**Biogeosciences
Discussions**

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Interactive comment on "Intra-annual variability of carbon and nitrogen stable isotopes in suspended organic matter in waters of the western continental shelf of India" *by* M. V. Maya et al.

Anonymous Referee #1

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General Comments

The manuscript presented by Maya et al. is an investigation of the δ13C and δ15N values of suspended particulate organic matter (SPOM), elemental C and N values, and SPOM pigment analysis, from the water column on the west Indian continental shelf region. They investigate the elemental and isotopic characteristics of SPOM at the inter-annual timescale with the aim of assessing the fidelity of δ15N as a denitrification proxy in this region. The authors conclude there the interpretation of δ15N purely as a denitrification proxy is, in fact, problematic.

The overall quality of the manuscript is relatively good, though there are a number of

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key concerns which need to be addressed, particularly in relation to the controls on elemental and isotopic C and N composition of SPOM (e.g. diagenetic effects); the sampling procedure and measurements of some of the data; an understanding of the true accuracy and precision of the data, and a clear representation and discussion of this; and the theoretical frameworks within which the data has been interpreted and discussed within.

It is my opinion that this manuscript is of a publishable quality, and will add an important debate to the literature, but requires major revisions to be undertaken before publication. This will allow the authors to improve the strength and clarity of their argument. I provide details of these proposed major revisions which I feel will improve the manuscript, and strengthen and clarify the arguments being made by the authors, and which I hope they find both helpful and insightful.

Specific Comments

I have a number of issues with this version of the manuscript. These include the (i) specific focus of the manuscript in relation to the clarity of the scientific issue being investigated, (ii) rationale behind the sampling approach, (iii) pre-analysis method relating to the elemental and isotopic C and N data, (iv) development of a clear understanding of the processes (i.e. literature review with clear thread of argument built up for the reader on C and N processes in the water column, and how they interact) controlling the elemental, isotopic and pigment concentrations in SPOM in these study are, and how this relates to the sampling strategy employed, (iv) clarity over the findings and how the authors reach the final conclusion on the fidelity of the δ15N as a problematic denitrification proxy. The comments/suggestions I make below require clarification, and may strengthen the overall presentation and scientific rigour of the manuscript presented for publication in Biogeosciences.

1. In general, the introduction is a little on the short side, and too general, with some reliance on references in place of a more detailed, structured argument. As such, it does

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not clearly lead into the overall aim of the paper (it could be done much more clearly, and focussed). I propose the authors consider the following points to restructure their introduction, strengthen the argument and bring clarity to what it is they are setting out to do and why it is important: a. The opening 2 sentences are very empty, and do not really set up the study other than to say we can measure kinetic isotopic fractionations. I'd rather see the authors replace these two sentences with more details from the references they provide at the end of sentence 2, and explain exactly why δ13C and δ15N in SPOM are a powerful tool for investigation "transformations in aquatic systems"...e.g. what transformations? What has been discovered in these studies? b. In sentences 9 – 10, the authors provide some details on key controls on these isotopic signatures in these environments, but overlook diagenetic processes, effects of acid pre-treatment of organic matter (see below; Number 3); photosynthesis; proportionality of end member contributions; proportions of refractory/non refractory organic components and lability of organic components; inorganic contributions (both C and N). This discussion is important, and needs some expansion in the context of this system under investigation, with some clear evidence from the literature that there is confidence in this region, and others, of what factors are the primary controlling factor and how this is known with any confidence. In other words, provide the reader with the proof that in the first instance, you can achieve what you say you can, and that this has been shown in past research. At the moment, it is very weighted towards δ15N, and very little on δ13C (in fact, this is typical of the paper, that δ13C is sub-ordinate to δ15N, and the authors may wish to re-evaluate this). c. At the moment, I feel the literature that leads up to the real understanding of the problem being investigated in this region is either non-existent or glossed over, and really needs to be brought into focus, discussed explicitly and leading into a clearly defined research question on denitrification. This will come from some expansion on the findings and short-comings of past research in this area and others. There is considerable room for a more focussed, and stronger, discussion.

2. The rationale behind the sampling strategy is unclear, with the exception of the seasonal context. Why did you pick the depths that you did, and why only 3 depths? What

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was the "error" linked with sampling location on return visits, and sampling depths? (i.e. you did not sample exactly the same location on each visit – does this have any implications?). Why sample on the dates you have sampled? What are the implications here given year on year variability in the overall coupled land-ocean-air system? (anything to note here?) I would like to see the author's clearly state the rationale for the sampling strategy in section 2.2, over and above the obvious seasonal factor.

3. I am concerned with the pre-analysis sample pre-treatment approach adopted by the authors with respect to elemental and isotopic C and N. In the first instance, there is not enough information provided on the acid-pretreatment method followed (here fumigation of samples using 6N HCl), nor on the analytical method (e.g. is this "dual-mode" isotope analysis. . .where elemental and isotopic C and N are measured simultaneously from the same pre-treated sample). At the moment, this is all glossed over and needs bulked up in the methods section to the point where readers can comprehensively follow the authors approach (i.e. competently repeat this analytical approach if they so wish)

An important body of literature exists on the effects of acid treatment of "bulk" organic matter (which is essentially what SPOM is, containing varying proportions of refractory and labile organic components). I refer the authors to the following 2 references which highlight these issues, and provide a good literature review within them that the authors need to be aware of, and reflect upon in this manuscript (it is, after all, a potential codicil to any interpretations presented here and elsewhere).:

Brodie, C.R., Leng, M.J., Casford, J.S.L., Kendrick, C.K., Lloyd, J.M., Zong, Y.Q., and Bird, M.I. (2011) Evidence for bias in C and N concentrations and δ13C composition of terrestrial and aquatic organic materials due to pre-analysis acid preparation methods. Chemical Geology. 282, 67 – 83.

Brodie, C.R., Heaton, T.H.E., Leng, M.J., Casford, J.S.L., Kendrick, C.P., and Lloyd, J.M. (2011) Evidence for bias in measured δ15N values of terrestrial and aquatic or-

ganic materials due to pre-analysis acid treatment methods. Rapid Communications in Mass Spectrometry. 25, 1089 – 1099.

Given this, the author's should consider giving the elemental and isotopic analysis a section in its own right within the manuscript so as to fully detail their method(s) and reflect on potential biasing to their measured values consequent of the pre-analysis approach. It should be borne in mind, particularly given the extent of the biasing, that this could preclude interpretation of some samples (particularly δ13C given such small differences). The authors should also bear in mind that SPOM is essentially "bulk" organic matter in the water column, comprising varying proportions of refractory and labile organic matter, and varying proportions of living and decaying materials from both terrestrial and marine origins.

In addition, it is not clear whether the elemental and isotopic measurements made have been made only on single samples, or whether they have been run in duplicate or triplicate. This needs to be clearly stated, and the one standard deviation over duplicate or triplicate measurements quoted on all samples.

Have the author's made measurement on pre-combusted Whatmann filters, capsules and acid to check for background C and N, and to correct for any contamination? If so, this needs to be stated, and if not, then this needs to be acknowledged as an unknown and a potential contributor to the variability in the data.

With respect to the discussion of these isotopic data, I am not clear why the discussion appears to be focussed on δ13C and δ15N averaged over all depths and within one season...i do not understand why...the approach to the discussion of the data should be made clear. To help show up differences between seasons/depths etc., the authors may consider some statistical analysis of their data, such as ANOVA, which may show up interesting "between" season difference.

4. There needs to be some detail on the statistical approach used by the authors (i.e. linear regressions presented in Figure 5). What is the rationale for analysing the data

in this manner, and why has a linear relationship been assumed in an inherently non-linear system? In addition, the linear model that represents the graphical fit (i.e. the equation) is not represented, and there is no error bars presented for the data. This all needs to be clarified and corrected. What does the r^2 value represent in the plot (considering potential bias from acid method, inorganic C and N)?

5. It is not clear how the authors have measured the dissolved O2 and nitrate data, or whether they have obtained this data from a published source. This needs to be clearly detailed in the methods section, with imprecision on the data noted. I'd like to see more critical evaluation of the relationship between the isotopic data and the O2 and nitrate data, such as in the context of diagenetic processes, for example. Can this be done?

6. With respect to Tables 1, 2 and 3, there are no errors stated for any of the data. This is not acceptable. All measurements carry an inherent imprecision (at least instrument precision, but usually greater) which needs to be stated.

Also, why have the authors taken the mean and SD of the entire data set (i.e. across all seasons and sample depths)? Why has this not been done on a seasonal basis/depth by depth across the seasons?

What does the SD represent? 1 or 2 standard deviations? Why is this mean value and SD important to the discussion that is focussed on seasonal differences/changes?

What does the unit uM mean? And why has elemental C and N data not been presented and discussed as ug C relative to the bulk sample measured, or as a percentage?

7. I am disappointed that there is no discussion on the potential role of diagenesis. This is an important consideration in water column SPOM, under varying oxygen conditions and seasonal phytoplankton changes, differing proportions of aquatic and terrestrial end members which could all contribute to physical and/or chemical alteration of SPOM. This needs to be fully discussed in the context of the results (constrained by

the understanding of acid pre-treatment biases), particularly as the author's come to the conclusion that their data "imply a limited utility of sedimentary δ15N as a water-column denitrification proxy in the region". I believe the manuscript (and its scientific understanding and discussion of the new data) will be strengthened by a wider discussion of diagenetic processes in this region, and other similar regions, and how it may play a key role. This is mentioned in one or two areas, but in no more than a "throw away context"....the discussion needs to reflect what is are important biological/physical processes in the water column, bearing in mind they could be different for C and N, as could the resultant magnitude of change on the signature.

8. The context with which the C/N and δ13C values have been interpreted and discussed within is highly questionable and, in my opinion (i.e. in the context of comments made here, assumptions on C/N values, but particularly δ13C values as an organic matter provenance index) probably incorrect in the context of bulk SPOM in the water column. Consider the following points: a. The authors interpret C/N values as an indicator for organic matter provenance, suggesting that, as all values are below 10, then the organic matter is predominately derived from aquatic sources. Whilst this can be widely cited as "fact", the author's should consider that C/N values in this "boxed up" fashion are not necessarily correct, with marine and/or freshwater algaes/macrophytes known to produce C/N values of > 30. b. The authors state that δ13C values of between -17.6 ‰ to -19.7 ‰ is typical of marine origin (Page 13, Line 23). What is the proof of this? δ13C as an indicator of provenance, such as marine versus terrestrial, as portrayed in this manuscript, is highly questionable. If the authors want this to stick, there needs to be a robust discussion and justification for reaching this interpretation, fully referenced with the nuances made explicit and dealt with. Otherwise, I encourage a re-evaluation of their position on this.

9. Check all references to ensure they are correct.

Technical issues (e.g. Typo's; units etc etc.)

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I have a number of small points for the authors to consider:

1. Page 3, Line 25. Use of phrase " in response to monsoonal forcing". Consider changing to "due to seasonal wind regime". Also on Line 25, remove "As described above" and replace with "One of".

2. Page 4, Line 7. The authors highlight trend over the $\sim$50yr. Consider the impact this statement makes, as you are measuring and discussing data on the seasonal timescale. Thinking on these timescales brings in additional processes which need to be carefully considered with respect to the reader...for example, on $\sim$50 year timescales, within sediment processes will be important, not just water-column processes. Some more detailed discussion of this, in the context of your findings from surface sediment measurements, could be undertaken. I also think this could be explained in more detail, be expanding upon the Agnihotri et al., 2008 and 2009 references.

3. Page 4, Line 18. "entire Indian Ocean Arabian Sea"...what does this mean?

4. Page 4, Line 22. Remove "... which enriches" and replace with "and increases nutrient supply to"

5. Page 5, Line 1 – 2. Change "extreme" and "of" to "local" and "in" respectively.

6. Page 5, Line 5. Why have you used the word "sustenance"?

7. Page 5, Line 14. Change "manifested by" to "evident from".

8. Page 5, Line 17 – 20. Remove the sentence beginning "As stated above....".

9. Page 6, Line 17. How many analysis were undertaken to provide the measurements of isotopic standard values and the standard deviations. Give an n = XX please.

10. Throughout the results, the units need to be re-considered. Please put elemental C and N as either ug C or %.

11. Page 7, Line 15. Why arithmetic means? What insight does it give, why is it useful?

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Why not geometric means?

12. Page 8, Line 1 – 2. What do these values relate to? All depths and sediment? Does this obscure the seasonal focus?

13. Throughout the results it is not clear whether the SD values provided are 1SD or 2 SD. This needs to be stated.

14. Page 9, Line 13. Word confusion ..."early during...".

15. Page 9, Line 24. You state "on average, the C/N ratios (6.55 ±1.39 ‰". C/N values do not have units of "‰'.

16. It strikes me as though there is a "year on year" variability within the system at any one time, but I don't really feel this coming through in the discussion and which may obscure the seasonal differences the authors discuss. I'd like to see some consideration of how the longer term variability/change, could potentially obscure the seasonal signature, and how the authors can really bring out this seasonal signature for discussion (and this links back to the opening remarks in the introduction linked to ∼50 years).

17. Page 11, Line 14 – 15. Relating to the only mechanisms being N2-fixation. Please provide references and a little more discussion on this remark, as it is the centre piece of the discussion at this point in the manuscript.

18. Page 12, Line 28 – 29. You mention "year to year variability"...and linking back to point 16 above, can you show how this spatio-temporal variability does not completely preclude you're interpretation on seasonal variability. For example, given the low ranges/differences in δ13C you have, can this be accounted for as a function of noise in the system? Or acid treatment?

19. Pages 13, Line 11 – 12. Please state explicitly the "several possibilities that have been suggested".

20. Page 13, Lines 14 – 21. You need to be clear here. You are right to say this is

a complex and dynamic system with large variability, but what "large variability"? what are the complexities of the system? More importantly, how does this really feed into your interpretations and understandings (see points 16 and 18 above).

21. Page 13, Line 25. You comment that the modest shift in δ13C could be a function of the proportion of diatoms and dinoflagellates in SPOM. Could it not be intre-annual, sub/decadal system variability? Inorganic materials? Acid treatment bias? Diagenetic processes? Are there any references you can use to support this point?

22. Page 14, Line 3. Sentence beginning "While such depletion is characteristic of terrestrial organic matter...". I am not convinced by this. Please provide a literature review (as previously stated above) for the proof that δ13C can be used as an unequivocal terrestrial v aquatic provenance tool. Much more consideration on what C/N values and δ13C values are really saying – much more discussion around these values, and their potential controls, is essential and cannot be glossed over.

23. Page 15, Line 13. Are you implying species composition is spatially heterogeneous? If so, what impact does this have on the elemental and isotopic signature within this study, over different depths, different seasons, and different years? How does ecological patchiness influence these elemental and isotopic compositions in space and time?

24. Page 16, Line 4. Is there any time lag that influence elemental and isotopic signature between the water column and surface sediments? i.e. different processes, and process rates in these two very different environments.

25. Page 16, Line 5 – 10. I think this will change after re-evaluation of the C/N and δ13C data.

Interactive comment on Biogeosciences Discuss., 8, 3923, 2011.