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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 ($\delta^{13}C$) 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 provenance 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 plants 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 ($(Ad/Al)_V$ = 0.4–0.6 and DHBA/V = 0.16–0.34) 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 $\delta^{13}C$ values for evaluating land use changes and the impacts of land use changes on aquatic ecosystems.

1. Introduction

The decomposition and eventual burial of organic matter (OM) in estuarine and coastal regions plays an important constraint on atmospheric CO_2 levels (Mackenzie, 1981; Liu et al., 2010). 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 CO_2 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

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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 $\delta^{13}C$ respectively) and C/N ratio are widely used tracers to quantify the sources and pathways of OM in estuarine sediments (Thornton and Mc Manus, 1994; Canuel et al., 1995; Graham et al., 2001; Hu et al., 2006 and references therein). The relative abundances 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 $\delta^{13}C$, is that it can be used to determine the terrestrial sources of OM in estuarine and coastal environments (Goñi et al., 1998; Bianchi et al., 2002, 2011). The compositional ratios of lignin phenols and their monomers (e.g., cinnamyl (C), vanillyl (V) and syringlyl (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. Because 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 by originating from the Western Ghats and 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, 1997; Panigrahy et al., 2010; Roy and Srivastava, 2012). This study aims to (1) investigate the distribution of sedimentary OM in estuaries along the WCI, (2) elucidate the sources of OM to estuarine sediments, and (3) 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: ~10^5 km^2) and Tapti (~10^4 km^2) are the two major rivers in this region along with numerous small rivers (watershed area: $\leq 10^3$ km^2), flowing into the eastern Arabian Sea. The range of length to elevation ratio (L/H) of WCI rivers varies from 0.07 to 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 ~7×10^{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, Fig. 1). Annual rainfall varies from 600 to >5000 mm (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 (~21°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 mg ha^{-1} yr^{-1}) than that in the Precambrian/lateritic region (10–15 mg ha^{-1} 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 Fig. 1). The percentage of dense forest, C_3, and C_4 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 plowed agriculture field), and mining (dredged mine tailings). Sediments were collected from middle of the estuary by boat using a Van-Veen grab (15 × 15 cm) during neap tide (average tidal height: 1–1.5 m). Sampling was undertaken in 2008 and 2009 during the early post monsoon season (October), when >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 $\delta^{13}C$ 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, ±5%) were measured in elemental analyzer (CHNOS; Vario EL III). Stable carbon isotope ratios ($^{13}C/^{12}C$) 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 $\delta^{13}C$ was ±0.1‰. Results are expressed as per mil (‰) deviation relative to the Vienna–Pee Dee Belemnite (V-PDB) standard and as defined below.

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

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