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Biogeosciences
Discussions

Interactive comment on "Downward fluxes of elemental carbon, metals and polycyclic aromatic hydrocarbons in settling particles from the deep Ionian Sea (NESTOR site), Eastern Mediterranean" *by* C. Theodosi et al.

C. Theodosi et al.

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We would like to thank Prof. C. Migon for the time and effort provided to review our study and his constructive comments that helped us improve our manuscript. All corrections suggested have been carried out in the revised version of the manuscript in which certain parts (Abstract, Introduction, Results and Discussion and Tables 1 and 2) have been changed appropriately in order to make the synthesis of both Reviewers' comments and suggestions. Overall, we believe that the manuscript has been improved in response to the Reviewers' helpful comments.

Reviewer #1: C. Migon (Referee) General comments: The manuscript deals with the variability of export flux at a Eastern Mediterranean site, using sediment trap deployments at different depths. The data set seems quite significant and valuable, and it is certainly a steady basis to address such a study. In addition, the manuscript is written in a pleasant straightforward form.

- My main concern is that the conclusions of this work are not clear. A key question, I think, is to understand what are the parameters that control the temporal variability of export fluxes. The data set used here presumably permits to provide responses, but I have not found clear conclusions (or, at least, suggestions). What is the role of atmospheric deposition of mineral matter? Does it cause export, or does it only ballast mass fluxes? This is very important to better understand the dynamics of mass fluxes. The wide range of parameters measured in the work of Theodosi et al. is very interesting, and should be used to compare the temporal variability of the respective emisisons sources of trace metals and of organics with that of the export flux, in order to understand the causal relationships: What parameter(s) drive(s) the export? External inputs of mineral matter or internal processes such as vertical mixing and/or biological productivity? I am convinced that, once the authors have focused their efforts on such a conclusive way, using all the potential of their data set, the manuscript will be of great significance.

Response: We also share the concern stated by the reviewer that a key question of this study is to understand what are the parameters that control the temporal variability of export fluxes of studied elements in the study area, since we believe that is essential for understanding pollutant's fate in this and any similar sediment trap study. However, as it is clearly stated in the beginning of the results and discussion section of our study (Page 19170, lines 22-26) in order to better assess the variability of the individual compounds fluxes reported in this study, we consider Mass flux and particulate organic carbon (POC) flux data in the study area which are not part of the dataset of this study but are reported by the adjoining paper Stavrakakis et al., 2013 BGD (this issue) and refer of course to the same set of samples. On this basis we use the data provided by Stavrakakis et al., 2013 in order to discuss in Section 3.3 the initial observation that fluxes of all studied elements, regardless of their origin, are strongly and significantly ($p<0.01$) intercorrelated, probably suggesting a common transport mechanism in the deep layers of the Ionian Sea (Nestor site). To this purpose we present in section 3.4. in a synthetic way major conclusions presented in Stavrakakis et al., 2013 BGD paper and unpublished data of Theodosi and Mihalopoulos in order to show that mass flux temporal variability in the study area, which of course represents the overall export of particulate material and associated primary pollutants, is subjected to strong seasonality which is driven by a combination of forcing (winter mixing or Saharan events, in particular extreme ones), biological (zooplankton) activity and also organic-mineral aggregation inducing a ballast effect. Moreover, it is clearly stated in the results and discussion section (Page 19176, lines 17-23) as an conclusion of the discussion in paragraph 3.4 and data presented in corresponding Figures 3,4, 5 and 7 of our study that the increase in dust deposition during 2007 and 2008 could explain the observed increase in mass flux between the same years , emphasizing the role of dust deposition in particular those that are induced by the more extreme Saharan events, whereas recorded maxima during May to September 2008 are likely attributed to mixed biogenic fluxes. We believe that the above approach is sufficient enough as a statement of what are the factors that control the temporal variability of export fluxes and a more detailed discussion will be presented in the adjoining paper Stavrakakis et al., 2013 BGD (this issue), since data on the temporal characteristics and fluxes of Mass flux, POC and ballast minerals are not part of the dataset of this study. The parameters have been addressed throughout the manuscript, however as suggested by the reviewer in the revised manuscript certain parts in the abstract, Introduction, results and discussion sections have been extensively changed in order to make the synthesis of both Reviewers' questions stated/comments/suggestions and improve both data and results presentation which may were misleading and/or confusing as a final outcome/conclusion in some cases.

Specific comments: - Introduction: 'The present study (. . .) and examines the role of seasonal changes in the biochemical composition of settling particles (Stavrakakis et al., 2012) as a driving force for their export to the deep Ionian Sea basins.' The meaning of this sentence is not clear. Does it suggest that mineral matter (or any other type of matter) is likely to determine export fluxes? (the term 'driving force' suggests that the occurrence of the export is caused by mineral matter). If any, this is very different of the ballasting effect, which only implies that the presence of mineral matter speeds up the sinking of matter. And marine fluxes are therefore expected to follow the same the seasonal patterns of atmospheric deposition, or, at least, it is expected that significant atmospheric events determine export fluxes, hence a coupling between the seasonal pattern of significant atmospheric events and that of export fluxes. Was it observed actually? This point remains unclear in the further discussion.

Response: As stated by the reviewer in order to be more accurate the appropriate changes have been performed in this part of the Introduction along with certain parts in the abstract, results and discussion sections in order to be more accurate in the presentation/interpretation of our results. Please follow our answer above.

- Section 3.1.1: 'Since EC is not participating in the food chain', I am not sure this is definitely stated. See e.g. Potter (1908), Cattaneo et al. (2010) or Weinbauer et al. (2012). Please check it.

Response: The reviewer is right and the comment has been deleted. Thank you very much for this comment.

- Section 3.1.2 last paragraph: 'Crustal matter flux was determined using Fe or Al as tracers of crustal elements, assuming a relative ratio of 4.5 % and 7.1 % for each sample, respectively (Guieu et. al., 2002; Wedepohl, 1995).' The use of these percentages is an obsolete method, I think: the content of Al, Fe, etc. in reference soils or rocks may vary quite significantly, and crustal matter is not made only of Fe and Al. In addition, I do not clearly see why the authors do that. If they intend to demonstrate that mineral matter is sometimes the most important constituent of the sinking material, it might be easier to compare the sum of Al, Fe, and mineral Si (at least) fluxes, and the total mass flux. It would be approximative, but less than the method used here.

Response: Indeed the reviewer is correct and there could have been other ways to calculate the "lithogenic matter" of the sinking material. However, lithogenic matter has been demonstrated in detail by the adjoining paper Stavrakakis et al., 2013 BGD (this issue), that is the reason why it has not be been discussed thoroughly and why we have addressed it as crustal matter instead, using two metal elements presented in this study as a reference/marker to approach ''lithogenic" matter contribution in the study area. Definitely there is wide range of factors lithogenic matter that could have been discussed but it was our intention to present it as a range. However, the result calculated, using Fe as reference that lithogenic matter ranged from 45% to 54% of total mass is in good agreement with the results presented for lithogenic matter by Stavrakakis et al., 2013 BGD (this issue).

- Then, the authors write 'The average crustal content of the sediment trap material in the study area, using Fe as reference, ranged from 45% to 54% indicating that crustal material is the most important constituent of sinking material, as demonstrated also by Stavrakakis et al. (2012).' I am not convinced by this demonstration. Indeed, some sediment trap samples exhibit high mineral content: this is expected at certain periods, such as the convective period (in areas of dense water formation), when the mineral matter accumulated above the thermocline is rapidly transferred to depths with minimal concentrations of biogenic matter, or when a significant Saharan dust event occurs and is packaged with biogenic material, at any time of the year. And so what? Once again (see my general comments), the authors should be more conclusive about that.

Response: Following the rationale stated in our initial answer the appropriate changes have been performed in this part in order to be more accurate in the presentation/interpretation of our results. We have to point out however that the fact that the average crustal material content, using a metal such as Fe as a reference, ranged

from 45% to 54% throughout the 17 months of the sediment trap deployment, in agreement with lithogenic matter data that have been demonstrated in detail by the adjoining paper Stavrakakis et al., 2013 BGD (this issue), is in fact an important aspect of the biogeochemistry of the ultra oligotrophic Eastern Mediterranean Sea, indicating that lithogenic matter is overall an important constitute of sinking particulate material. In no case we disagree with the possible occasions of high mineral content at certain periods stated by the reviewer.

Technical corrections: - Introduction, page 19167, lines 10-13: The sentence makes no sense. - The mineralisation protocol may not be adapted to refractory metals. Can the author provide results of CRM mineralisation and analysis? - The reference Buat-Ménard 1989 is not correct in the reference list. - The reference Heimbürger et al. (Biogeosciences Discussion, 2010) should not be cited (never published in BG).

Response: Appropriate corrections have been performed regarding page 19167, lines 10-13 and references Buat- Ménard 1989 and Heimbürger et al., 2010 (BGD). The accuracy of the analytical method has been tested with the use of three certified marine sediment reference materials, MESS-3, GBW 07313 and BCSS-1. Recoveries obtained ranged from 90.0 to 104.1% for all studied elements (V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb). In the case of Al the recovery was ∼60% and all results were corrected accordingly. As in the case of major and trace elements, the precision of the analytical method used for PAHs determination was also evaluated by analyzing the National Institute of Standards (NIST) standard reference sediment SRM 1941a (Organics in Marine Sediment). The determined values ranged between 93 and 106% of the certified values.

Interactive comment on Biogeosciences Discuss., 9, 19165, 2012.