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# ***Interactive comment on “Transfer of lipids through marine water columns to sediments – insights from stable and radiocarbon isotopes” by S. G. Wakeham and A. P. McNichol***

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Below is review 1, with our responses in bold italics; red indicates the changes that will be made upon revision (see attached pdf if colors do not show here):

This manuscript discusses the sources of organic carbon in surface sediments of Black Sea, Arabian Sea and Ross Sea. Contributions of ‘marine biomass, terrigenous vascular plant, and relict sources’ are evaluated using lipid biomarkers, stable carbon and radiocarbon analysis. To better understand the global carbon cycle and its impact on climate change, it is important to learn sources of OC in marine sediments, which is still not well-studied. Radiocarbon analysis of specific lipid biomarkers is a powerful tool for

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marine OC sources apportionment in the past 15 years and it is applied in this study. I realize that nice samples and data were obtained in this work, but the authors fail to show an interesting story. Some terms are not defined, some conclusions are not easy to understand because a lack of detailed explanation. The key points of some sections are not clear that I need to read several times to have an idea what valuable information I can obtain. The manuscript needs to be reorganized to make the manuscript easily understandable to the reader and highlighted the key points.

Specific comments: Title: P9761: I suggest modification of the title. As mentioned in the abstract, the manuscript focuses on the sources of OC, but not lipid biomarker. Lipid biomarker is a tool for OC source apportionment. Ok, we will modify the title slightly to: “Transfer of organic carbon through marine water columns to sediments – insights from stable and radiocarbon isotopes of lipid biomarkers”.

Abstract: P9762 Line7: What’s the definition of ‘relict sources’? “Relict” is a commonly used term in geology, but to clarify we have changed “relict sources” to “relict kerogen sources.” See also lines 3-6, p 9765.

P9762 Line7: ‘sediment trap material’. It takes me some time to remember that ‘sinking particulate matter’, ‘sediment trap material’, ‘particulate organic matter/POM/bulk POM’ used in this manuscript are the same thing. We agree that these terms are interchangeable, as are sediment organic matter, SOM etc used throughout. Actually “bulk POM” and “bulk SOM” are used to specifically distinguish the unfractionated material from the extracted SLE (see comment below) or specific isolated biomarkers. We do not feel that these need to be changed. POM and SOM were first defined on p 9764, line 27.

P9762 Line7-11: ‘Marine biomass in. . .respectively.’ P9762 Line15- 18: ‘These results. . .marine POC.’ I suggest you explain a little about how you get these conclusions, even though you have mentioned in the text. I feel that’s more important than or as important as the conclusion itself. We are not sure what is requested here. Since

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this is in the abstract, it is a summary of results and discussion that follow and are developed in the main body, from which the abstract is derived. However, we will modify (changes in color) the abstract to: . . . “The goal was to develop a multi-parameter approach to constrain relative inputs of organic carbon (OC) from marine biomass, terrigenous vascular plant, and relict kerogen sources. Using an isotope mass balance, we calculate that marine biomass in sediment trap material from the Black Sea and Arabian Sea accounted for 66-100% of OC, with lower terrigenous (3-8%) and relict (4-16%) contributions. Marine biomass in sediments constituted lower proportions of OC (66-90%), with consequentially higher proportions of terrigenous and relict carbon (3-17% and 7-13%, respectively). Ross Sea data were insufficient to allow similar mass balance calculations. These results suggest that whereas particulate organic carbon is overwhelmingly marine in origin, pre-aged allochthonous terrigenous and relict OC becomes proportionally more important in sediments, consistent with pre-aged OC being better preserved during vertical transport to and burial at the seafloor than the upper ocean-derived marine OC.”

By the way, what’s the definition of ‘pre-aged OC’? “Pre-aged OC” is a term commonly used in the radiocarbon literature to designate allochthonous OC that has been aged prior to being delivered to its present depositional setting. Since it is widely used, we do not think a definition is needed here. But see line 10, p 9764 and lines 3-6, p 9765.

Introduction: P9763 Line9: “marine OC’ may contain ‘terrigenous plant and relict sediment OC’. So what’s the real meaning of ‘marine OC’ herein? Again, we are not sure what the reviewer is asking. “Marine OC” is a commonly used term for autochthonous OC, as opposed to allochthonous terrigenous and relict kerogen OC. It is true that OC in the ocean will be a mix of autochthonous marine and allochthonous terrestrial and relict OC, but we do not feel that changing the terminology here is needed.

One extra question: Are there any previous studies on sources of marine OC in the same study areas? Without statement of historical work, it is not clear what knowledge the present work will added. At least, I know Eglinton et al., 1997, Science also ‘com-

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bined biomarker/stable carbon/radiocarbon studies of marine particulate matter', studying the sample area (e.g. Black Sea and Arabian Sea). To our knowledge, there are no comparable sediment trap OM-sediment SOM compound-specific biomarker/stable C/ radiocarbon isotope studies in the literature, especially not for these areas. The Eglinton et al paper 1997 cited here and on p 9764 line 7 does indeed give from  $^{14}\text{C}$  data for sedimentary lipids in the Black Sea and Arabian Sea, but not in sediment trap material (marine particulate matter as the reviewer suggests), which is the novel feature of this paper. Kusch et al (cited p 9782) report radiocarbon data for some alkenes in several core tops (no trap material) in the western Black Sea.

But we will add the following to p 9778, line 12: "A similar spread in  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  values for marine, vascular plant and relict hydrocarbon biomarkers had been previously reported for Black Sea and Arabian Sea sediments (Eglinton et al., 1997)."

Results and discussions: P9772-4 Section3.2-3.3: When compound-specific stable carbon/radiocarbon analysis of sources biomarkers is used to estimate sources of OC, why it is still necessary to measure stable carbon/radiocarbon of bulk OC? There is a tremendous literature on isotope compositions of bulk POM and SOM, so by including these here, it puts these samples into a wider perspective. Further, we use the compound-specific results as proxies for bulk OC, which really is what is of importance to biogeochemists.

In this section, sometimes abbreviated names of the seas (BS, AS and RS) are used, sometimes non-abbreviated names are used. It takes me some time to remind what the abbreviation means, because they are not as commonly used as 'OC'. I suggest avoid using abbreviated names of the seas since the names are actually not long. We feel that the abbreviations are not a problem and they have been defined when first used.

Several points make Section 3.3 difficult to follow:

1) The discussion starts from BS and AS, switch to RS, back to BS and AS, again

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switch to RS, then to AS and RS. To us, this order of the two paragraphs in this section labeled “bulk radiocarbon isotopes” is logical as we are talking about two separate sample sets (OC vs SLE): paragraph 1) presents radiocarbon of bulk BS, AS and RS trap and sediment OC; paragraph 2) then gives radiocarbon for BS, AS and RS trap and sediment SLE’s.

2) DIC probably means dissolve inorganic carbon, but it is not introduced in the text above, and the authors also don’t mentioned DIC was measured before this data is showed. It is confusing that why the discussion switch to DIC herein. Yes, DIC does mean dissolved organic carbon; we thought the term was widely accepted. But we will change to “pre-bomb and post-bomb mixed layer DIC (dissolved inorganic carbon). . . .” DIC was not measured in this paper, so it was not included in methods; the values given are from the literature as cited. But mixed layer DIC is important for setting the  $^{14}\text{C}$  of the autochthonous marine OC component, effectively one end-member.

By the way, what’s SLE (P9774, Line12 and also P9773, Line5). SLE was defined when first used on p 9769 line 6.

3) There is no prior explanation of ‘pre-bomb and post-bomb’ (P9773, Line25). Even though I know the change about atmospheric  $^{14}\text{C}$  concentrations before and after nuclear weapon test, it is still not easy to make clear what the authors intend to tell herein. Again “pre-bomb” and “post-bomb” are widely used terms in the radiocarbon community and we do not fell that they need to be redefined here. Pre- and post-bomb terms are related to the DIC question noted above.

P9780 Section3.6: Components of OC can vary a lot in radiocarbon age, why the radiocarbon ages of bulk OC can be used in the mass balance method? The goal of this paper was to use lipid biomarkers to tease apart the isotopic contributions from the marine, terrestrial, and relict components, and then to try to apportion sources and show how the relative contributions from each changes between the water column POM and the underlying sediments, i.e. bulk OC. Using the biomarkers, we thought

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would give a better opportunity to determine the relevant endmembers, given that, as the reviewer points out, components of OC can vary a lot in radiocarbon age. Thus the  $^{14}\text{C}$  of the biomarkers is used to estimate the relative inputs from the different OC sources.

Below is review 2, with our responses in bold italics; red indicates the changes that will be made upon revision:

The Wakeham and McNichol paper examines the stable and radiocarbon composition of a quite wide range of lipid biomarkers from a unique set of marine particulate samples, including both water column particles and surface sediments from the Black Sea, Arabian Sea and Ross Sea with contrasting oceanic settings. Both the sample set and the compound-specific  $^{14}\text{C}$  data are very precious, given the laborious nature and stringent analytical standard required for this type of analysis. Some of the results are the first attempt applied to the specific environment and will add valuable information on the source and fate of lipid compounds in the ocean. In this regard, the paper is very worthy of publication.

The authors further attempt to constrain the relative inputs of marine, terrigenous, and relict OC sources by utilizing a multiparameter mixing model. While this approach has been used in quite many papers previously, it is not very clearly explained here, particularly the end-member values. For instance, both Cadded and Cother are mentioned. What's the difference? Does Cadded include both CT and CR? If so, why is  $_{14}\text{C}_{\text{Cadded}}$  assumed to equal  $_{14}\text{C}_{\text{Crelict}}$ ? I think this needs to be clarified as it has a decisive effect on the result of the mixing model solution. Our model differs from many that have been used because we are not able to use the  $\delta^{13}\text{C}$  values (see comment below). This forces us to make assumptions that are not necessary in other models. The mention of both Cadded and Cother is an editing mistake; Cother will be edited to Cadded. Clarification of the confusion is attempted with the following editing of the text between lines 554-557 and 570-574.

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554-557 For each sample, there is a  $\Delta^{14}\text{C}$  value assigned to the bulk SLE extract, fresh marine, fresh terrestrial and a relict/terrestrial mix. Bulk material is assumed to be a mixture of fresh marine and other “added” material, where the added material refers to the fresh terrestrial and relict/terrestrial mix. Given this, we can derive an equation the relative amounts of marine and “added” material.

570-574 Truly relict material has a  $\Delta^{14}\text{C}$  value of  $-1000\text{‰}$  and fresh terrigenous material has the values determined in this study ( $\Delta^{14}\text{C}_{\text{CT}}$ , Table 5). As stated earlier, the measured value of  $\Delta^{14}\text{C}_{\text{CR}}$  appears to be a mixture of truly relict material and terrigenous material with a suite of ages. If we assume that the value we measured for “relict” material (Table 5) is a good representation of  $\Delta^{14}\text{C}_{\text{added}}$ , then we can assign a unique solution to the mass balance.

Also, on Page 9780, it says “the small differences in  $\delta^{13}\text{C}$  coupled with significant error make it difficult to use the stable isotopic composition as a discriminating factor in determining the sources of the bulk material”. But it seems that  $\delta^{13}\text{C}$  values in Table 4 are still used for the calculations. Why so? How are the  $\delta^{13}\text{C}$  values chosen?  $^{13}\text{C}$  values, obtained by the same averaging as for  $^{14}\text{C}$ , are indeed included in Table 4, but as stated in the text their range was small and as such they were not helpful in distinguishing OC source so they were not used in mass balance.

Finally, as compared with marine-derived lipids, terrestrially derived lipids are relatively poorly represented in Tables 1-3 with only 3 compound classes, although they are probably the most abundant and workable types in the solvent extractable lipids. But considering the large range of  $\Delta^{14}\text{C}$  values found for various marine lipids (in Arabian Sea, for example), how much confidence do you have in having these three types of lipids to represent the average  $^{14}\text{C}$  content terrestrial OC? As compared with marine biota, lipids are a relatively smaller component in the terrestrial biomass or OC. Some recent work has shown that other major terrestrial biopolymers (lignin) may have different  $^{14}\text{C}$  ages in surface sediments. How will this affect the end-member values and hence the result of the mixing model? We don’t know how to answer this except to say

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that we had to work with what we were able to measure. Other compounds like lignin would indeed have been helpful, but in most of the samples available, there would have been too little lignin to work with as the trap and several sediments would have contained little lignin, and in any event at the time of analysis compound-specific lignin methods were not available. The results of the mixing model are not presented as the absolute answer but as an indication of what the data suggest is happening.

Specific comment: Page 9771, Line 15: Pearson and Eglinton (2000) is not found in the references. Yes, it will be added.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/11/C5349/2014/bgd-11-C5349-2014-supplement.pdf>

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Interactive comment on Biogeosciences Discuss., 11, 9761, 2014.

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