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Comparative organic geochemistry of Indian margin (Arabian Sea) sediments: estuary to continental slope

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Abstract

Surface sediments from sites across the Indian margin of the Arabian Sea were analysed for their carbon and nitrogen compositions (elemental and stable isotopic), grain size distributions and biochemical indices of organic matter (OM) source and/or degradation state. Site locations ranged from the estuaries of the Mandovi and Zuari rivers to depths of ~ 2000 m on the continental slope, thus spanning nearshore muds and sands on the shelf and both the semi-permanent oxygen minimum zone (OMZ) on the upper slope (~ 200–1300 m) and the seasonal hypoxic zone that impinges on the shelf. Source indices showed mixed marine and terrigenous OM within the estuaries, and overwhelming predominance (80 %+) of marine OM on the shelf and slope. Thus, riverine OM is heavily diluted by autochthonous marine OM and/or is efficiently remineralised within or immediately offshore of the estuaries. Any terrigenous OM that is exported appears to be retained in nearshore muds; lignin phenols indicate that the small terrigenous OM content of slope sediments is of different origin, potentially from rivers to the north. Organic C contents of surface shelf and slope sediments varied from < 0.5 wt % in relict shelf sands to over 7 wt % at slope sites within the OMZ, decreasing to ≤ 1 wt % at 2000 m. Major variability (~ 5 wt %) was found at slope sites within the OMZ of similar depth and near-identical bottom-water oxygen concentration. A strong relationship between organic C and sediment grain size was seen for sediments within the OMZ, but lower C loadings were found for sites on the shelf and below the OMZ. Diagenetic indices confirmed that lower C content below the OMZ is associated with greater extent of OM degradation, but that C-poor shelf sediments are not consistently more degraded than those within the OMZ. Together, the results indicate that OM enrichment on the upper slope can be explained by physical controls (winnowing and/or dilution) on the shelf and progressive OM degradation with increasing oxygen exposure below the OMZ. Reduced oxygen exposure may contribute to OM enrichment at some sites within the OMZ, but hydrodynamic processes are the overriding control on sediment OM distribution.

BGD
11, 3387–3422, 2014

1 Introduction

The Arabian Sea is exceptional both for the monsoons that drive intense, seasonally variable productivity, and for its mid-depth oxygen minimum zone (OMZ, ~ 200–1300 m). The ring of organic-matter-rich sediments that lines the margins of the Arabian Sea coincides roughly with the OMZ, a feature that led O_2 availability to be proposed as the primary control on sediment organic matter (OM) distributions (e.g. Paropkari et al., 1992, 1993; van der Weijden et al., 1998), and the Arabian Sea OMZ to be suggested as the modern equivalent of settings with OM-rich deposits found in the geological record (Demaison and Moore, 1980). However, the margins of the Arabian Sea differ markedly in productivity, and OMZ sediments experience differing degrees of O_2 depletion and thus have different benthic communities and degrees of bioturbation (Cowie, 2005). There is also variability in the magnitude and location (depth range) of sediment organic C maxima. Moreover, there is often a mismatch in the depths of C maxima and O_2 minima, and major variability in C content can occur without parallel variability in O_2 (e.g. Pedersen et al., 1992; Calvert et al., 1995; Cowie et al., 1999, 2009). This and other evidence has led to multiple other (interrelated) factors, including productivity, winnowing and cross-margin sediment transport, bottom topography and OM-mineral interactions (etc) to be invoked as important contributing controls. The interactions and relative importance of these factors remain the subject of considerable research and debate (Cowie, 2005, and references therein).

A further potential influence on margin sediment OM content and composition is OM source. A notable feature of the Arabian Sea is that sediments from all margins have generally been shown to contain OM that is overwhelmingly of marine origin, often even in nearshore shelf sediments. This is perhaps not surprising for the western margins (e.g. Smallwood and Wolff, 2000), where there are no major rivers depositing sediments. However, on the basis of stable isotopic, biomarker and petrographic evidence, it also appears to be true even of the Pakistan margin, directly offshore of the Indus River (e.g. Cowie et al., 1999; Schulte et al., 2000; Jeffreys et al., 2009) and for

BGD
11, 3387–3422, 2014

the Indian margin (e.g. Calvert et al., 1995; Agnihotri et al., 2008; Kurian et al., 2013). The damming of the Indus, completed in the 1970s, dramatically reduced sediment export (e.g. Syvitski and Milliman, 2007), which might explain present-day paucity of terrigenous OM in offshore sediments. However, the same marine predominance is also found throughout Holocene sediment records from the Pakistan margin (e.g. Schubert et al., 1998). For the Indian margin, the lack of a clear terrigenous OM signature in shelf and slope sediments is perhaps surprising given the number of significant rivers that discharge on the western Indian coast, and have particularly large runoff during the SW monsoon periods. The fate of the suspended sediments from these rivers, and if/how they contribute to shelf and slope OM deposits, remain unclear.

The Indian margin is also of particular interest because, in addition to the semi-permanent mid-depth OMZ that impinges on the upper slope, a belt of intense O_2 depletion develops from south to north along the entire western Indian shelf during the summer monsoons, usually peaking in September–October (Naqvi et al., 2000, 2006, 2009). This represents the largest coastal hypoxic zone on Earth, and a further potential influence on shelf sediment OM content and composition.

However, previous assessments of sediment OM distributions on the Indian margin have lacked either comprehensive cross-margin sampling or systematic determination of parameters necessary to delineate OM source and degradation state, as well as content. We present here results from a range of analyses of sediments taken from transects spanning the western Indian margin (off Goa), from estuaries to the continental shelf and across the upper slope, spanning both the seasonal coastal hypoxic zone and the semi-permanent OMZ on the continental slope. The broader objective was to elucidate the interactions and relative importance of factors including source, hydrodynamic processes and O_2 availability as OM distributional controls.

BGD
11, 3387–3422, 2014

2 Methods

2.1 Setting, sampling locations and methods

Sediment samples were collected at sites across the upper Indian continental margin, from various points within the estuary confluence of the Mandovi and Zuari rivers (Fig. 1a) and across transects spanning the shelf and/or upper slope (to ~ 2000 m), north, offshore and south of the mouth of the Mandovi/Zuari estuary (Fig. 1b and c). Station details are presented in Table 1. Firstly, push cores (8.5 cm i.d.) were collected with the manned submersible *Shinkai 6500* on RV *Yokosuka* cruise YK0811 in 2008, at stations (500–2000 m depth) forming two transects (Yokosuka N and Yokosuka S) to the north of the Mandovi/Zuari estuary (Fig. 1b). Secondly, shelf sediments were collected on RV *Sindhu Sankalp* cruises in October 2010 and May 2011 (Fig. 1b and c). These were collected over 3 transects, directly offshore and north and south of the Mandovi/Zuari estuary confluence (referred to as the Ratnagiri, Goa and Karwar transects, respectively). Notably, the Goa transect also extended to a depth of 2056 m, thus fully spanning both the shelf and the permanent OMZ on the upper slope. Sediments were collected either by box core or grab, which were subsequently sub-cored with 8.5 cm i.d. plastic barrels. Finally, sediments from the Mandovi/Zuari estuary were collected by grab on a small coastal vessel. Sediment cores from selected stations were vertically sectioned at 1 cm intervals, and sediments were then freeze-dried, with weights being determined before and after drying.

Together, these sites span an estuarine gradient (river to mouth) as well as the continental shelf and upper continental slope. Notably the margin transect includes stations above, within and below the permanent mid-water OMZ (dissolved oxygen (DO) $\leq 50\,\mu M$, ~ 250–1300 m). The shelf sites span the full depth range (~ 20 m to shelf break [~ 200 m]), and experience extreme seasonal variability in bottom-water DO concentrations, from fully oxygenated during intermonsoon months to extreme hypoxia during the summer southwest monsoon (Fig. 3). The shelf-to-slope transects also span a wide range of sediment types, from fine muds nearshore and beyond the

BGD
11, 3387–3422, 2014

shelf break, to mid-shelf relict carbonate sands (Ramaswamy and Nair, 1989; Rao and Rao, 1995; see below).

Finally, suspended sediment samples from both rivers were collected with large-volume bottle sampling at sites upstream of the furthest inland seawater incursion, in October 2010 and May 2011 (filtered onto pre-weighed glass fibre filters, 0.7 µm nominal pore size).

2.2 Analytical

Sediments were analysed for their organic C (C_{org}) and total N (TN) contents and stable C and N isotopic compositions using CE Instruments NA2500 elemental analyser connected to a VG Isogas Prism III isotope ratio mass spectrometer. Freeze-dried sediments were decalcified by vapour-phase HCl acidification (Hedges and Stern, 1984) followed by addition of 2–3 drops of purified 6N HCl. Acetanilide was used as the calibration standard for elemental data, while $\delta^{15}N$ and $\delta^{13}C$ were respectively determined relative to air and the PACS-2 reference standard from the National Research Council Canada ($\delta^{13}C_{org} = -2.228$ ‰). Replicate analyses of selected samples ($n = 2$–5) produced precision (% standard deviation; %sd) of < 2 % and < 3.3 % for $\%C_{org}$ and %TN, respectively, and standard deviations of < 0.12 ‰ for $\delta^{13}C$ and 0.16 ‰ for $\delta^{15}N$. Grain size analyses were conducted by laser diffractometry on slurries of sediments disaggregated in an aqueous solution of sodium hexametaphosphate. Amino acids were determined by the method of Cowie and Hedges (1992a), which involved reverse-phase HPLC of 6N HCl hydrolysates and fluorometric detection of ortho-phthaldialdehyde derivatives. Quantification was relative to charge-matched internal standards added after hydrolysis. Replicate analyses of selected samples ($n = 2$–3) produced a %sd of < 7 % of the mean for all amino acid parameters other than trace component yields and mole percentages (≤ 12 %). Lignin phenols were analysed by the method of Ertel and Hedges (1992) as modified by Goñi and Montgomery (2000) and involved gas chromatographic separation and flame-ionisation detection of phenols liberated by al-

BGD
11, 3387–3422, 2014

kaline CuO hydrolysis, and quantified relative to internal standards added immediately post hydrolysis. Precision (%sd) for individual phenols in replicate analyses of selected samples (n = 2–3) was < 10 % of mean values in most estuary and shelf samples, but were markedly higher for slope sites where phenol levels were close to detection limits. Precision for total phenol yields was < 20 % in all cases. All concentrations were corrected for sediment salt content, which were determined either by combining porewater contents with bottom-water salinity values or by silver nitrate titration of dried sediment suspensions in distilled water.

3 Results

Results of all elemental, stable isotopic, biochemical and grain size analyses are presented in Table 1. Details of all stations, including locations, depths and bottom-water DO concentration (at the time of sampling) are recorded in Table 1.

4 Discussion

4.1 Cross-margin and down-core organic matter distributions

As illustrated in Fig. 2, sediment organic C concentrations (%C_{org}, wt %) range from ~ 0.2 wt % in selected estuary and mid-shelf deposits (all coarser sediments, see below) to a maximum of ~ 7 % at selected upper slope sites (~ 500–800 m). Below the lower boundary of the permanent mid-water OMZ (~ 1300 m), there is a progressive drop, reaching ~ 1–1.5 wt % at 2000 m.

Notably, while maximal %C_{org} values are found at sites within the core of the OMZ, there is dramatic variability in %C_{org} at given depths within the OMZ, especially in the more northern (Yokosuka) transects. This is in contrast to DO concentrations, which, apart from seasonal fluctuation at the upper OMZ boundary (Fig. 3), are comparatively constant, with season and at any given depth within the OMZ (as observed in

BGD
11, 3387–3422, 2014

repeat CTD profiles). There is also a large range of $\%C_{org}$ values in shelf sediments (i.e. above the permanent OMZ), with values in shallow nearshore deposits notably reaching values (up to ~ 4 %) similar to many observed on the slope (within the OMZ). Thus, the observed variability in sediment organic C content is clearly not associated only with variations in DO. The cross-margin distributions are consistent with others reported previously for the Indian margin (e.g. Calvert et al., 1995), which also have shown maximal concentrations on the upper slope, but also, for some transects, major variability within the OMZ and, on occasion, maximal C_{org} values at or below the lower OMZ boundary.

By contrast, similar cross-margin transects from the Pakistan margin of the Arabian Sea (Cowie et al., 1999, 2009) showed less pronounced $\%C_{org}$ maxima on the upper slope (~ 4 % max.) and these were found at the lower boundary of the OMZ (~ 1000–1200 m), whereas DO was minimal at 300–400 m depth. Most notably, within any given transect area on the Pakistan margin $\%C_{org}$ values were remarkably constant at a given depth and DO value. Thus, the scatter observed within the OMZ on the Indian margin (Fig. 2 and Calvert et al., 1995) was not apparent off Pakistan.

4.2 Organic matter sources

The fate of terrigenous OM that enters estuaries and the coastal ocean is a subject of long-standing debate (e.g. Hedges, 1992) and current research. For the present study, it is also important to establish the extent of terrigenous OM inputs in order to deconvolve observed cross-margin trends in C_{org} concentration. Distributions of parameters that serve as potentially diagnostic indices of terrigenous (vs. autochthonous/marine) OM inputs are plotted in Fig. 4. These include stable C isotopic compositions ($\delta^{13}C_{org}$ [‰], Fig. 4a), total lignin phenol yields (Λ, mg/100 mg C_{org}; Fig. 4b) and molar organic-C-to-total N ratios ($(C/N)_a$, Fig. 4c).

Firstly, $\delta^{13}C_{org}$ values for sediments from the Zuari/Mandovi estuary sites ranged from −23.6 to −25.2 ‰ (Fig. 4a, Table 1). These compare to more negative values of

BGD
11, 3387–3422, 2014

−27.2 to −30.6 ‰ found in suspended particulate organic matter (SPOM) from upriver sites on the Zuari and Mandovi rivers (Table 1). These values in turn are in line with previous studies which showed SPOM $\delta^{13}C_{org}$ values ranging from ∼ −21 towards the mouths to ∼ −32 ‰ towards the upstream ends of the estuaries, with values varying with season/discharge and tidal stage (Maya et al., 2011; Khodse and Bhosle, 2012; Kessarkar et al., 2013). Like these SPOM data, the results of the present study therefore clearly indicate mixed OM inputs to sediments across the Zuari and Mandovi estuaries, with varying proportions of marine and terrigenous OM at the different locations.

The $\delta^{13}C_{org}$ values of shelf sediments (Fig. 4a) become sharply heavier (more marine) even at the shallowest sites, with all but one site (K2, 24 m depth, Karwar transect) having values of −21.3 ‰ or heavier (with low to mid-latitude planktonic signatures typically being in the range of ∼ −18 to −22 ‰, Emerson and Hedges, 1988). There is some fluctuation in $\delta^{13}C_{org}$ values (−19.4 to −21.3 ‰) across the shelf (all 3 shelf transects) but relatively uniform values beyond the shelf break, with a possible trend towards slightly more positive values below 1300 m. These results clearly indicate a strong and relatively uniform predominance of marine OM in the sediments at all sites except the shallowest and closest to shore. The more negative signature in the nearshore sediments on the Karwar transect (which is still positive relative to the estuarine sediments), may reflect a predominant nearshore transport from N to S of any terrigenous SPOM that exits Zuari/Mandovi estuary. Finally, it is notable that the lack of clear trend in $\delta^{13}C_{org}$ across the slope and OMZ is in stark contrast to trends observed on the Pakistan margin (Cowie et al., 1999, 2009), where distinctly more negative $\delta^{13}C_{org}$ signatures within the OMZ were attributed to the imprint of chemosynthetic bacteria and/or to enhanced OM preservation. The lack of trend across the Indian margin may therefore be due to better ventilation and less pronounced hypoxia than off Pakistan (there is a progressive intensification of hypoxia from S to N), leading to absence of chemosynthetic processes and/or to less enhanced preservation of OM (see further discussion below).

BGD
11, 3387–3422, 2014

Total lignin phenol yields (Fig. 4b) and molar C/N ratios (Fig. 4c) provide very similar indications to $\delta^{13}C_{org}$ signatures. Total C_{org}-normalised lignin phenol yields (Λ) are quite variable in the estuarine sediments, with a maximum of 5.4 mg/100 mg C_{org}. However, there is a steep decrease offshore, with maximal values found at the shallowest nearshore sites (Λ = 0.4 to 25.4 mg/100 mg C_{org}) on the Goa, Ratnagiri and Karwar transects, respectively. At all sites at depths greater than 100 m, on all transects, Λ values are $\leq$ 0.2 mg/100 mg C_{org}. Carbon-to-nitrogen ratios are more ambiguous tracers of marine vs. terrestrial OM inputs due the common and variable effects of diagenetic imprints. However, the range of (C/N)a values in the estuarine sediments (10.0–14.5) again suggests varying proportions of marine and terrigenous OM (Fig. 4c). Moreover, lower, more typically marine values ($\sim$ 7–11) are found on the shelf, even in nearshore deposits, and at sites beyond the shelf break (although there is considerable scatter across the Yokosuka slope transects). There is also a possible trend towards lower values at greater depth (below the OMZ) due to lowering of C/N ratios with advanced degradation (Cowie et al., 1999, 2009).

A cross-plot of lignin phenol yields and $\delta^{13}C_{org}$ values (Fig. 5a) provides strongly coherent source indications. Sites from within the Mandovi/Zuari estuary system show variable lignin phenol yields and $\delta^{13}C_{org}$ values that fall within the range of values previously recorded for SPOM across the length of the estuary, but more positive (marine) than values recorded at upriver sites. These results confirm mixed marine and terrigenous OM inputs to the estuarine sediments, though it would appear that the lignin yield of terrigenous inputs is variable (i.e. there is not a uniform lignin yield for the terrigenous OM end-member). The two shallowest, nearshore sites on the Ratnagiri and Karwar transects clearly show significant terrigenous OM inputs, based on both parameters, but all sites further offshore on these transects, and all sites on the Goa and Yokosuka transects, have Λ values $\leq$ 0.54 mg/100 mg C_{org} and $\delta^{13}C_{org}$ values of -21 ‰ or heavier. For illustrative purposes, taking a $\delta^{13}C_{org}$ for the terrigenous OM end-member of -29 ‰ (average of values for upriver SPOM, Fig. 6a) and a value of $\sim$-19.5 ‰ for the marine OM end-member (approximate x-axis intercept at Λ = 0) gives

BGD
11, 3387–3422, 2014

an estimated marine OM contribution of 84 % or greater for all shelf and slope sites on all transects, other than the shallowest nearshore sites on the Ratnagiri and Karwar transects (81 % and 65 %, respectively). This overwhelming predominance of marine OM across most of the shelf and slope, alongside the contributions of marine OM to the estuarine sediments (41–57 %, by the same calculation), indicates that the large majority of terrigenous OM carried by the Zuari and Mandovi rivers is retained within or close to the estuary system. Alternatively, as the large majority of OM in both riverine and estuarine particulates and in coastal sediments typically is intimately attached to associated mineral surfaces (Hedges and Keil, 1995), the results indicate that terrigenous OM export is greatly outweighed by local autochthonous OM production, and terrigenous OM is presumably remineralised and replaced by marine OM on mineral surfaces (Keil et al., 1997; Mayer et al., 1998).

Lignin phenol compositions yield further insights. A cross-plot of the ratio of syringyl-to-vanillyl phenols (S/V) against the ratio of cinnamyl-to-vanillyl phenols (C/V) (Fig. 5b) can indicate the types of vegetation contributing lignin to a given sample. All three phenol types are present in all samples. However, sites within the Mandovi–Zuari estuary system, and shallow nearshore shelf sites, plot closer to the origin, consistent with mixed conifer and deciduous plants that characterise the coastal and Western Ghats region drained by the Mandovi and Zuari Rivers (Roy et al., 2006). In contrast, slope sites show relatively elevated S/V ratios and, especially on the northernmost transect (Yokosuka N), elevated C/V ratios. Though lignin yields (and terrigenous OM inputs) are low at all slope sites, these results suggest a greater relative prevalence of non-woody angiosperm inputs (e.g. grasses) on the slope, especially further to the north. One explanation would be southward offshore transport of terrigenous OM from northern rivers, including the Narmada and Tapti, and possibly the Indus, which have larger discharge than the Mondavi or Zuari, and drain catchments dominated by grasslands (e.g. Roy et al., 2006). Notably, clay mineral compositions of nearshore shelf and outer shelf and slope sediments also differ (dominated by montmorillonite and illite/kaolinite, respectively; Ramaswamy and Nair, 1989; Rao and Rao, 1995; Kessarkar et al., 2003).

BGD
11, 3387–3422, 2014

Clays on the outer shelf and slope were similarly attributed to along-slope transport of lithogenic material with the prevailing southward offshore current. Again, this would indicate that terrigenous OM output from the Mandovi and Zuari is limited, and either locally remineralised or retained in the narrow belt of nearshore muddy sediments.

Stable nitrogen isotopic signatures are potentially ambiguous as marine/terrestrial OM source indicators due to fractionation associated with processes such as fixation, denitrification and OM decay. However, there is a cross-margin trend broadly in line with those seen in Λ, $\delta^{13}C_{org}$ and (C/N)a (Fig. 6a). Estuarine sediments exhibit comparatively negative values of 0.7–5.9 ‰, consistent with varying contribution of more negative terrestrial OM. Nearshore muddy sediments have values that rise to ~ 6–7, consistent with a greater marine OM contribution, but coarser sediments in the ~ 50–200 m depth range show heavier values (4–6 ‰), which are not paralleled by change in Λ or $\delta^{13}C_{org}$, and therefore are not evidently source-related. Beyond the shelf break, the finer sediments show values in the range of ~ 5.3–7.5 ‰ to a depth of ~ 1400 m, with greatest variability on the Yokosuka N transect, where sediment grain size distributions are also most variable (see below). Below the OMZ (~ 1300 m and below) there is a possible trend towards more positive values, reaching values of 7.1–7.4 at ~ 2000 m on the Yokosuka S and Goa transects. Overall, it is not clear whether observed distributions of N isotopic signatures are caused primarily by source, diagenetic or other factors, but a notable feature is that values are not as positive as those seen over the same depth range (~ 200–2000 m) off Pakistan (e.g. ~ 6.6–8.5 ‰ on the Indus margin, spanning the OMZ; Cowie et al., 2009). This trend to heavier $\delta^{15}TN$ values from S to N along the eastern margin of the Arabian Sea has previously been attributed to a parallel intensification of denitrification associated with progressively greater oxygen depletion (e.g. Kurian et al., 2013, and refs therein). Total hydrolysable amino acid yields (THAA, mg/100 mg C_{org}; Fig. 6b) are affected by both OM source and selective diagenetic effects (Cowie and Hedges, 1992b). Thus, while values for the Goa transect appear to show a decrease in THAA values at slope sites below the OMZ, this is not evident for the Yokosuka S transect, and there is otherwise no clear pattern across the

BGD
11, 3387–3422, 2014

margin; estuarine, shelf (nearshore muds and relict sands) and upper slope sediments show considerable scatter with no consistent differences with depth or sediment type. A similar lack of clear cross-margin trend in THAA values has been observed on the Pakistan margin (Suthhof et al., 2000; Vandewiele et al., 2009).

4.3 Preservation state and controls on OM distribution

Because of the low and uniform contribution of marine OM at all sites offshore of the nearshore muddy deposits, factors other than source appear to be responsible for observed cross-margin trends in sediment OM content. Previous studies in the Arabian Sea have concluded oxygen availability to be a key factor (e.g. Paropkari et al., 1992, 1993; van der Weijden et al., 1998), typically based on correspondence between mid-slope C_{org} enrichment and the OMZ. Moreover, differences in OM degradation state across the OMZ also have pointed to an O_2 effect, with enhanced preservation generally being linked to O_2 depletion within the OMZ (e.g. Schulte et al., 2000; Suthhof et al., 2000; Sinninghe Damste et al., 2002; Vandewiele et al., 2009). However, differences in preservation state are slight compared to the several-fold range in $\%C_{org}$ values found below vs. within the OMZ, and, moreover, other studies have found clear exceptions to any relationship between O_2 and either C_{org} content or OM quality. For example, Calvert et al. (1995), in a synthesis of results from the Indian margin, demonstrated multiple cases of C_{org}-enriched sediments at sites below the OMZ, and no clear cross-margin trends in hydrogen indices (a measure of hydrocarbon richness). Rather, they showed a strong positive correlation between $\%C_{org}$ and sediment grain size, expressed as %(Silt+Clay), for all slope sites falling in the depth range of roughly 200 m to $\sim$ 1500 m, with lower $\%C_{org}$ loadings found above and below these depths. These findings are evidence of a further important contributing factor; hydrodynamic processes. Thus, variability in C_{org} loading within the 200–1500 m depth range was attributed to hydrodynamic equivalence of OM and fine sediment and/or to sorption of OM onto finer particles. Organic-poor sediments on the shelf were attributed to extensive reworking and/or winnowing of OM from carbonate sand deposits on the mid- and outer shelf, or

BGD
11, 3387–3422, 2014

to dilution of nearshore muds with organic-poor terrestrial clays. The paucity of OM at sites below 1500 m was attributed to decreasing input to the sediment due to progressive offshore decrease in productivity and to greater decay within the increasing water column.

Bottom-water O_2 concentrations and grain size distribution characteristics for sediments collected in the present study are shown in Fig. 7. Oxygen concentrations (Fig. 7a) exhibit the expected cross-margin trend for the intermonsoon (April/May) sampling period during which sediments from the Ratnagiri, Goa and Karwar transects were collected, thus showing oxygenated conditions on the shelf. However, as indicated in Fig. 3 and by bottom-water O_2 concentrations recorded at some of the Goa shelf stations during the late monsoon (Fig. 7a, October), the entire shelf experiences dramatic seasonal fluctuations in DO concentration, reaching $<\sim 10\,\mu M$ across the entire shelf during the monsoon, and 0 µM (sulfidic) at some inner shelf sites (Naqvi et al., 2000, 2006, 2009). Below a depth of ~ 200 m, values on the upper slope are comparatively stable, and reach a minimum ($< 5\,\mu M$, but non-zero) between depths of ~ 200 m and 800 m. Below this, values progressively rise to a maximum of ~ 100–110 µM at ~ 2000 m. Apparent differences between transects across the lower OMZ boundary (~ 800–1000 m; Fig. 7a) are most likely due to sampling method (direct on-bottom measurement on Yokosuka transects vs. near-bottom CTD casts on Goa transect). However, there may also be real spatial and/or temporal variation bottom-water DO levels across the lower OMZ boundary; (e.g. considerable fluctuation was observed at a single location over a 1 day benthic lander deployment, apparently related to tidal currents; H. Kitazato; personal observation).

Sediment grain size distributions show clear cross-margin variation, both in %(Silt+Clay) (Fig. 7b) and in median grain size (Fig. 7c). Consistent with previous studies (e.g. Ramaswamy and Nair, 1989; Rao and Rao, 1995; Kessarkar et al., 2003) there is a narrow nearshore belt of muds (< 25 mm median, > 85 %(Silt+Clay)) at depths shallower than ~ 50 m, and a belt of coarser sediments extending to ~ 200–300 m (depending on transect). On the slope, sediments below ~ 400 m are generally

BGD
11, 3387–3422, 2014

finer (< 61 µm median), with an apparent gradual (slight) decrease with depth, reaching 9–14 µm median at ~ 2000 m. These trends are paralleled in %(Silt+Clay) values (Fig. 7b), but this parameter more clearly shows that there is considerable variability in grain size distributions for slope sediments from the Yokosuka N transect.

A plot of $\%C_{org}$ against bottom-water DO concentration for shelf and slope surface sediments (Fig. 8a) shows no immediate evidence of an overriding effect of DO on sediment OM content. However, inclusion of shelf sediments is potentially misleading because of the wide range of DO concentrations experienced on the shelf due to seasonal hypoxia (ranges of DO concentrations are indicated for selected shelf sites). Slope sediments, from sites > 200 m depth on the Goa and Yokosuka transects offer a clearer picture as they span the permanent mid-water OMZ, and thus experience near-constant depositional redox conditions (Fig. 8b). In this case, there is a progressive decrease in $\%C_{org}$ values from a site at the lower OMZ boundary (1290 m) to sites below, as bottom-water DO levels rise, suggesting a possible oxygen effect. However, there is also a wide range of $\%C_{org}$ values amongst sites with very low DO values within the OMZ. In some cases, this occurs at proximal sites; i.e. at equal depths as well as DO concentrations. Thus, while increasing DO levels may cause the decrease in $\%C_{org}$ below the OMZ, it is clear that O_2 is not the universal or overriding control on C_{org} distributions across the slope.

This finding is in agreement with that of Calvert et al. (1995); the same relationships between $\%C_{org}$ and sediment grain size they observed for other Indian margin sediments is also found for the present sample set, for both slope and shelf sediments. Specifically, $\%C_{org}$ values for sediments within the permanent OMZ (> 200 m to ~ 1100 m) show a strong positive correlation with %(Silt+Clay), while values for sites from the shelf and below the OMZ (depths indicated by labels) show lower relative C_{org} loadings (Fig. 9). Thus, while C_{org} enrichments are certainly found within the OMZ, hydrodynamic processes are the overriding control, and explain the wide range of $\%C_{org}$ values observed at sites with low and relatively uniform DO values within the core of the OMZ.

BGD
11, 3387–3422, 2014

What remains to be resolved is the cause(s) of lower C_{org} loadings on the shelf and below the OMZ. Three amino acid parameters that provide indications of OM preservation state can offer further insights on the role that enhanced OM preservation in the absence of oxygen might play in causing observed cross-margin OM distributions. These are the percentages of total N in the form of amino acids (%AA-TN; Cowie and Hedges, 1994; Fig. 10a), the percentages of total amino acids in the form of the non-protein amino acids β-alanine and γ-amino butyric acid; %(BALA+GABA); Cowie and Hedges, 1994; Fig. 10b) and a Degradation Index based on multivariate analysis of whole amino acid suites across a sample set representing a full diagenetic spectrum (DI; Dauwe and Middelburg, 1998; Dauwe et al., 1999; Fig. 10c). Although these parameters may be sensitive at different stages of OM alteration (e.g. Cowie and Hedges, 1994), the clearest signal shown by all three parameters is that in both the Yokosuka and Goa transects, extending below the OMZ, there is a consistent trend towards greater degree of alteration that parallels the increase in DO levels from ~ 1200 m at the base of the OMZ to the maximum sampling depth of 2056 m. Thus, the lower $\%C_{org}$ values observed below the OMZ appear to be linked to increasing extent of OM decay, as previously observed on the Pakistan margin (Vandewiele et al., 2009), and which can be linked to a progressive rise in O_2 exposure time (e.g. Hartnett et al., 1998; Hedges et al., 1999).

At sites within the OMZ (~ 200 m to 1300 m), %AA-TN values vary without clear trend with depth or difference between transects (Fig. 10a). Values for %(BALA+GABA) and DI (Fig. 10b and c) similarly show no clear trend with depth. However, while the Yokosuka transect sites generally show lower %(BALA+GABA) values (less degraded), DI values are generally more negative (i.e. more degraded) than at corresponding sites on the Goa transect. Reasons for the slight contrasts between the three parameters are unclear, though it has previously been shown that %(BALA+GABA) values become most reliable as tracers of degradation state at late stages of alteration (Cowie and Hedges, 1994). Overall, results indicate no trend in degradation state within the OMZ, and a lower level of degradation than at sites below.

BGD
11, 3387–3422, 2014

For the shelf sites, %(BALA+GABA) and DI values (Fig. 10b and c) show consistent differences between nearshore muds and mid-to-outer shelf relict sands, but again provide contrasting indications of degradation state. Whereas the nearshore muds appear less degraded in terms of DI values (more positive, Fig. 10c), they appear more degraded in terms of %(BALA+GABA) values. Again, reasons for these discrepancies are unclear, but it is possible that the more terrigenous nearshore muds or the carbonate-rich sands have distinctive amino acid suites, and these sample types were not amongst those used in assessing either parameter as indices of degradation state (Cowie and Hedges, 1994; Dauwe and Middelburg, 1998; Dauwe et al., 1999). Although there are also differences in %AA-TN values (Fig. 10a) between the nearshore muds and some of the relict sands, there is more scatter and no consistent cross-shelf pattern. Overall, the three parameters suggest that OM in shelf sites is similar to or less degraded that sites within the OMZ (e.g. when comparing muds at nearshore sites and on the slope); thus, there are no clear signs of more degraded OM at sites above the OMZ as is seen at sites below the OMZ.

The key finding from the degradation indicators is therefore that the progressively more advanced OM degradation state at sites below the OMZ indicates that the parallel decrease in $\%C_{org}$ values (Fig. 2), and the low values relative to %(Silt+Clay) (Fig. 10), are not due to decreasing OM input as argued by Calvert et al. (1995), but to increasing decay with longer O_2 exposure (e.g. Hartnett et al., 1998; Hedges et al., 1999). On the other hand, the lack of consistent difference in degradation state between shelf and upper slope sediments from the OMZ, even in relict shelf sands, is consistent with conclusions drawn by Calvert et al. (1995), and indicates that differences in sediment OM content on the shelf are due more to physical effects (e.g. winnowing or dilution with mineral material) than to any difference in OM preservation related to O_2 availability. This lack of O_2 effect is to be expected at nearshore sites with short O_2 exposures (Cowie and Hedges, 1992c; Hartnett et al., 1998), especially with the impact of seasonal hypoxia across the entire shelf.

BGD
11, 3387–3422, 2014

Finally, down-core distributions of OM content and all compositional patterns over the upper 30–50 cm showed at most slight change (data not presented; Cowie unpublished). Cross-margin differences in sediment OM content and composition observed in surface sediments therefore are maintained down-core. This phenomenon, also observed on the Pakistan margin, even at OMZ sites devoid of macrofauna and thus without masking of down-core profiles by bioturbation (Cowie et al., 1999, 2009), indicates that in situ OM alteration is generally limited. Thus, sediment OM contents and compositions are predominantly determined by processes occurring prior to deposition, within the water column or across the benthic interface.

5 Conclusions

In overview, the main findings of the present study are as follows:

- Source indices confirm mixed marine and terrigenous OM inputs to estuarine sediments, but little terrigenous OM outside the estuaries, indicating efficient remineralisation and/or retention within nearshore muds and extensive dilution with autochthonous marine OM.
- Lignin phenols indicate that terrigenous OM in slope sediments may derive from along-slope transport of material from larger rivers to the north.
- Organic matter enrichment in upper slope sediments is due to a combination of physical processes (winnowing and dilution) on the shelf and progressive decay of OM with increasing oxygen exposure below the OMZ.
- Major variability in sediment OM content within the OMZ is strongly linked to grain size distributions. Thus, while low oxygen exposure may contribute to OM enrichment in the OMZ, hydrodynamic processes are the overriding control.

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BGD
11, 3387–3422, 2014

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BGD
11, 3387–3422, 2014

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BGD
11, 3387–3422, 2014

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BGD
11, 3387–3422, 2014

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BGD
11, 3387–3422, 2014

Table 1a. Site data and surface sediment organic matter compositional data.

Station	Depth m	Lat. deg. N	Long. deg. E	DO (μM)	%salt	C_{org} %	TN %	(C/N)a	$\delta^{13}C_{org}$ ‰	δ^{15}N-TN ‰	THAA[a]
Estuary Sites											
Zuari 1	< 3	15.4110	73.9100	nd	4.0	2.36	0.19	14.4	−23.62	5.42	17.38
Zuari 3	< 3	15.3675	73.9770	nd	0.6	0.21	0.02	13.0	−23.76	2.01	16.48
Zuari 5	< 3	15.3032	74.0150	nd	0.5	0.19	0.02	11.1	−25.02	3.68	20.19
Canal 6	< 3	15.4350	73.9340	nd	2.4	2.08	0.18	13.6	−24.34	5.92	15.42
Canal 7	< 3	15.4795	73.9500	nd	2.0	2.31	0.19	14.3	−25.17	4.67	17.85
Mandovi 9	< 3	15.5364	73.9300	nd	1.1	0.19	0.02	13.8	−25.08	1.08	15.68
Mandovi 10	< 3	15.5398	73.9600	nd	0.8	0.12	0.01	10.0	−23.59	0.70	21.05
Mandovi 11	< 3	15.5068	73.9100	nd	1.0	0.27	0.02	13.3	−24.99	1.75	14.41
Yokosuka Transect N											
1123 R10	500	17.5583	71.1891	0.5	15.4	6.87	0.81	9.9	−20.91	6.31	20.67
1123 R7	575	17.5555	71.1924	0.6	16.3	6.96	0.80	10.2	−20.95	5.92	15.06
1117 Y6	693	17.5365	71.1769	1.1	4.2	2.09	0.27	8.9	−20.34	6.15	18.03
1117 Y8	746	17.5333	71.1753	1.3	5.9	3.51	0.44	9.3	−20.53	5.30	16.42
1112 R8	793	17.5278	71.1733	1.4	6.4	4.13	0.47	10.2	−20.40	6.01	17.06
1119 R4	812	17.5249	71.1704	2.8	7.5	4.50	0.51	10.3	−20.37	5.65	14.91
1115 R9	813	17.5248	71.1696	2.3	5.7	4.94	0.58	9.9	−20.42	6.03	15.22
1112 R6	814	17.5252	71.1721	1.8	5.3	4.72	0.55	10.0	−20.22	6.02	16.33
1110 Y8	928	17.5430	71.1050	4.7	4.7	2.41	0.23	12.5	−19.79	5.99	13.47
1116 Y3	1000	17.5304	71.1002	9.7	4.6	2.87	0.38	8.8	−20.51	5.38	18.79
1110 R7	1139	17.5258	71.0850	22.7	6.3	3.92	0.46	10.0	−20.16	6.27	16.96
1114 Y10	1145	17.5275	71.0806	21.2	5.7	4.34	0.55	9.1	−20.59	7.49	15.71
1116 R10	1052	17.5297	71.0936	17.8	5.4	4.40	0.51	10.2	−20.14	6.11	15.74
1114 Y3	1156	17.5254	71.0822	22.4	11.4	4.56	0.56	9.6	−20.32	5.90	18.01
Yokosuka Transect S											
1109 R4	540	16.9804	71.9217	1.7	5.2	3.24	0.38	9.9	−20.38	5.53	16.57
1105 R6	795	16.9794	71.8683	1.1	7.2	5.84	0.67	10.2	−20.40	6.29	18.17
1101 Y4	798	16.9793	71.8678	2.2	10.3	5.57	0.63	10.3	−20.41	6.20	13.80
1100 Y2	900	16.9663	71.8518	4.7	6.6	4.75	0.57	9.7	−20.64	6.80	16.20
1098 Y2	2000	16.7831	71.3356	108.6	7.2	0.98	0.15	7.4	−19.48	7.09	18.70

BGD
11, 3387–3422, 2014

Table 1a. Continued.

Station	Depth m	Lat. deg. N	Long. deg. E	DO (μM)	%salt	C_{org} %	TN %	(C/N)a	$\delta^{13}C_{org}$ ‰	δ^{15}N-TN ‰	THAA[a]
Ratnagiri Transect											
R2	31	16.7135	73.2079	48.7	4.9	2.07	0.22	11.2	−21.30	6.04	15.80
R4	52	16.6660	73.0512	66.0	9.5	2.31	0.27	9.9	−20.21	7.10	20.94
R6	82	16.5608	72.6289	78.4	3.5	0.82	0.08	11.5	−20.15	6.15	20.24
R9	227	16.5383	72.2284	3.1	1.8	0.74	0.09	9.7	−19.84	3.98	13.17
Goa Transect											
G4	20	15.5182	73.7036	78.7	9.5	2.80	0.32	10.2	−21.01	6.95	16.94
G5	28	15.5133	73.6518	85.4	9.6	3.23	0.31	12.0	−21.16	6.82	16.82
G6	37	15.4989	73.5827	88.2	9.2	3.13	0.30	12.0	−20.77	6.96	16.39
G7	46	15.4820	73.5150	90.2	7.8	3.45	0.36	11.2	−20.72	6.96	19.12
G8	60	73.4530	73.4020	31.7	1.4	0.52	0.08	7.9	−19.42	4.86	19.22
G9	71	15.4277	73.2827	57.2	3.0	0.69	0.11	7.3	−19.93	4.94	19.27
G10	100	15.3685	73.1307	31.7	3.5	1.20	0.13	10.7	−20.65	5.97	15.38
G11	127	15.3413	73.0035	22.6	2.2	0.64	0.07	10.4	−20.26	4.09	19.68
G12	164	15.2354	72.9810	76.8	2.4	0.91	0.10	10.3	−20.23	3.88	20.02
G12B	200	15.2253	72.9299	3.9	5.5	2.80	0.31	10.7	−20.89	6.28	19.46
G12C	346	15.3567	72.8241	3.8	9.4	2.39	0.26	10.5	−19.77	6.76	14.93
G12D	543	15.3063	72.8078	2.8	8.1	6.74	0.74	10.6	−20.24	6.13	21.28
G12E	760	15.2767	72.7644	5.7	5.4	6.60	0.66	11.7	−20.17	6.38	14.53
G13	960	15.2801	72.6742	24.4	6.6	4.82	0.51	11.1	−20.15	6.51	14.70
G13B	1290	15.2050	72.6107	37.7	9.7	4.12	0.43	11.3	−20.16	6.57	12.58
G14	1642	15.1170	72.4067	70.1	5.9	1.59	0.16	11.9	−19.80	6.94	11.47
G15	2056	14.9968	71.0000	104.5	5.9	1.47	0.17	9.8	−19.85	7.43	12.11
Karwar Transect											
K2	24	14.4698	74.2416	29.1	8.1	3.79	0.34	12.8	−22.84	5.85	nd
K3	34	14.4679	74.1725	34.4	7.8	2.74	0.29	10.9	−20.97	6.60	18.80
K5	52	14.3975	74.0004	72.6	2.0	0.53	0.05	11.5	−21.09	5.24	19.03
K7	67	14.3195	73.7729	83.8	1.6	0.27	0.03	11.8	−21.22	4.53	22.01
K8	235	14.1713	73.2607	2.5	4.7	2.70	0.29	10.9	−20.49	6.27	nd
K9	500	14.1714	73.2316	4.4	7.1	6.60	0.69	11.1	−20.19	6.43	12.57

[a] yields in mg/100 mg C_{org};

[b] mole %;

Median = median grain size; Clay, silt and sand are percentages by volume. Other parameters are as defined in the text.

BGD
11, 3387–3422, 2014

Table 1b. Site data and surface sediment organic matter compositional data.

Station	%(BALA +GABA)[b]	%AA-TN	DI	Λ[a]	V[a]	S[a]	C[a]	Median µm	Clay %	Silt %	Sand %
Estuary Sites											
Zuari 1	2.93	32.8	0.55	4.60	1.883	2.074	0.151	nd	nd	nd	nd
Zuari 3	2.38	26.3	0.42	0.15	0.051	0.046	0.005	220.4	5.3	6.5	88.2
Zuari 5	1.51	28.3	0.27	nd	nd	nd	nd	334.8	7.0	9.3	83.8
Canal 6	2.34	26.2	0.76	5.36	2.357	2.462	0.166	nd	nd	nd	nd
Canal 7	2.49	32.1	0.58	1.99	0.778	0.941	0.094	14.8	26.0	50.0	24.0
Mandovi 9	2.28	26.9	0.55	3.29	1.295	1.421	0.150	209.4	9.5	16.1	74.5
Mandovi 10	3.30	26.7	−0.06	nd	nd	nd	nd	nd	nd	nd	nd
Mandovi 11	2.78	23.6	0.61	1.57	0.608	0.731	0.078	149.8	9.5	17.2	73.3
Yokosuka Transect N											
1123 R10	1.44	26.7	0.28	0.01	0.001	0.003	0.002	11.4	19.2	73.3	7.5
1123 R7	1.63	23.7	0.14	0.01	0.001	0.001	0.002	12.6	18.5	71.1	10.4
1117 Y6	1.71	21.6	−0.48	0.01	0.003	0.002	0.003	61.3	13.1	37.3	49.6
1117 Y8	1.48	21.2	−0.12	0.01	0.001	0.002	0.001	55.4	9.7	42.2	48.1
1112 R8	1.54	24.2	0.00	0.01	0.001	0.001	0.003	20.3	14.9	49.9	35.2
1119 R4	1.84	21.4	−0.16	0.01	0.001	0.002	0.002	29.2	13.6	48.8	37.6
1115 R9	1.68	20.8	0.00	0.01	0.003	0.002	0.002	15.2	17.4	55.8	26.8
1112 R6	1.96	22.5	0.05	0.01	0.001	0.001	0.002	16.6	16.8	55.8	27.4
1110 Y8	2.11	22.7	−0.18	0.01	0.002	0.003	0.004	28.2	14.8	47.6	37.5
1116 Y3	1.99	22.6	−0.45	0.02	0.003	0.004	0.004	23.0	16.5	47.3	36.2
1110 R7	2.14	23.7	−0.10	0.01	0.001	0.003	0.002	13.2	18.6	67.1	14.3
1114 R10	1.93	22.0	−0.02	0.01	0.002	0.002	0.002	11.7	20.8	63.5	15.7
1116 Y10	1.92	22.0	−0.11	0.01	0.001	0.001	0.001	9.3	26.2	60.6	13.3
1114 Y3	1.90	22.4	0.02	0.01	0.001	0.001	0.002	8.4	28.6	60.5	10.9
Yokosuka Transect S											
1109 R4	2.60	21.5	0.13	0.02	0.003	0.004	0.002	38.2	14.8	41.2	44.0
1105 R6	1.96	25.7	0.01	0.01	0.002	0.003	0.001	11.5	18.5	74.0	7.5
1101 Y4	1.72	20.5	0.04	0.01	0.003	0.003	0.001	12.1	19.6	70.8	9.6
1100 Y2	1.86	21.7	−0.01	0.01	0.002	0.002	0.002	12.0	21.0	64.7	14.3
1098 Y2	3.49	19.5	−0.77	0.02	0.004	0.004	0.002	8.9	28.0	63.1	8.9

BGD
11, 3387–3422, 2014

Table 1b. Continued.

Station	%(BALA +GABA)[b]	%AA-TN	DI	Λ[a]	V[a]	S[a]	C[a]	Median µm	Clay %	Silt %	Sand %
Ratnagiri Transect											
R2	3.18	22.9	0.61	1.52	0.617	0.599	0.070	10.4	25.4	69.1	5.5
R4	3.04	29.4	0.17	0.55	0.129	0.135	0.024	7.7	34.0	61.8	4.2
R6	2.06	30.7	0.10	nd	nd	nd	nd	102.8	21.3	21.7	57.0
R9	1.54	15.5	−0.23	nd	nd	nd	nd	199.4	11.6	19.8	68.7
Goa Transect											
G4	2.88	23.7	0.81	0.42	0.100	0.215	0.029	14.1	15.3	78.5	6.2
G5	2.88	27.8	0.89	nd	0.134	0.160	0.084	13.4	17.2	76.7	6.2
G6	2.54	27.1	0.70	nd	0.097	0.126	0.024	16.4	12.7	81.2	6.1
G7	2.51	29.0	0.74	nd	0.115	0.127	0.018	14.2	19.2	72.5	8.4
G8	1.80	19.0	0.09	nd	nd	nd	nd	176.0	8.8	13.9	77.3
G9	1.58	17.8	−0.05	nd	nd	nd	nd	176.1	8.4	12.8	78.8
G10	1.21	21.1	0.12	nd	nd	nd	nd	65.4	11.0	38.1	51.0
G11	1.41	25.5	0.20	nd	0.037	0.039	0.006	149.0	9.5	16.9	73.6
G12	1.11	26.1	0.41	nd	0.061	0.013	0.002	196.7	10.2	13.5	76.3
G12B	1.75	27.7	0.46	0.14	0.019	0.030	0.008	48.8	18.2	34.5	47.2
G12C	1.47	22.1	0.14	0.07	0.011	0.023	0.006	114.2	13.7	30.5	55.9
G12D	2.46	31.6	0.29	0.09	0.010	0.016	0.006	6.8	32.5	63.2	4.3
G12E	2.68	23.3	0.37	0.08	0.009	0.025	0.005	8.4	26.9	68.2	4.9
G13	3.08	22.6	0.15	0.07	0.015	0.023	0.007	11.0	22.1	69.8	8.1
G13B	3.08	19.9	0.17	0.06	0.008	0.016	0.006	9.0	27.0	66.6	6.4
G14	5.15	18.9	−0.24	0.06	0.022	0.010	0.005	5.6	41.6	52.8	5.6
G15	5.52	16.7	−0.60	0.09	0.011	0.024	0.009	6.2	38.2	57.7	4.2
Karwar Transect											
K2	nd	nd	nd	2.00	0.794	0.830	0.086	17.6	13.4	73.7	12.9
K3	1.75	28.6	0.39	nd	nd	nd	nd	15.1	20.2	67.5	12.2
K5	1.16	27.9	0.23	nd	nd	nd	nd	83.1	11.6	26.2	62.2
K7	1.04	31.8	0.03	nd	nd	nd	nd	179.2	5.4	8.4	86.2
K8	nd	nd	nd	nd	nd	nd	nd	17.1	21.5	45.7	32.8
K9	2.83	19.6	0.11	0.14	0.037	0.040	0.006	6.5	36.6	57.8	5.6

[a] yields in mg/100 mg C_{org};

[b] mole %;

Median = median grain size; Clay, silt and sand are percentages by volume. Other parameters are as defined in the text.

BGD
11, 3387–3422, 2014

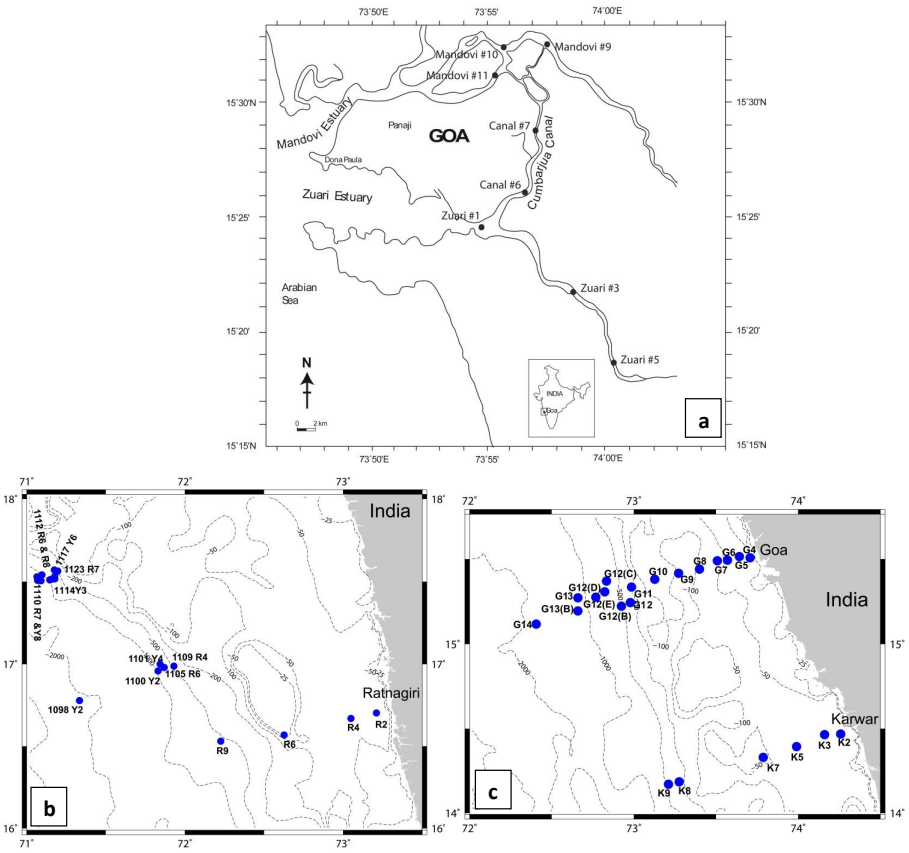

Fig. 1. Sediment sampling locations; **(a)** within the Mandovi Zuari estuary confluence, **(b)** Yokosuka and Ratnagiri transects, **(c)** Goa and Karwar transects.

BGD
11, 3387–3422, 2014

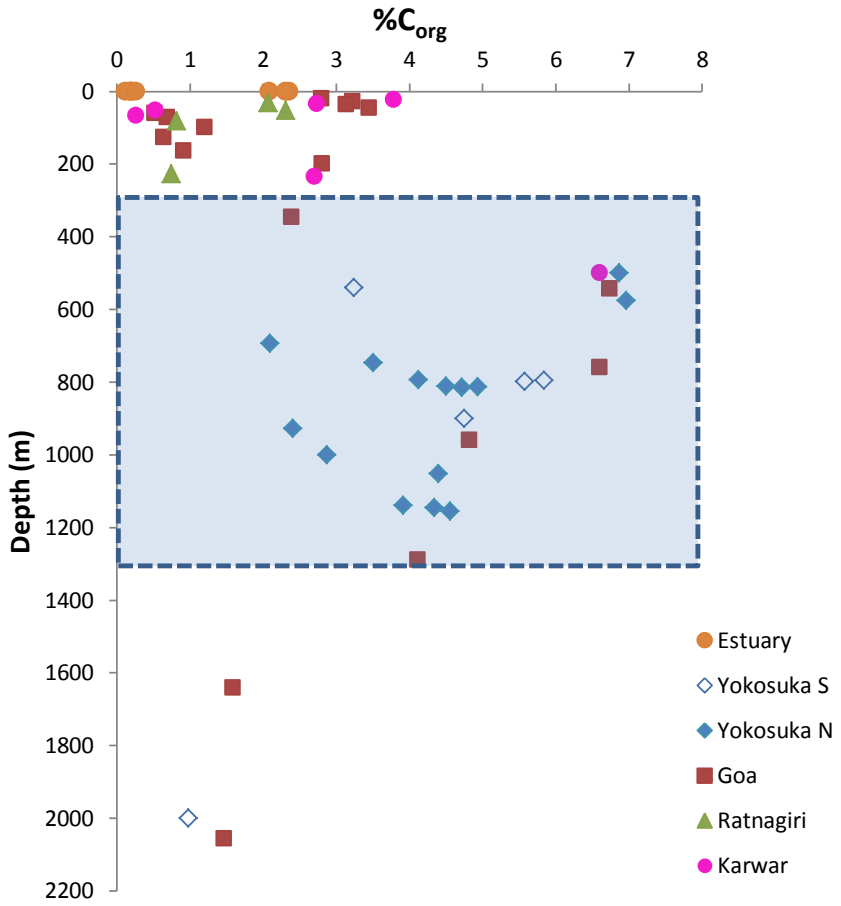

Fig. 2. Organic carbon weight percentage (%C_{org}) in surfical sediments (0–2 cm) from estuary, shelf and upper slope sites on the Indian margin of the Arabian Sea. Shaded area indicates approximate depth of permanent mid-depth OMZ (<~ 50 µM).

BGD
11, 3387–3422, 2014

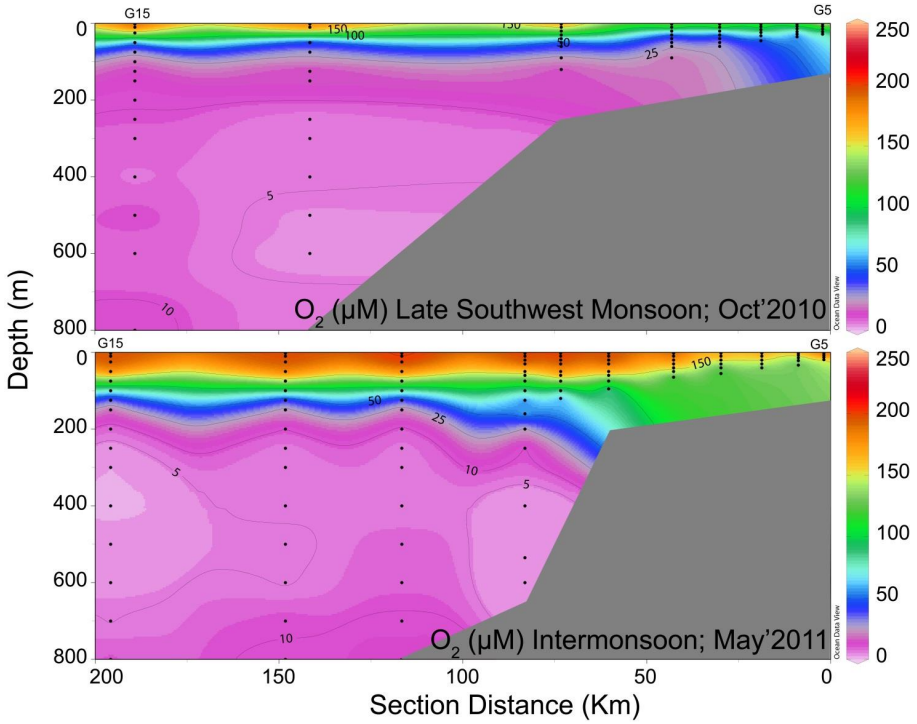

Fig. 3. Cross-margin plots (to 800 m) of dissolved oxygen concentration (µM) during the late monsoon season (October 2010, upper panel) and intermonsoon season (May 2011, lower panel).

BGD
11, 3387–3422, 2014

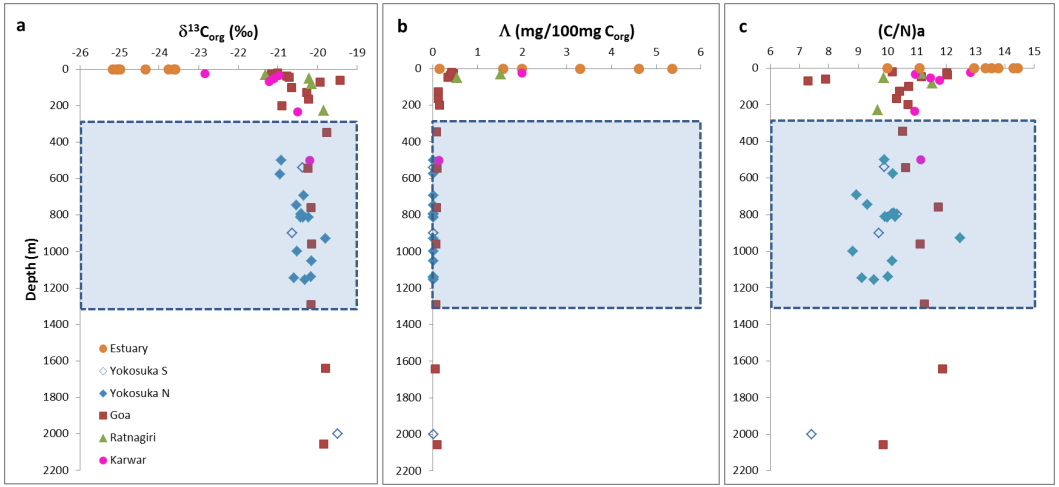

Fig. 4. Plots against station depth (m) of **(a)** stable C isotopic composition ($\delta^{13}C_{org}$, ‰); **(b)** total lignin phenol yield (Λ, mg/100 mg C_{org}), and **(c)** molar ratios of organic C to total N ((C/N)a), for surficial sediments from estuary, shelf and slope sites. Shaded area indicates approximate depth of permanent mid-depth OMZ (<~ 50 µM).

BGD
11, 3387–3422, 2014

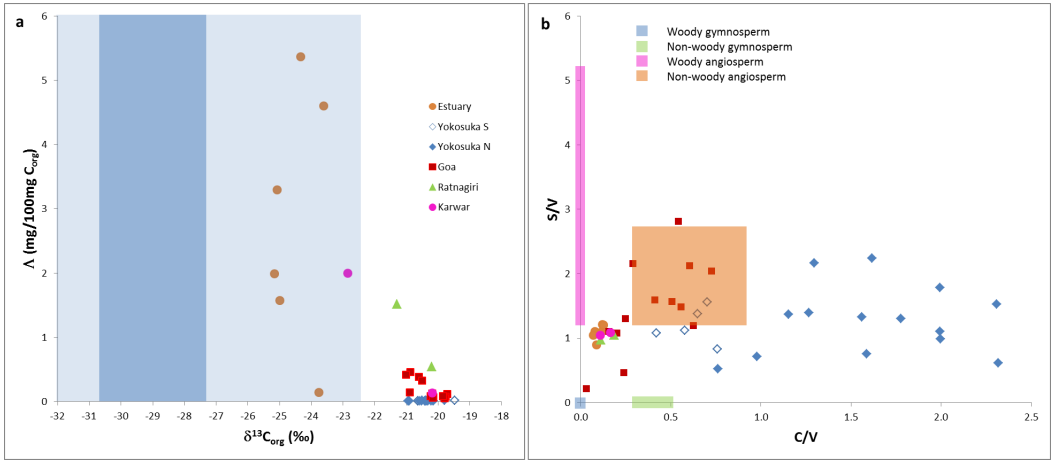

Fig. 5. Plots for surficial sediments of **(a)** total lignin phenol yield (Λ, mg/100 mg C_{org}) against stable C isotopic composition ($\delta^{13}C_{org}$, ‰), and **(b)** ratios of total syringyl to total vanillyl phenols (S/V) against ratios of total cinnamyl to total vanillyl phenols (C/V). Shaded areas in panel **(a)** indicate the range of $\delta^{13}C_{org}$ values found in upriver SPOM samples (darker shading, this study) and across the Mandovi and Zuari estuaries (previous studies; see text). Shaded areas in panel **(b)** indicate value ranges for tissues from a suite of N. American plants (Hedges and Mann, 1979).

BGD
11, 3387–3422, 2014

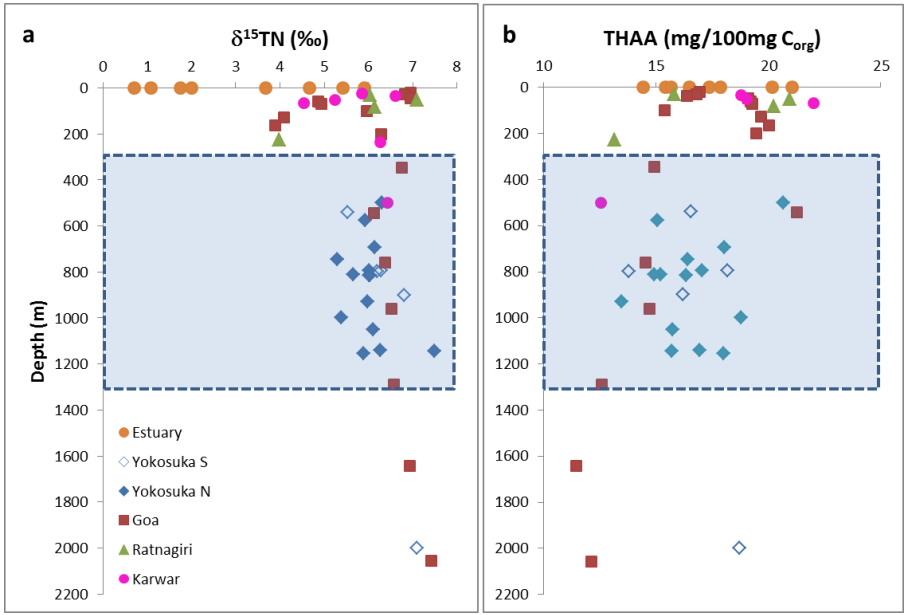

Fig. 6. Plots against station depth (m) of **(a)** stable total N isotopic composition (δ^{15}TN, ‰), and **(b)** total C_{org}-normalised yield of hydrolysable amino acids (THAA, mg/100 mg C_{org}), for surficial sediments from estuary, shelf and slope sites. Shaded area indicates approximate depth of permanent mid-depth OMZ (<~50 µM).

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11, 3387–3422, 2014

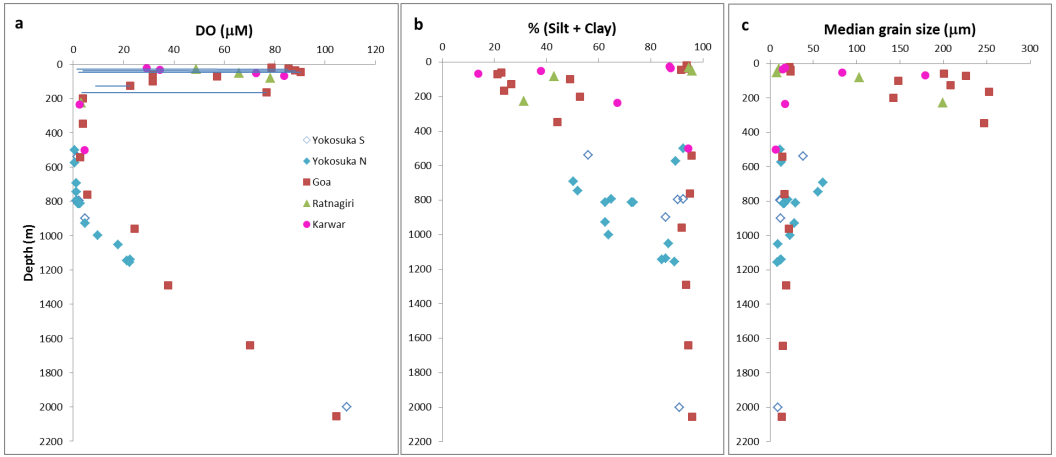

Fig. 7. Plots against station depth (m) of **(a)** bottom-water dissolved oxygen concentration (DO, µM) at time of sampling, **(b)** percentage of silt and clay (by volume) in surficial sediments, and **(c)** median grain size (µm) in surficial sediments, from shelf and slope sites. DO concentrations were either measured directly from a submersible (Yokosuka transects) or in near-bottom bottle samples. All sediment samples and DO data for Goa, Ratnagiri and Karwar transect sites were collected during intermonsoon (normoxic) period. Horizontal lines for 5 Goa transect shelf sites indicate bottom-water DO values encountered during the monsoon season (shelf hypoxia).

BGD
11, 3387–3422, 2014

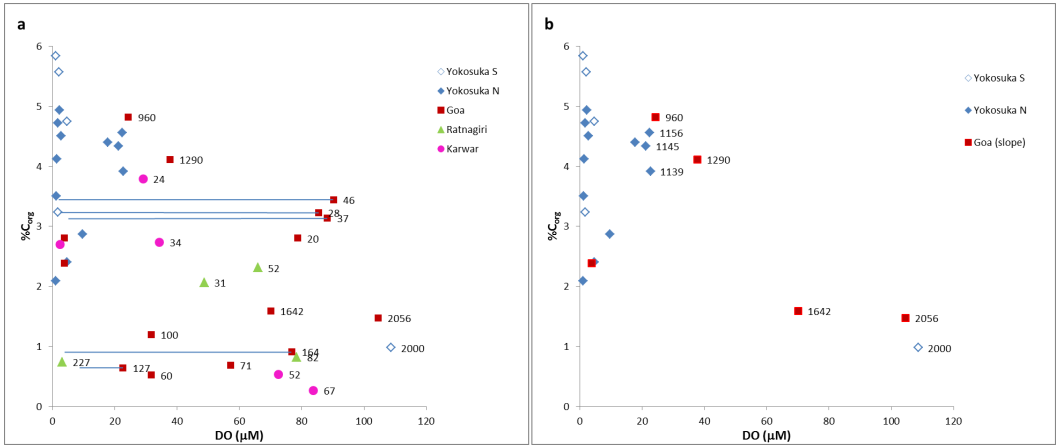

Fig. 8. Plots of surface sediment organic C content ($\%C_{org}$) against bottom-water dissolved oxygen concentration (DO, μM); **(a)** all sites, and **(b)** for slope sites (> 200 m) for the Goa and Yokosuka transects. DO concentrations were either measured directly from submersible (Yokosuka transects) or in near-bottom bottle samples. All sediment samples and DO data for Goa, Ratnagiri and Karwar transect sites were collected during intermonsoon (normoxic) period. Horizontal lines for 5 Goa transect shelf sites indicate bottom-water DO values encountered during the monsoon season (shelf hypoxia). Data labels show station depths for shelf sites and slope sites near and below the lower OMZ boundary (>∼1000 m).

BGD
11, 3387–3422, 2014

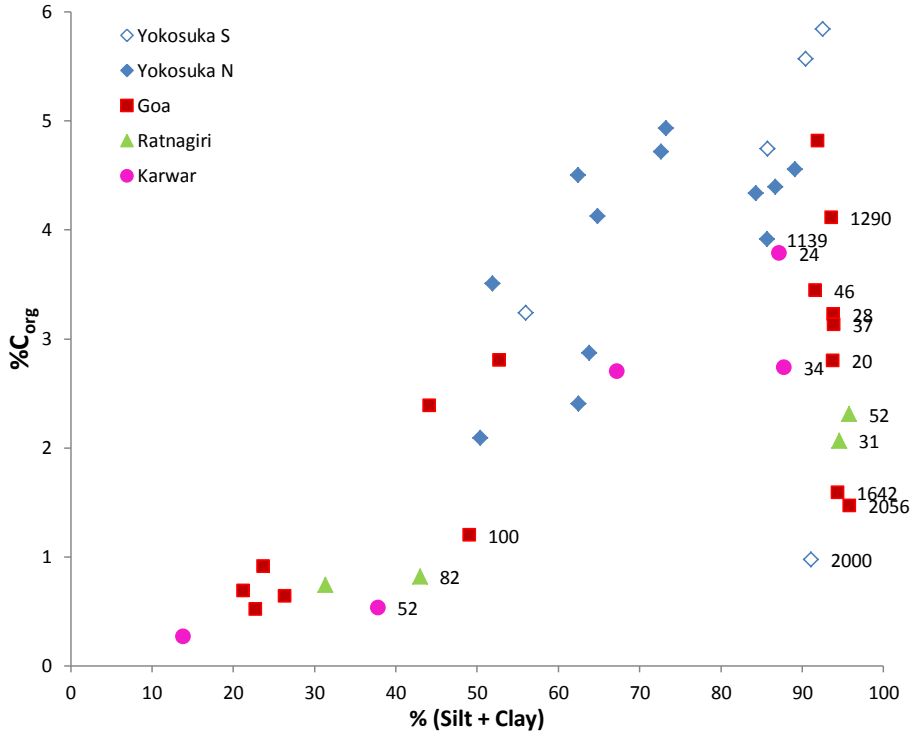

Fig. 9. A plot of organic C content (%C_{org}) against percentage (by volume) of silt and clay (%(Silt+Clay)) in surficial shelf and slope sediments. Marker labels show station depths for selected sites.

BGD
11, 3387–3422, 2014

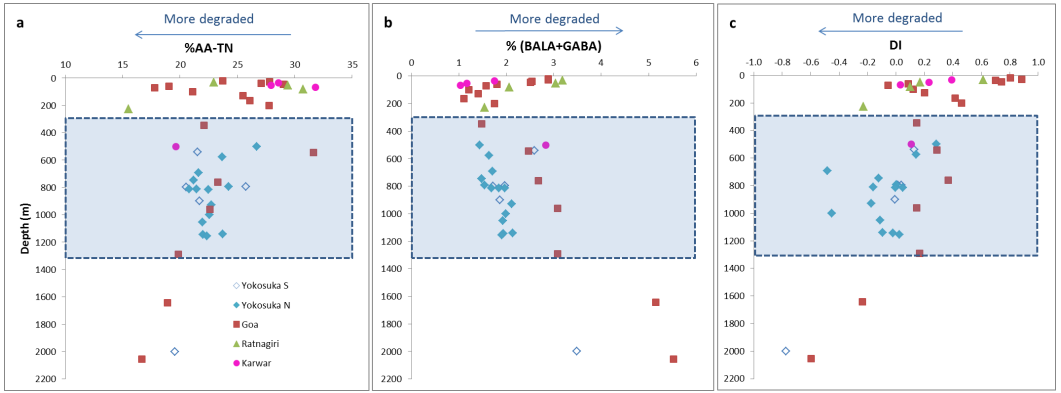

Fig. 10. Plots against station depth (m) of **(a)** percentage of total N as hydrolysable amino acids (%AA-TN), **(b)** mole percentage of total hydrolysable amino acids in the form of β-alanine and γ-aminobutyric acid (%(BALA+GABA)), and **(c)** Degradation Index (DI) as per Dauwe and Middelburg (1998), Dauwe et al. (1999), for surficial shelf and slope sediments. Shaded area indicates approximate depth of permanent mid-depth OMZ (<~50 µM).

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11, 3387–3422, 2014