coumaric acid (PCD) + ferulic acid (FAD)]. The total lignin phenol is expressed either as  $\Lambda 8$  (normalized with  $C_{org}$ ) and/or  $\Sigma 8$  (normalized with weight of the sediment) throughout this study<sup>28</sup>. A series of non-lignin products: *p*-Hydroxyphenols (*p*-hydroxybenzaldehyde (Pl) + *p*-hydroxyacetophenone (Pn) + *p*-hydroxybenzoic acid (Pd)) and 3,5-dihydroxybenzoic acid (DHBA) are also extracted through CuO oxidation procedure. The Pn can be derived from lignin, whereas Pl and Pd can also be derived from protein rich materials<sup>29</sup>, so Pn/P is often indicative of non-plant materials present in the SPM<sup>30</sup>. The development of maturing degree of terrestrial OM can be monitored through DHBA/V ratio, which has been commonly used as source indicator for terrestrial OM within soil horizons. Other possible sources of DHBA includes tannins and flavonoids. The DHBA/V can therefore indicate degradation state of plant OM in soil, as DHBA increases during advancement of plant cell decay<sup>31</sup>. The diagenetic nature of plant tissues within the sample was evaluated using ratios (Ad/Al)<sub>v</sub> (i.e. Vd/Vl) and (Ad/Al)<sub>s</sub> (i.e. Sd/Sl). The S/V and C/V ratios were used to determine the abundance of angiosperm vs. gymnosperm and/or woody vs. non-woody tissues in the sample<sup>28</sup>. The general paradigm of lignin degradation is C–S–V, where C is most labile and degrades faster than S and V. The degradation sequence is subjected to change during the processes such as sorption and/or soil OM incorporation<sup>32</sup>. Therefore, to avoid misinterpretation lead by the use of only S/V and C/V, the S, V and C further normalized with  $\Lambda 8$  to produce lignin phenol vegetation index (LPVI;), which firmly can indicate towards the actual diagenetic characteristics of lignin<sup>33</sup>. The LPVI is calculated as follows;

$$LPVI = \left[ \frac{S(S+1)}{(V+1)+1} \right] \times \left[ \frac{C(C+1)}{(V+1)+1} \right] \quad [\text{Eq. 2}]$$

One-way ANOVA (analysis of variance) was carried out after the Komogorov-Smirnov normality and homogeneity test to understand the significance of spatial variability in the sedimentary chemical parameters across the Narmada and Tapi. Statistical significance (95% ( $p \leq 0.05$ ) and 99% ( $p \leq 0.01$ )) of the variations in lignin phenol,  $\delta^{13}C_{org}$ ,  $C_{org}/N$ , TN and  $C_{org}$  were calculated. All the statistical analyses performed using SPSS 10.0 (Windows).

### 3. Results

#### 3.1 Elemental and isotopic properties

The contents of  $C_{org}$  were varied between 25.2% and 33.8% in the vegetation samples, with a lowest value of 17% found in algae *Anabaena ambigua*. The contents of  $C_{org}$  in soil samples were ranged between 0.17% and 1.41%, with higher values in agriculture soils. The ranges of  $C_{org}$  (0.4%–1.3%) and TN (0.01%–0.07%) in sediments of Tapi were higher than the ranges of  $C_{org}$  (0.2%–0.8%) and TN (0.01%–0.03%) in sediments of Narmada (Table 2). The ranges of  $C_{org}/N$  were nearly similar in sediments of Narmada (12.5–58.8) and Tapi (18.6–60.0). The  $\delta^{13}C_{org}$  of vegetation samples *Saccharum spp.* (V2), *Sorghum spp.* (V3) and *Zea mays* (V4) were higher and ranged between -11.5‰ and -12.8‰, which indicated plant of  $C_4$  nature. The  $\delta^{13}C_{org}$  in soil samples varied between -18‰ and -28.1‰, and largely dependent upon the overlying vegetation. The ranges of  $\delta^{13}C_{org}$  were found relatively lower in the sediments of Tapi (-25.6‰ to -20.9‰, mean:  $-22.9 \pm 1.9$ ‰) and higher in Narmada (-23.1‰ to -14.3‰, mean:  $-19.9 \pm 3.1$ ‰). The stations within the upper Tapi estuary (T1 and T2) have  $C_{org}$  content significantly ( $p \leq 0.05$ ; ANOVA) higher than the stations within upper Narmada estuary (N1 and N2). The sediments from the areas close to urban cities e.g. in the middle region of Tapi (at T3 near Surat) and Narmada (at N3 and N4 near Bharuch) have higher  $C_{org}/N$  ratio as compared to the other stations (Table 2; Figure 2). The  $\delta^{13}C_{org}$  values increased towards estuarine region in both the rivers, with an extremely higher value of -14.3‰ recorded at the sea end station of Narmada. The ranges of  $C_{org}/N$  and  $\delta^{13}C_{org}$  found in Narmada and Tapi sediments were within the limits of those found in river-estuary systems along tropical and non-tropical regions of the world (Table 3).

#### 3.2 Lignin phenol yield and compositional ratios

The range of  $\Sigma 8$  (mass normalized yield of eight lignin phenols (S+V+C)) was between 101 mg/10g dry wt. and 556 mg/10g dry wt. in the vegetation samples collected along Narmada and Tapi river-estuary systems. The  $\Sigma 8$  in sediment ranged broadly between 0.18 mg/10g dry wt. and 1.4 mg/10g dw (mean:  $0.6 \pm 0.5$  mg/10g dw.) in Narmada, whereas it ranged from 1.3 mg/10g dw. to 1.7 mg/10g dw. (mean:  $1.5 \pm 0.2$  mg/10g dw.) in Tapi. The values of  $\Lambda 8$  (i.e.  $C_{org}$  normalized yield of eight lignin phenols) were broadly ranged between 0.24 mg/100mg  $C_{org}$  and 2.0 mg/100mg  $C_{org}$  in Narmada, with average value lower ( $1.1 \pm 0.6$  mg/100mg  $C_{org}$ ) as compared to that in Tapi ( $\Lambda 8 = 1.2$ – $3.1$  mg/100mg  $C_{org}$ , mean:  $2.1 \pm 0.8$  mg/100mg  $C_{org}$ ). The range of C/V was lower in Narmada (0.07–0.47, mean:  $0.25 \pm 0.16$ ) as compared to that in Tapi (0.22–0.46, mean:  $0.33 \pm 0.1$ ). Similarly, the range of S/V was lower in Narmada (0.14–1.10, mean:  $0.71 \pm 0.35$ ) than Tapi (0.79–1.06, mean:  $0.91 \pm 0.12$ ).

The range of  $(Ad/Al)_V$  (acid to aldehyde monomers of V phenol) was higher in Narmada (0.48–0.90, mean:  $0.70 \pm 0.16$ ) as compared to that in Tapi (0.32–0.41, mean:  $0.36 \pm 0.03$ ). The range of  $P/(V+S)$  (ratio between total P-hydroxyl phenol to sum of V and S phenol) was larger in Narmada (0.15–0.92, mean:  $0.45 \pm 0.29$ ) than Tapi (0.27–0.39, mean:  $0.32 \pm 0.05$ ). The range of DHBA/V (ratio between DHBA and total V phenol) was nearly similar in Narmada (0.01–0.21, mean:  $0.1 \pm 0.08$ ) and Tapi (0.1–0.11, mean:  $0.1 \pm 0.01$ ). The range of Pn/P (ratio between *p*-hydroxyacetophenone and total P phenol) was higher in Narmada (0.07–0.21, mean:  $0.12 \pm 0.05$ ) compared to that in Tapi (0.06–0.09, mean:  $0.08 \pm 0.01$ ). The range of LPVI was much higher in Narmada (4–359, mean:  $176 \pm 158$ ) than Tapi (17–23, mean:  $19 \pm 3$ ). Spatial distribution of  $\Lambda_8$  in sediments indicated presence of higher plant OM in Tapias compared to Narmada (Figure 2). The average limits of  $\Lambda_8$ , S/V, C/V and  $(Ad/Al)_V$  found in the sediments from Narmada and Tapi are within the limits of those found in river-estuary systems along the tropical and non-tropical regions of world (Table 3).

## 4. Discussion

### 4.1 Characteristics and distribution of OM in Narmada and Tapi

The values of  $C_{org}/N$  usually exceed 23 in fresh terrestrial plant remains, and ranged between 4.7 and 11 in algae and  $\sim 4$  in bacteria<sup>12</sup>. The values of  $\delta^{13}C_{org}$  were lower in  $C_3$  plants ( $-22\%$  to  $-35\%$ ) and higher in  $C_4$  plants ( $-11\%$  to  $-15\%$ ) as well as algae ( $-22\%$  to  $-28\%$ ) are conducive to difference in the photosynthetic pathways of plants. The  $C_{org}/N$  ratio in sediments from Narmada and Tapi ranged broadly between 12.5 and 60.0, and  $\delta^{13}C_{org}$  ( $-14.3\%$  and  $-25.6\%$ ), altogether indicate OM generated from mixed source (i.e. mixture from plants ( $C_3$  and  $C_4$ ) and river/estuary algae). Except the  $C_{org}/N$  ratio which was higher than 50, the  $C_{org}/N$  ratio in the Narmada and Tapi ranged from 12.5 to 25.0. Both  $C_{org}/N$  and  $\delta^{13}C_{org}$  in natural environments such as river-estuary systems largely vary due to mixing of multiple sources of  $C_{org}$  therefore often provide ambiguous information about the source (Table 3). The elevated  $C_{org}/N$  (50.0–60.0) and higher  $\delta^{13}C_{org}$  ( $-20.3\%$  to  $-22.6\%$ ) at stations N3, N4 (upper Narmada estuary) and T3 (upper Tapi estuary) in the vicinity of urban cities indicate OM sourced from plant detritus and with less nitrogen compounds, which is in line with the higher  $\Lambda_8$  found in sediments of those stations (Figure 2). Domestic sewage has usually lower  $C_{org}/N$  (7–10), which is abundant with nitrogenous components<sup>34</sup>. The alternative explanation to this process could be degradation of OM and input of degraded soil OM, which preferentially increased the  $C_{org}/N$  ratio. OM degradation in soil due to in-sufficient rainfall and rapid land use change causes removal of lighter  $^{12}C$ , which increased the  $\delta^{13}C_{org}$  value<sup>35</sup>. The degraded soil OM presumably mobilized into these stations during wet discharge period in both the river-estuary systems.

The relative abundance of V, S and C phenols vary in different plant tissues. Therefore, the ratios S/V and C/V can be indicative of the presence of angiosperm vs. gymnosperm and woody vs. non-woody tissues, respectively<sup>12</sup>. The ranges of C/V and S/V in Narmada and Tapi highlights the OM derived from angiosperm, non-woody tissues, except at station N3, where a fraction of OM was derived from gymnosperm woody tissues (Figure 3a). The Lignin Phenol Vegetation Index (LPVI) is used to better understand the actual diagenetic state of plant OM in sediment. The use of LPVI has an advantage of providing relatively accurate information about plant OM degradation mechanism, against its evaluation based on only C/V and S/V ratio, because the C/V and S/V ratios can be altered during the OM decomposition, which may be due to the preferential and disproportionate removal of C and S phenols than V<sup>36</sup>. The ranges of LPVI found in Narmada and Tapi sediments indicated dominance of OM from woody angiosperm and non-woody gymnosperm plant tissues<sup>33</sup> (Table 1). Based on the relationship between C/V and S/V, samples from stations N5, N1 and T4 showed higher C/V and S/V and therefore indicates presence of non-woody angiosperm leaves and grass tissues in those sediments. On the other hand, the sediments from stations N6 and N3 (i.e. lower most and upper most estuarine station, respectively) showed dominance of gymnosperm wood tissues (Figure 3). Such disparity in the OM source information can be addressed by an alternative explanation that plant OM in these sediments have been preferentially degraded with specific phenols (C and S) during the course of transport and/or mixed with previously degraded material, presumably from soil. This is consistent with results of nearly similar mean C/V and S/V ratios but contrasting LPVI values in both the rivers (Table 2). Relatively higher LPVI in Narmada sediments as compared to that in Tapi is due to presence of more degraded plant OM in former. Plant OM degrades in soils due to bacterial or fungal action that alters its molecular composition<sup>37</sup>. The residual fraction of plant OM degrades further by microbial community after entering into river continuum and this process fuels gross respiration and out gassing of CO<sub>2</sub>. Such degraded plant OM (lignin) was abundant in sediments of Narmada than Tapi, which were also indicated by elevated ratios of P/(V+S) and (Ad/Al)<sub>v</sub> present in the sediments of Narmada (Table 2; Figure 3b). Besides, higher mean sedimentary  $\delta^{13}\text{C}_{\text{org}}$ , lower  $\Lambda_8$  and low S/V and C/V in Narmada indicated that a fraction of OM was mobilized from plants other than leaves, probably from soil<sup>38</sup>. Furthermore, the OM is humified in soils, which were indicated by nearly identical DHBA/V ratios in both the rivers. The DHBA/V > 0 indicated OM humification in soils<sup>36</sup>.

Inter-relationship among the lignin phenol indices such as LPVI, (Ad/Al)<sub>v</sub> and DHBA/V provide important insights into the mechanism of plant OM degradation. Figure-3c, showed a strong negative correlation between LPVI and (Ad/Al)<sub>v</sub> in Narmada ( $R^2 = -0.82$ ) as



compared to that in Tapi. This highlights the selective removal of C and S phenols from the sediments of Narmada. Alternatively, significant positive correlation between DHBA/V and LPVI ( $R^2=0.95$ ) was found in the sediments of Narmada as compared to that in Tapi, which reveal towards an ambiguity in lignin diagenesis that might have removed V instead of C or S (Figure 3d). However, such type of degradation is not unprecedented and could be possible during lignin diagenesis predominantly from acidic soils<sup>32</sup>. Our data do not rule out either possibility, as the ranges of LPVI were contrastingly different in both the river-estuary systems of this study (Table 2). Also, the sedimentary OM in both the systems presumably represents a long-term average that has undergone alteration off the stream as affected by natural (less rainfall) and anthropogenic (land use change) processes. However, this signal is not so clear in Tapi in this study. Relatively lower Pn/P in Tapi than Narmada is indicative of fraction of OM contributed by algae. This is because the aldehyde (p-hydroxybenzaldehyde) and acid (p-hydroxybenzoic acid) monomers of P phenol can be sourced from both plant and algae whereas; Pn is solely present in plant<sup>39</sup>. On an average, sediments from both Narmada and Tapi constitute a significant fraction of plant derived OM mixture preferentially degraded with labile components (C phenols) such as grass like tissues and relatively fresh (lower  $(Ad/Al)_v$ ) as compared to other rivers in tropics as well as non-tropical region of the world.

#### 4.2 Quantification of potential OM sources and their contributions

Figure 4a indicated that based on the compositional ranges of  $N/C_{org}$  (0.02 to 0.08) and  $\delta^{13}C_{org}$  (-14.3‰ to -25.5‰) present in the sediments from Narmada and Tapi, the OM in these systems originated from multiple sources such as  $C_3$  plants,  $C_4$  plants and algae. The use of  $N/C_{org}$  against  $C_{org}/N$  was preferred as to obtain statistically robust results in end member mixing models. This is because higher values of denominator (i.e.  $C_{org}$ ) behave linearly to maintain the consistency with carbon-normalized ratio such as  $^{13}C_{org}/^{12}C_{org}$  in the model calculation (i.e.  $\delta^{13}C_{org}$ )<sup>40-41</sup>. The catchments of Narmada and Tapi are dominated with  $C_3$  as well as  $C_4$  vegetation, therefore the signatures of  $\delta^{13}C_{org}$  in a mixture of  $C_3$  and  $C_4$  plants will yield ambiguous result, which can be isotopically indistinguishable from algae<sup>40-41</sup>. Furthermore, by doing so, the role of soil OM as observed by higher DHBA/V ratio in this study, will be underestimated. The soil OM that exhibit  $\delta^{13}C_{org}$  correspondingly with overlying vegetation will be underestimated if only the OM contributions from  $C_3$  plants,  $C_4$  plants and algae are evaluated. Therefore, the use of lignin phenol helped us to delineate among complex isotopic signatures of the mixture of  $C_3$  and  $C_4$  plants vs. algae. The  $C_3$  and  $C_4$  plants have distinct  $\delta^{13}C_{org}$  but nearly similar  $N/C_{org}$ , whereas the river/estuarine algae have identical  $N/C_{org}$ , but exhibit different  $\delta^{13}C_{org}$  (< -22‰ to < -28‰) due to differences in the concentrations and sources of dissolved inorganic carbon in them<sup>41</sup>. Therefore,

taking N/C<sub>org</sub> of both C<sub>3</sub> and C<sub>4</sub> plants as vascular plant end member with fresh tissues we can estimate the overall contribution of fresh plant OM to the sediment. Plant OM mobilized through soil undergoes degradation, which preferentially alter  $\Lambda 8$  values significantly as compared to the signatures of N/C<sub>org</sub> and  $\delta^{13}\text{C}_{\text{org}}$ . Therefore, the soil contains relatively less lignin and a N/C<sub>org</sub> between plant mixture (C<sub>3</sub> and C<sub>4</sub>) due to plant OM degradation. This is in contrast with fresh tissues from C<sub>3</sub> and C<sub>4</sub> plants those contain higher lignin phenols ( $\Lambda 8 > 5$  mg/100mgOC) and lower N/C<sub>org</sub> ratio. The algae don't synthesize lignin phenol and produce higher N/C<sub>org</sub> ratio ( $> 0.13$ )<sup>38 & 41</sup>. The compositional limit of vascular plant, soil and algae along with the sediment samples from Narmada and Tapi is shown in Figure 4b. The N/C<sub>org</sub> and  $\Lambda 8$  values of end-members were; vascular plant (0.015 and 5 mg/100mgC<sub>org</sub>), soil (0.04 and 0.3 mg/100mgC<sub>org</sub>) and algae (0.14 and 0.009 mg/100mgC<sub>org</sub>) collected from literature and this study. The relative contribution of different OM end-members/sources are calculated based on simple mixing model below.

$$f_{\text{plant}} + f_{\text{soil}} + f_{\text{algae}} = 1 \quad [\text{Eq. 3}]$$

$$f(\text{N/C}_{\text{org}})_{\text{plant}} + f(\text{N/C}_{\text{org}})_{\text{soil}} + f(\text{N/C}_{\text{org}})_{\text{algae}} = (\text{N/C}_{\text{org}})_{\text{sample}} \quad [\text{Eq. 4}]$$

$$f(\Lambda 8)_{\text{plant}} + f(\Lambda 8)_{\text{soil}} + f(\Lambda 8)_{\text{algae}} = (\Lambda 8)_{\text{sample}} \quad [\text{Eq. 5}]$$

Where  $f_{\text{plant}}$ ,  $f_{\text{soil}}$  and  $f_{\text{algae}}$  are the fractions of OM derived from fresh vascular plant tissues (C<sub>3</sub> as well as C<sub>4</sub>), soil containing relatively degraded plant tissues and algae, respectively. The individual percentage of OM contribution is normalized to 100% in order to achieve mass balance. The sensitivity of the model was examined by altering the elemental and biomarker compositions of end-members ( $\pm 2\sigma_{\text{sd}}$ ). Absolute errors for end-members are estimated as ~15% for vascular plants and soil and 18% for algae. The contribution of degraded plant OM mobilized through soil was found to be ~40–97% in Narmada compared to 3–60% in Tapi (Figure 4c). The distribution indicated stations close to the urban cities have more degraded plant OM compared to the stations in upper and lower reaches. Contributions of algae is limited to the estuarine stations in both the rivers and found to be ~50% in Narmada and ~35% in Tapi. Contribution of OM from fresh vascular plant is predominated in Tapi (20–63%) compared to Narmada (2–35%) (Figure 4c).

The collective results of this study indicated that a substantial portion of OM in sediments from Narmada originated from degraded plant OM mobilized through soil, owing to the intensive land use change practice that is prevalent throughout the west coast of India. Other potential cause for this is the declined natural fluvial load to the river basin due to construction of dams and paucity of rainfall,

which probably gave rise to higher soil input to the aquatic sediment, especially during high discharge period<sup>42</sup>. The degraded plant OM mobilized through soils will no longer be a food source to the biological community, also it will restrict further re-mineralization in riverine as well as in coastal environment. This whole process will affect the terrestrial and oceanic carbon cycling in the adjacent Arabian Sea. Therefore, this study indicating response of terrigenous OM to the interaction of natural and anthropogenic processes in large tropical monsoon-fed Indian river systems, highlights the importance of further studies, which will be helpful to assess the information on potential implication of terrestrial OM delivery from monsoonal systems and its fate in river-estuary systems prior to their delivery into the oceanic carbon cycling across Indian continental margin.

## 5. Conclusion

Based on the changes in elemental, isotopic and molecular properties of sediment in Narmada and Tapi we draw the following conclusions:

- (1) The sedimentary OM in Narmada and Tapi is derived from mixed sources: vascular plants (C<sub>3</sub> and C<sub>4</sub>), soil and algae. The compositional ratios of lignin phenols indicated that plant OM has undergone degradation and mobilized through soil into the sedimentary environment;
- (2) Results of end member mixing model indicated that contribution of degraded plant OM mobilized through soil was ~40% –97% in Narmada and 3% –60% in Tapi. Contributions OM from algae is limited to the estuarine stations in both the rivers and found to be ~50% in Narmada and ~35% in Tapi. Contribution of OM from fresh vascular plant is predominated in Tapi (20% - 63%) as compared to Narmada.
- (3) Lignin phenol concentrations and compositional ratios indicate that sedimentary OM is dominated by woody and non-woody angiosperm plant tissues, with preferentially degraded phenols in them. The plant OM mobilized through soil is influenced by land-use modifications and affected by humification in soil environment.

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## Figure Caption

**Figure 1:** Study area map: location of sampling stations on lower reaches of Narmada and Tapi river systems.

**Figure 2:** Spatial distribution of bulk elemental isotopic and biomarker properties in sediments from Narmada and Tapi river system. Solid black and white circles are sediment samples from Narmada and Tapi River respectively. The station numbers are depicted close to the data points.

**Figure 3:** (a) Property–property plot of C/V and S/V ratio with compositional ranges of different plant tissues which is adopted from literature<sup>12</sup>; (b) Plot of oxidative degradation of V and S phenol monomers in sediment samples, the compositional range of fresh plant tissues is from literature<sup>29</sup>; (c) Negative correlation between LPVI and degradation of V phenol indicating LPVI is a function of plant organic matter degradation in Narmada sediment and (d) Positive correlation between LPVI and degradation of plant OM in soil indicating non-preferential diagenesis of lignin monomers in soil due to land use change associated humification process.

**Figure 4:** Property-property plots of (a)  $C_{org}/N_{vs} \delta^{13}C_{org}$  (b)  $\Lambda_8$  vs.  $C_{org}/N_{in}$  in the sediments from Narmada and Tapi along with potential OM sources ( $C_3$  plant,  $C_4$  plant and algae). (c) Calculated proportion OM contributed from different sources to the sediment based on the results of end-member mixing model.

## Table Captions

**Table 1:** Use of lignin and non-lignin phenol yields and compositional ratios in aquatic environmental studies and their interpretation.

**Table 2:** Elemental, isotopic and biochemical marker properties of plants, soils, algae and sediments collected from the Narmada and Tapi river-estuary system. Vegetation samples are categorized as: higher plant; *Tectonagrandis* (V1), agriculture plants; *Saccharum spp.* (V2), *Sorghum spp.* (V3), *Zea mays* (V4) *Gossypium spp.* (V5), *Oryza sativa* (V6), river algae; *Anabaena ambigua* (V7), submerged aquatic grass; *Mayacaceae* (V8) and *Alismataceae* (V9). Soils are categorized as mountainous soils (S1-S3), agriculture soils (S4-S9) and river bank soils (S10-S12).

**Table 3:** Comparison of elemental and isotopic ratios of organic carbon and lignin phenol ratios in some of the river-estuary sediments from tropical and non-tropical regions of the world.



**Table 1**

Definition	Notation	Potential indicator of sources
Syringyl phenol (Syringaldehyde (C <sub>9</sub> H <sub>10</sub> O <sub>4</sub> )+acetosyringone (C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> )+syringic acid (C <sub>9</sub> H <sub>10</sub> O <sub>5</sub> ))	S	Present in angiosperm woody and non-woody plant tissues, traces occasionally found in non woody gymnosperm tissues.
Vanillyl phenols (vanillin (C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> ), acetovanillone (C <sub>9</sub> H <sub>10</sub> O <sub>3</sub> ) and vanillic acid (C <sub>8</sub> H <sub>8</sub> O <sub>4</sub> ))	V	Present in all type of plant but exclusively found in gymnosperm woody tissues.
Cinnamyl phenols (p-coumeric acid (C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> ) and ferulic acid (C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> ))	C	Present in non-woody tissues of gymnosperm and angiosperm plants (e.g. grasses and leaves)
p-hydroxyl phenols (p-hydroxybenzaldehyde (Pl:C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> ), p-hydroxyacetophenone (Pn:C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> ) and p-hydroxybenzoic acid (Pd:C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> ))	P	Pn is lignin derived mainly from gymnosperm and non-woody angiosperm plant tissues. Pl and Pd can also sourced from non-lignin compounds such as protein rich plankton and bacteria.
3,5-dihydroxy benzoic acid (C <sub>7</sub> H <sub>6</sub> O <sub>4</sub> )	DHBA	Present in soils (both mineral and vegetation mediated), also found in estuarine brown macro algae.
Carbon normalized lignin yield (unit: mg/100mgOC)	Δ8	Relative fraction of terrigenous vascular plant organic matter to total organic carbon in sample.
Mass normalized lignin yield (unit: mg/10g dry wt.)	Σ8	Relative abundance of terrigenous vascular plant organic matter in sample
Ratio between syringyl and vanillyl phenols	S/V	S/V=0 (gymnosperm plant tissues); S/V=1–6 (angiosperm plant tissues) <sup>12,16</sup>
Ratio between cinnamyl and vanillyl phenols	C/V	C/V <0.1 (woody-plant tissues); C/V >0.1 (non-woody plant tissues) <sup>12,16</sup>
Ratio between vanillic acid and vanillin	(Ad/Al) <sub>v</sub>	Oxidative degradation of V phenol by white rot fungi and bacteria. (Ad/Al) <sub>v</sub> <0.3 (non-degraded/ fresh tissues); (Ad/Al) <sub>v</sub> >0.6 (degraded plant tissues) <sup>16,22</sup>
Ratio between syringic acid and Syringaldehyde	(Ad/Al) <sub>s</sub>	Oxidative degradation of S phenol by white rot fungi and bacteria. (Ad/Al) <sub>s</sub> <0.14 (non-degraded/ fresh tissue); (Ad/Al) <sub>s</sub> >0.16 (degraded plant tissues) <sup>16,22</sup>
Ratio between total p-hydroxyl phenols and sum of totalvanillyl and syringyl phenols	P/(V+S)	Degradation V and S phenols due to demethylation by brown rot fungi. Increased ratio indicative of diagenesis of plant organic matter <sup>2</sup>
Ratio between p-hydroxyacetophenone and total p-hydroxy phenols	Pn/P	Indicator of autochthonous production, as Pn is solely generated by vascular plants, whereas Pl and Pd can be sourced from plant as well as plankton/bacteria <sup>21</sup>
Ratio between 3,5-dihydroxy benzoic acid and total V phenol	DHBA/V	Indicator of lignin degradation due to humification. DHBA/V of fresh plant litter in soil equal to zero; DHBA/V ~0.05 is for vegetated soil and DHBA/V>0.8 is for mineral rich soil <sup>17</sup>
Lignin phenol vegetation Index	LPVI	Indicator of plant lignin diagenesis during degradation of plant tissues. LPVI=1 (gymnosperm wood); 12-27 (non-woody gymnosperm tissues); 67-415 (angiosperm woods) and 378-2782 (non-woody angiosperm tissues) <sup>12</sup> .

**Table 2:** Elemental, isotopic and biochemical marker properties of plants, soils, algae and sediments collected from the Narmada and Tapti river-estuary system. Vegetation samples are categorized as: higher plant; *Tectonagrandis* (V1), agriculture plants; *Saccharum spp.* (V2), *Sorghum spp.* (V3), *Zea mays* (V4) *Gossypium spp.* (V5), *Oryza sativa* (V6), river algae; *Anabaena ambigua* (V7), submerged aquatic grass; *Mayacaceae* (V8) and *Alismataceae* (V9). Soils are categorized as mountainous soils (S1-S3), agriculture soils (S4-S9) and river bank soils (S10-S12).

### Plants

Sample	V1	V2	V3	V4	V5	V6	V7	V8	V9
OC (%)	32.5	33.8	35.1	32.0	31.6	31.0	17.0	26.1	25.2
TN	0.52	0.92	1.01	1.22	2.34	1.71	2.25	2.43	2.30
C/N	62.7	36.9	34.8	26.3	13.5	18.1	7.5	10.7	10.9
$\delta^{13}\text{C}$ (‰)	-28.3	-12.8	-11.5	-11.5	-28.5	-29.5	-20.1	-14.9	-12.7
$\Sigma 8$ (mg/10g dw)	123.4	555.6	332.5	415.7	107.2	178.6	9.5	101.3	171.8
$\Delta 8$ (mg/100mg OC)	3.80	16.44	9.47	12.99	3.39	5.76	0.56	3.88	6.82
S/V	0.71	0.57	0.54	0.63	0.95	1.25	0.59	0.04	2.64
C/V	0.16	0.87	0.85	0.63	0.56	1.48	0.11	0.02	0.38
(Ad/Al) <sub>v</sub>	0.55	0.59	1.13	1.24	0.62	0.29	0.10	5.36	0.38
P/V+S	0.40	0.10	0.84	0.09	0.38	0.28	2.18	0.17	0.11
DHBA/V	0.08	0.01	0.02	0.01	0.30	0.03	1.18	0.11	0.14
Pn/P	0.25	0.18	0.14	0.21	0.04	0.20	0.05	0.34	0.07
LPVI	69	466	421	356	505	2525	40	1	811

### Soils

Station	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
OC	1.24	0.17	0.40	1.04	1.41	0.90	0.94	1.23	1.20	0.19	0.20	0.22
TN	0.13	0.01	0.03	0.09	0.10	0.06	0.08	0.06	0.12	0.02	0.01	0.02
C/N	9.8	19.3	12.4	12.2	14.4	14.0	12.1	19.5	10.4	11.9	15.7	11.0
$\delta^{13}\text{C}$ (‰)	-22.3	-23.7	-25.0	-23.8	-21.1	-19.4	-18.0	-20.6	-19.5	-28.1	-25.2	-25.8
$\Sigma 8$ (mg/10g dw)	1.67	0.13	0.16	1.80	2.48	1.30	1.23	0.40	1.62	0.03	0.01	0.17
$\Delta 8$ (mg/100mg OC)	1.35	0.76	0.39	1.73	1.76	1.44	1.31	0.32	1.35	0.14	0.06	0.78
S/V	0.41	1.62	0.28	1.07	0.39	0.98	1.08	0.78	0.92	0.33	0.30	0.37
C/V	0.14	0.50	0.13	0.25	0.21	0.45	0.57	0.36	0.38	0.20	0.31	0.28
(Ad/Al) <sub>v</sub>	0.67	0.58	0.36	0.40	0.39	0.35	0.53	0.73	0.31	0.97	1.19	0.65
P/V+S	0.49	0.98	1.03	0.23	0.16	0.70	0.19	0.32	0.55	1.39	1.20	0.45
DHBA/V	0.09	0.08	0.08	0.14	0.13	0.10	0.10	0.47	0.09	0.18	0.10	0.05
Pn/P	0.10	0.06	0.02	0.17	0.17	0.05	0.18	0.19	0.07	0.07	0.07	0.25
LPVI	30	777	15	193	41	385	606	211	285	32	49	56

## River-estuary sediments

Station	Narmada						Tapti			
	Estuary			River			Estuary		River	
	N6	N5	N4	N3	N2	N1	T4	T3	T2	T1
OC (%)	0.40	0.80	0.40	0.70	0.20	0.50	0.40	0.60	1.30	1.10
TN (%)	0.03	0.03	0.01	0.01	0.01	0.03	0.02	0.01	0.07	0.06
C/N	12.5	25.0	58.8	50.0	22.8	16.7	22.2	60.0	20.0	18.6
$\delta^{13}\text{C}$ (‰)	-14.3	-20.3	-22.7	-20.3	-21.1	-23.1	-22.1	-22.5	-20.9	-25.6
$\Sigma 8$ (mg/10g dw)	0.33	0.19	0.56	1.40	0.18	0.54	1.26	1.42	1.60	1.74
$\Delta 8$ (mg/100mgOC)	0.82	0.24	1.40	2.00	0.91	1.08	3.15	2.37	1.23	1.58
S/V	0.14	0.89	0.91	0.54	0.88	1.10	1.06	0.82	0.92	0.79
C/V	0.07	0.47	0.19	0.10	0.25	0.39	0.46	0.28	0.32	0.22
(Ad/Al) <sub>v</sub>	0.84	0.90	0.58	0.77	0.60	0.48	0.36	0.32	0.41	0.35
P/V+S	0.24	0.92	0.24	0.15	0.56	0.44	0.31	0.39	0.31	0.27
DHBA/V	0.03	0.21	0.07	0.01	0.11	0.16	0.10	0.11	0.11	0.10
P <sub>n</sub> /P	0.16	0.07	0.11	0.21	0.10	0.08	0.09	0.06	0.09	0.08
LPVI	4	369	118	32	156	359	18	23	18	17

**Table 3:** Comparison of elemental and isotopic ratios of organic carbon and lignin phenol ratios in some of the river-estuary sediments from tropical and non-tropical regions of the world.

River(country)	C/N T	d13C T	L8 T	CV T	SV T	AdAIV T	Ref.
<i>Tropical region</i>							
Godavari (India)	16.9±7.6	-24.2±1.8	2.90±1.7	0.55±0.6	1.00±0.2	0.50±0.2	Pradhan et al., 2014a
Minor rivers (India)	18.5±4.5	-25.4±0.8	4.33±1.9	0.22±0.0	1.13±0.2	0.52±0.1	Pradhan et al., 2014b
Savarmati (India)	16.5±3.0	-17.3±0.1	0.30±0.1	0.50±0.4	1.30±0.6	0.80±0.2	Pradhan et al., 2014b
Kapus (Indonesia)	19.5±17.7	-29.3±0.6	1.50±0.7	0.60±0.3	0.80±0.2	1.20±0.4	Loh et al., 2012a
Landak (Indonesia)	28.8±8.8	-29.4±0.3	1.10±0.5	0.50±0.1	0.80±0.1	1.10±0.3	Loh et al., 2012a
Mempawah (Indonesia)	22.0±11.3	-28.7±0.7	2.30±0.8	0.60±0.1	0.80±0.1	1.10±0.3	Loh et al., 2012a
Wenchang (Hainan, China)	10.2±4.8	-23.3±2.7	2.90±1.8	0.20±0.1	0.90±0.1	0.80±0.9	Bao et al., 2013
Narmada (India)	33.3±19.9	-22.9±2.0	2.12±0.9	0.33±0.1	0.91±0.1	0.36±0.0	This study
Tapti (India)	32.1±18.9	-19.9±3.2	1.09±0.6	0.25±0.2	0.71±0.3	0.70±0.2	This study
<i>Non-tropical region</i>							
Mississippi	10.5±1.0	-23.7±0.8	1.64±0.5	0.03±0.0	0.93±0.3	0.27±0.1	Bianchi et al., 2002
Rio Tapajós	15.0±		4.80±2.5	0.13±0.0	0.85±	0.45±	
Amur			0.10±0.0	0.37±0.2	0.53±0.4	2.71±0.6	
Colombia	16.8±4.9	-24.8±1.2	2.18±1.5	0.22±0.2	0.41±0.2		
Delaware	12.5±4.0	-21.7±1.4	4.37±3.7	0.42±0.2	0.49±0.3		
Broadkill	13.4±3.1	-18.9±0.6	4.44±2.8	0.29±0.1	0.30±0.1		
Fjord	20.1±7.5	-26.9±1.2	6.35±2.1	0.11±0.1	1.20±0.1	0.27±0.2	
Koping	11.4±5.7	-24.8±0.7	1.00±0.3	1.81±0.2	0.82±0.1	2.49±1.0	Loh et al., 2012b
Yangtze (China)	14.7±10.1	-24.0±0.1	2.3±1.6	0.2±0.1	1.0±0.7	0.79±0.5	Li et al., 2014

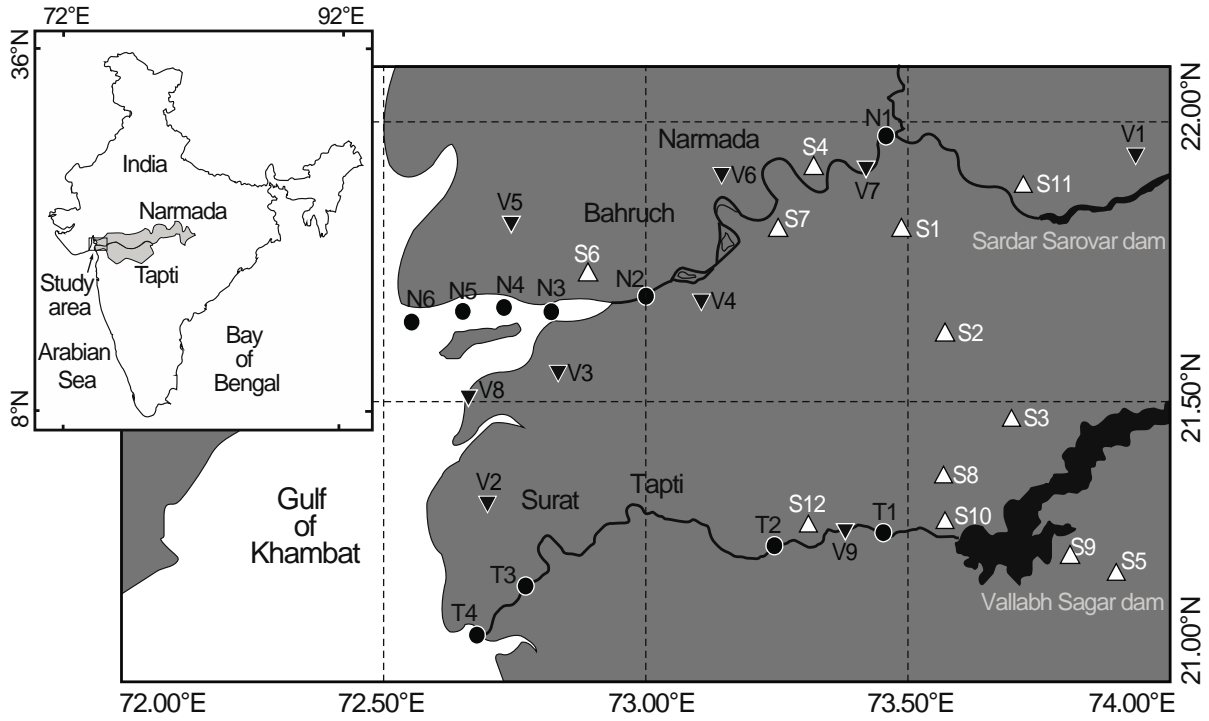


Figure 1

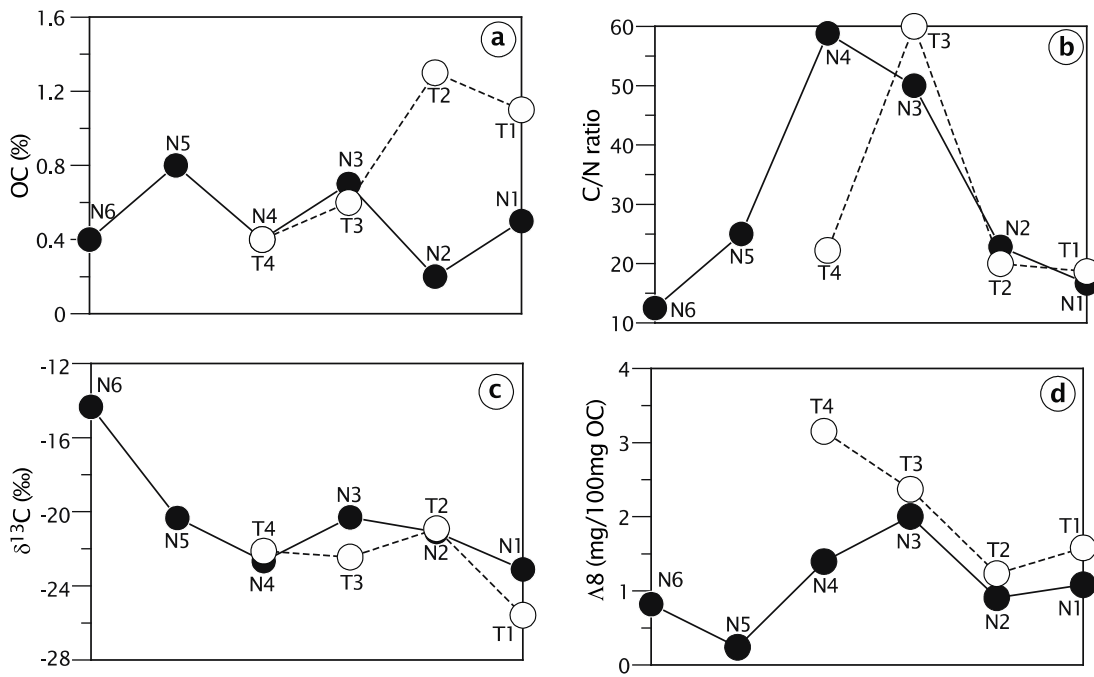


Figure 2

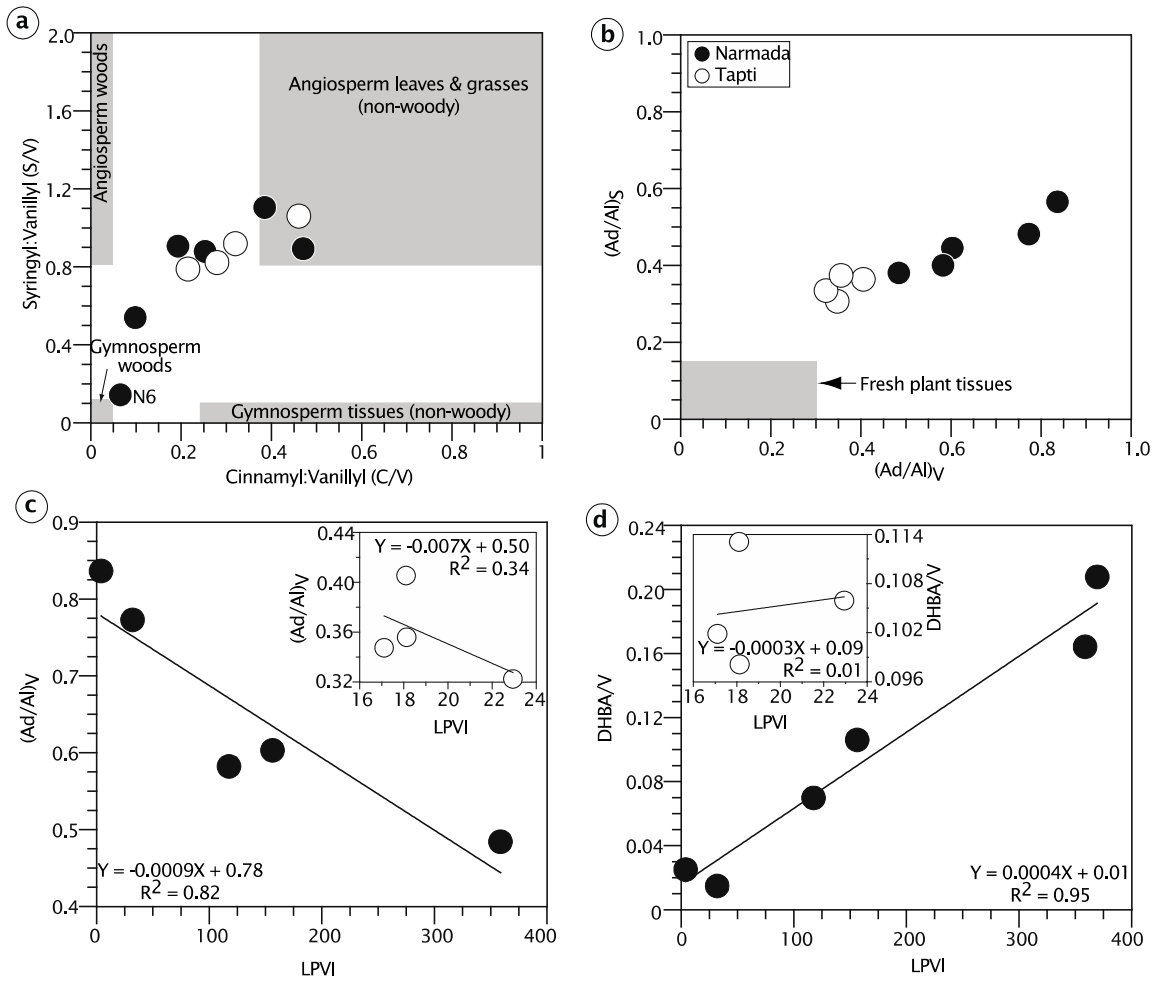


Figure 3

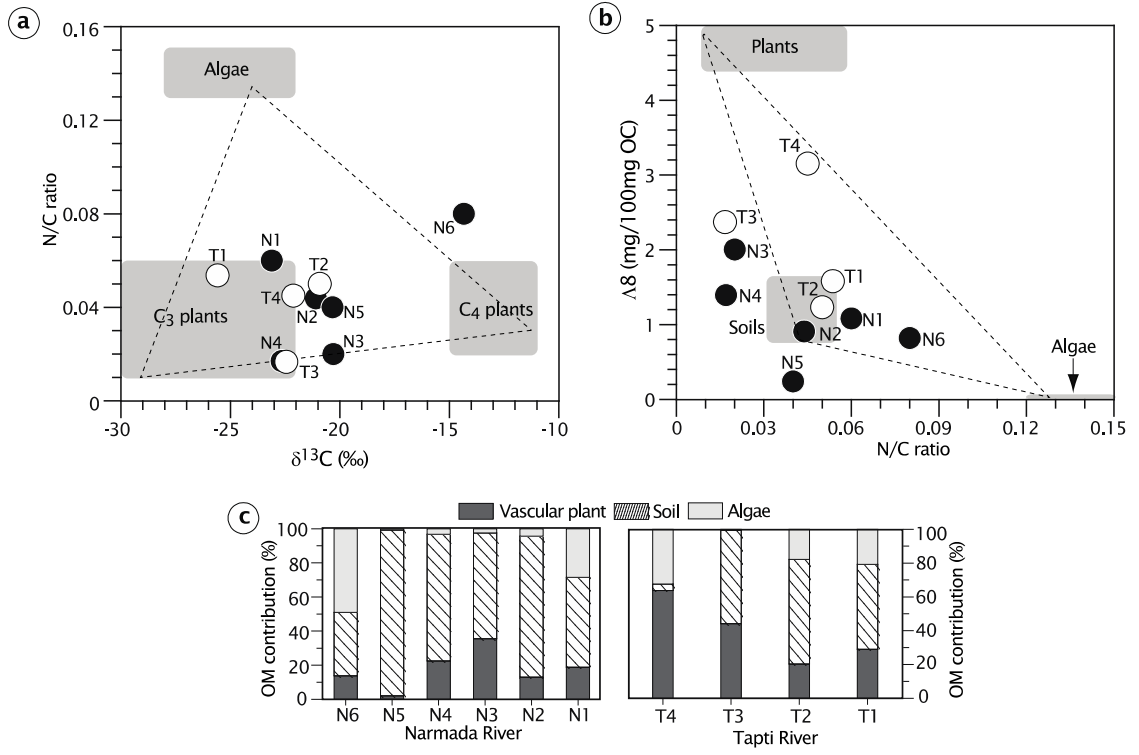


Figure 4