

Review Maya et al. (2011): Variability of N and C isotopes of suspended organic matter, bgd-8-3923-2011

General comments:

The manuscript by Maya et al. is a well-written study of nitrogen and carbon cycling in coastal waters off Goa/India. The title reflects the contents, and the manuscript is kept in a clear and fluent language.

The authors present a time series of stable carbon and nitrogen isotope measurements of suspended particulate organic matter (SPOM) from the western continental shelf of India (WCSI), 10km off the coast. Since this type of data is still very sparse for the Indian Ocean/Arabian Sea this is a valuable data set and, as such, well worth publishing in *Biogeosciences*. The applied techniques are state-of-the-art analytical methods (irm-GC-MS and HPLC) and sufficiently described in the methods chapter. The data presentation is appropriate (although I found a mistake in one plot, see detailed/technical comments below). Cover of the literature is generally good. The one or the other statements needs to be backed-up with references (see detailed comments below).

According to the introduction, the primary aim of the study is to better understand the intra-annual variability of C and N cycling over the WCSI in order to explain the observation of increasing oxygen-depletion in the water column over the past 50 years and decreasing $\delta^{15}\text{N}$ values observed in the underlying sediments which might be related, e.g., to fertiliser supply. The aspect of anthropogenic influence, however, hardly appears in the rest of the manuscript. With the “summary and conclusions” being primarily a summary a true conclusion referring back to the aim defined in the introduction is currently missing.

The discussion repeats some of the data descriptions of the results chapter. There is some potential for shortening and streamlining here. On the other hand, there are some points missing out in the discussion, in particular, alternative sources of suspended organic carbon and the differences between the two monsoon events covered by the time series. The discussion currently ignores, e.g., the potential contribution of soil organic matter during the monsoon season which could have implications for the interpretation of some of the data. Furthermore, the pattern of the SPOM data exposes clear differences between the monsoon seasons of 2007 and 2008 and associated upwelling conditions. Some of these differences obviously result from the different timing of the onset of atmospheric circulation change, i.e. the onset of the monsoon and associated upwelling, rainfall and freshwater runoff. The discussion would therefore greatly benefit from meteorological data (precipitation, wind). The authors may even think about discussing the aspect of *inter*-annual SPOM variability. Taking soil OM supply and inter-annual variability into consideration will complement the discussion and improve the manuscript. I suggest the authors include these aspects and will give the reasoning in more detail below.

Overall, I would recommend publication of this fine data set in *Biogeosciences* once the suggested changes have been considered and mistakes have been corrected.

Detailed comments:

Abstract: The abstract should present the key research motivation early on (understanding the biogeochemical cycles of C and N on the WCSI, human impact and the recent development of sedimentary ^{15}N).

Chapter 2.1 Study area: Maybe this section should be part of the 'introduction' instead of the 'methods' chapter since it describes the sampling site rather than any analytical procedure.

Page 3926, lines 20-26 and Figure 1: I can't quite picture the circulation regime. Although both the SW and the NE monsoon are said to oppose the direction of the WICC this results in upwelling in one case and downwelling in the other. Intuitively, I would have assumed upwelling to occur during the offshore NE monsoon, for example. I suppose the described circulation pattern is either a result of the specific angles between coastline, wind direction and coastal current or controlled by remote re-organisation of the Indian Ocean surface circulation as mentioned in Schott and McCreary (2001)? It would be helpful if the contrasting wind regimes (SW and NE monsoon) and the pathway of the West India Coastal Current/WICC could be included in Figure 1.

Since atmospheric forcing appears to play a key role for the upwelling and downwelling regimes on the WCSI is there any wind data available (directions and speed) that could be plotted with the time series?

Schott and McCreary (2001) mention an undercurrent opposing the surface current between April and September. Is this undercurrent known from the study site? Temporarily opposing surface current and undercurrent might represent an important oceanographic feature because it could mean that, at times, suspended organic matter of different provenance and/or age could be present in the water column due to lateral advection. This would be an important issue when comparing surface and bottom water samples.

Page 3928, line 8: What is the precision of the elemental analyzer? How was the C/N ratio calculated (atomic ratio or by weight)?

Page 3930, line 11: How were the concentrations of dissolved oxygen (O_2) and nitrate (NO_3^-) determined? (missing in 'methods' chapter)

Page 3930, line 23: I don't think one should calculate averages of the isotope data from both the 2007 and 2008 SW monsoon events. As the authors mention later in their discussion and as apparent from Figure 3 the situation in August and September 2008 is considerably different from September 2007: concentrations of SPOM as reflected by C and N concentrations are much higher and the SPOM in the surface water (0-9m) is a whopping 6-7‰ heavier in August/September '08 than in September '07. This is significant! The differences become even more obvious when comparing the pigment of September '07 and August '08. I wonder if there is meteorological data available for these periods that might help explaining these differences? In any case, the data from the 2007 and 2008 monsoon events should be described and interpreted separately. Accordingly, the cross plots in Figure 5 should be adjusted or, at least, samples from the pre-monsoon and monsoon seasons of different years should be represented by different symbols.

Page 3930, lines 25-27: I fail to spot the described difference in surface and bottom water $\delta^{13}\text{C}$ composition for the SW monsoon period in the data in Table 2. On the contrary, $\delta^{13}\text{C}$ values appear to vary very little throughout the water column in August and September 2008. There is no data for the bottom water in September 2007 and the described depth trend probably derives from calculating average values for the surface water across two monsoon seasons - which I think is not feasible regarding the inter-annual variability. Instead, the most pronounced difference in $\delta^{13}\text{C}$ values between surface/subsurface waters and bottom waters appears in the pre-monsoon season, on 24 April '07. A pronounced 3‰ shift in $\delta^{13}\text{C}$ values also appears on 2 April '08 which, furthermore, is the only date when $\delta^{13}\text{C}$ values and C/N ratios show a consistent depth trend and near-perfect correlation ($r^2 = 0.96$).

Here is a general thought:

Sometime during March/April the coastal circulation regime apparently switches from downwelling to upwelling. Could it be that during this short transitional period the water column is less dynamic but rather stagnant with no strong surface current? In this case, the water column might appear more homogenous and thus facilitating the establishment of consistent depth trends, e.g., in isotope composition and C/N ratio, that otherwise are obscured by the stratification resulting from lateral advection of surface waters. In April 2008, e.g., the water column appears well mixed (Figure 2), or rather homogenous since 'mixed' suggests a dynamic process. The $\delta^{13}\text{C}$ values and C/N ratios could result from eolian supply of plant material that has just started to sink through the water column. In 2007, this situation appears to have occurred earlier, maybe in March. The depth profiles of $\delta^{13}\text{C}$, C/N and O_2 from 5 April 2007 may represent the transfer of the eolian-derived terrestrial OM towards the bottom and the onset of stratification due to lateral advection of southern-sourced surface waters. The following set of samples (24 April 2007) already features strong stratification with a clear step in the oxygen and isotope profiles. Most pre-monsoon depth profiles show such steps in the data below 9m or 18m water depth, often with 1‰ shifts in the carbon isotope profile, except for the samples from late March '08 (the stagnant period?). Is there any data on the lower boundary of the coastal surface current?

Page 3933, lines 2-4: The sentence "We carried out... during this season." can be deleted.

Page 3933, lines 14-15: The statement that low $\delta^{15}\text{N}$ values "can only be caused by nitrogen fixation" needs references. Reynolds et al. (2007) give an additional/alternative explanation for low $\delta^{15}\text{N}$ values: instead of directly taking up isotopically light N_2 from the atmosphere phytoplankton/cyanobacteria may also use ^{15}N -depleted ammonia (NH_4^+) excreted by zooplankton.

Page 3934, lines 15-22: The binary end-member model for C/N ratios (1 marine and 1 terrestrial end member) by now is a bit dated. As I have already mentioned in an earlier comment on this manuscript (see BGD online discussion) organic material from terrestrial sources can in fact reveal C/N ratios significantly lower than 12, strongly degraded soil organic matter, in particular. For the pre-monsoon period, however, the authors might actually exclude any contribution of nitrogen-rich soil-derived OM due to the fact that terrestrial run-off is minimal at this time of the year. This aspect will gain importance for the data of the monsoon season. I was wondering, though, if the lightest $\delta^{13}\text{C}$ value and the second highest C/N ratio of the

pre-monsoon period determined on 2 April 2008 at the surface could results from dust input. Plant-derived organic compounds are common components of aerosols (see, e.g., Schefuss et al., 2003) and would indeed have a high C/N ratio and light isotopic value provided they derive from C3 plants.

Page 3935, lines 10-12: “It’s hard to pin down... although several possibilities have been suggested” such as...?? It would be good to have the options listed.

Page 3935, lines 22/23: “The $\delta^{13}\text{C}$ of SPOM generally ranged from -17.6 to -19.7% , and was thus typically of marine origin.” This is the 2008 monsoon, only! The sentence may be deleted altogether since the data should already be described in the results chapter.

Page 3935, lines 24/25: “The modest enrichment of ^{13}C in SPOM during the **2008** SW monsoon ... may be attributed to the dominance of diatoms and dinoflagellates.” The statement that diatoms and dinoflagellates are isotopically heavier needs a reference, here.

Page 3936, lines 3-5: “While such depletion is characteristic of terrestrial organic matter, the corresponding C/N value (5.7) is not indicative of the terrestrial origin. We are unable to explain this anomaly.” As I have mentioned above and in my earlier comment on this manuscript soil OM would be a good candidate to significantly lower the C/N ratio. Additionally, clay minerals associated to soil material supply may introduce ammonium and/or bind some of the ammonium present in the water column during this period (Naqvi et al., 2006) and, thus, reduce the C/N ratios even further. This explanation would be consistent with increased freshwater supply from the nearby Mandovi and Zuari estuaries to the coastal surface waters as indicated by the reduced salinity presented in Figure 4b of Naqvi et al. (2006). Suprit and Shankar (2008) also associate the drop in salinity of the coastal surface waters during the SW monsoon to freshwater supply through the short but numerous rivers along the Indian east coast draining the windward slopes of the Western Ghats. Menon et al. (2011) present satellite data of chromophoric dissolved organic matter (CDOM) and suggest a terrestrial origin of CDOM in the Mandovi estuary during the monsoon season in response to increased river run-off. Furthermore, their satellite data reveals a river plume off the Zuari estuary in September 2005. Unfortunately, such data is not available for the previous months (due to cloud cover, presumably). Nevertheless, these findings illustrate that during the monsoon season river-derived organic material does reach offshore areas where it might be dispersed with the coastal current. In contrast, during the pre- and post-monsoon phases discharge from the Mandovi and Zuari Rivers is negligible (Purnachandra Rao et al., 2011). Thus, introduction of nitrogen-rich and ^{13}C -depleted material may be considered for the late 2007 SW-monsoon data (September 07), only. There is, apparently, discharge data available for the Mandovi River (see Suprit & Shankar, 2008) which could be included in Figure 3 along with meteorological data (rainfall, wind direction).

Regarding the significant differences observed not only between the 2007 and 2008 monsoon events but also between the pre-monsoon phases (compare, e.g., March '07 and March '08 pigment data) the authors might consider discussing some *inter*-annual variability of SPOM composition, even though the time series does not cover two full annual cycles, admittedly. They themselves make a case for such an approach by

describing an “early onset of upwelling ... on 24 May 2007”, assuming that “N₂ fixation ... probably varies substantially from year to year” and, eventually, finding that the “data for the two years are somewhat divergent”. Could it be that the monsoon season in 2007 was longer and/or more intense than the in 2008? Again, meteorological data could provide the means to pin down the observed differences, thus, resulting in a more convincing data interpretation.

Page 3937, lines 1-7: Here, an increase in the $\delta^{13}\text{C}$ value of more than 3‰ from -23.8‰ to -19.3‰ associated with constantly low C/N ratios is suggested to indicate predominantly marine OM whereas a similar $\delta^{13}\text{C}$ value of -24.7‰ combined with a (moderately) higher C/N ratio is suggested to indicate terrestrial OM supply. Assuming a constant marine OM origin when one proxy clearly varies while the other remains constant is tricky. What about a mix of nitrogen-rich but ¹³C-depleted soil OM and nitrogen-rich as well as ¹³C-enriched marine OM? The impact of soil OM export on common proxies to assess marine and terrestrial OM amounts and the resulting severe underestimation of terrestrial OM sedimentation has been described for tropical river systems elsewhere (Weijers et al., 2009; Holtvoeth et al., 2005). Decreasing proportions of soil OM after the SW monsoon could very well result in the observed pattern of decreasing $\delta^{13}\text{C}$ values and constant C/N ratios from September to December 2007. In January ‘08, there is indeed evidence for the supply of ‘conventional’ terrestrial input, i.e. of plant matter. This time, the C/N ratios do increase. This could be interpreted as eolian input which would complement the assumption of atmospheric nitrogen supply during the winter made earlier in the discussion.

Page 3937, line 21: The possibility of atmospheric deposition of nitrogen and terrestrial run-off are mentioned in the manuscript but not properly discussed. There is evidence in the data for eolian input of nitrogen and carbon at times (e.g., 31-Jan-08 and 2-Apr-08) that could possibly be backed up with data on wind directions – if available. No data has been presented for the timing and amounts of fluvial run-off.

Page 3938, lines 1, 2: I am not very familiar with the post-sedimentary effect of early OM diagenesis on the nitrogen isotopic composition. Is it not very likely that diagenetic processes in the surface sediments increase the proportion of the heavy isotope? Although the possibility of diagenetic enrichment is mentioned in the abstract there is currently no discussion of this aspect in the manuscript. Please, add a few lines on this matter.

Page 3938, lines 5-9: As mentioned above, there is a very good chance of soil OM supply during the monsoon season that would keep C/N ratios low but modifies the carbon isotope signature. Please, consider this aspect for the monsoon/post-monsoon period in the discussion.

It would be nice to see a scheme or conceptual model illustrating how the composition of SPOM changed over the period of the time series with regard to marine productivity (shifting, e.g., from phytoplankton to cyanobacteria), eolian input and terrestrial run-off. It could display a succession of events such as “upwelling”, “trichodesmium bloom”, “fluvial soil OM supply”, “bottom water oxygen deficit”, “eolian plant OM supply” and the like. Although all of this can be filtered out of the data displayed in the figures and the data discussion I think this would help the reader

a great deal in picturing what was going on at the site before, during and after the monsoon seasons of 2007 and 2008. Such a scheme could be presented in the conclusions chapter or combined with Figure 3 and meteorological data (if available).

Technical corrections:

Page 3926, line 18: delete “Indian Ocean”

Page 3933, line 15: correct *Trichodesmium*

Page 3935, lines 10, 12 and 18: Please, specify Naqvi et al. (2006) as 2006**a** or **b** according to the reference list.

Table 1: replace “24 May 2007” with “24 **April** 2007”

Figure 2: Please, add units of contour lines (μM) to figure or figure captions.

Figure 3: The figure displays the **wrong data for 2-Apr-08!!** This appears to be a copy of the data from 31-Jan-08. Correct according to Table 1.

Figure 5: Please, separate the samples from the 2007 and 2008 pre-monsoon and monsoon periods by using different symbols. In fact, it might be worth plotting the data separately. Check how correlations change then.

References:

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