

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.

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We would like to thank Dr. L. Heimburger for the time and effort provided to review our manuscript and his constructive comments that helped us improving our manuscript. All corrections suggested have been carried out in the revised version of the manuscript. In addition certain parts (Abstract, Introduction, Results and Discussion and Tables 1 and 2) have been re-worked to make the synthesis of both Reviewers' comments and suggestions. Overall, we believe that the manuscript has been improved in response to their helpful comments.

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Reviewer #2: L. Heimburger (Referee) General comments: In the manuscript, Theodosi and co-workers study the quality the vertical export flux in the EMed Sea using sample of 5 sediment traps moored between May'07 and March'08. The samples were analyzed for elemental carbon, PAH and metals. The manuscript is very well written by requires revisions.

- My main concern is that the authors do not explore their intensive dataset. Their data is not enough put in comparison with previous studies either (other than MED). For instance the authors published on trace metals in sediment traps of the Black Sea (Theodosi et al., 2013) which they do not compare with. Data on major and trace metal contractions of trapped particles are scarce and worth comparison.

Response: In the initial manuscript it was not our intention to perform comparisons with regions other than the MED and generally other ecosystems such as the Black Sea, which was the reason no such data has not been included. However as suggested by the reviewer, in the appropriate section (paragraph 3.2 and Table 2 of the revised manuscript) a comparison has been performed with the aforementioned paper by Theodosi et al. 2013 in the Black Sea.

- The authors go not much beyond the ideas of a paper that I submitted to BGD (Heimbürger et al., 2010b). In this paper we presented amongst other arguments a strong correlation of all trace metal fluxes. Calculated metal fluxes are no independent variables and cannot be treated as such, as one of the reviewers pointed out correctly at the time. This is why the paper never made it to publication in BG. Please do not cite this discussion paper. If correlations are presented to trace a common metal source it must be in terms of concentrations. Please show a correlation matrix for the selection of your metals.

Response: In page 19174 line 3 of the submitted BGD manuscript it is stated that the comparison between various metals and PAHs (page 19174 lines 3-26 and page 19175 lines 7-16) to infer statistically significant correlation between studied elements, refers

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to mass ratios. The Reviewer's comment that calculated metal fluxes are no independent variables and cannot be treated as such is correct and the fact that fluxes of all studied elements, regardless of their origin, are strongly and significantly ($p < 0.01$) intercorrelated is used only as an initial statement suggesting a common transport mechanism in the deep layers of the Ionian Sea (Nestor site), which is further addressed in detail at paragraph 3.4 of the BGD manuscript. The appropriate section of the revised manuscript has been approached differently in order to make clearer that comparison between various metals and PAHs refers to mass ratios. Also a correlation matrix for the selection of the studied elements in terms of mass ratios has been included.

- There is to my knowledge only one other publication on metal concentrations of trapped particles in the MED and it should be compared with (Roussiez et al., 2012). Please make the effort to compare your dataset also with other regions.

Response: We thank the reviewer for his suggestion and in the revised version a comparison has been performed both with Roussiez et al., 2012 and the Black sea.

- Perhaps the paper could even be divided in two: a EC, PAH paper and one on metals only. The way it is presented for now is confusing and especially the metal part comes a bit short in terms of data description, analysis and statistics.

Response: We would like to thank the reviewer for this suggestion, however, we strongly believe that the most important aspect of this study is the fact that allows for the first time simultaneous determination of primary pollutants fluxes (EC, metals and PAHs) in the deeper basins of the Mediterranean Sea and the opportunity to study their common transport pathways and factors controlling their export to deep oceanic waters. To our knowledge this is the first time that such amount of tracers with different origins are used to better understand the transport pathways of the particulate matter. Although splitting this work in two is a "gain" for us we believe that the second work (or part B) will lack in terms of originality. We thus prefer to thoroughly re-work in the revised manuscript certain parts to make the synthesis of both reviewers' helpful

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comments and suggestions on improving data description, analysis and the intercomparison/interaction between the studied elements groups.

Specific comments:

- Introduction: Overall too exhaustive relative to the manuscript length P19167115: dissolved or particulate? The manuscript is dealing with particles only. P1916811: Cu is mentioned twice. I don't understand

Response: Appropriate changes have been performed in the introduction section of the revised manuscript.

- Materials and methods: P19169125: is this acid attack strong enough for refractory metals? No aqua regia of HF? No CRM is available that comes close to trapped particles. What did you use? What are the recoveries?

Response: Since no Certified Reference Material (CRM) for metals in suspended particulate matter is currently available, 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 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.

- Composition of settling particles: P19171110: How does coating with soluble material decrease the EC concentration? If POC is remineralized with depth than the portion of refractory EC must increase.

Response: We agree with the reviewer comment. To avoid speculations (as mechanisms are not clear) we prefer to delete the statement.

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- Major and trace metals: Please describe metal concentrations in detail.

Response: An initial presentation on metal concentrations has been included in section 3.1.2., whilst more details on the origin, comparison with literature data and seasonal, depth related distribution of natural and anthropogenic compounds are discussed in the appropriate sections.

- Did you check for possible contamination of the sample bottles of the automated sediment trap? How?

Response: Sample bottles of the automated sediment trap have been acid-cleaned with hydrochloric acid and carefully washed with milli-Q water prior to use. The formaldehyde used for the filling of the cups was Suprasolv grade (ultra-clean).

- P19172I3: trended? P19172I3: increment? P19173I19: DYFAMED is supposedly open ocean (Marty, 2002; Heimbürger et al., 2012) P19173I25: as said earlier you are not allowed to correlations on dependent variables, all element fluxes contain the mass flux variable P19174I7: add between

Response: The appropriate corrections have been done in the revised manuscript. Regarding the comment on mass ratio/fluxes correlations please follow our earlier response.

- In the following, please proof read English, there are some occasional errors. Throughout the manuscript be clear if you describe element fluxes or concentrations. Table 1: show how rich the dataset actually is but is useless at the same time. Please organize better. I suggest putting the vertical depths as lines and the elements as variables. Better present as two tables: one on concentrations and one on fluxes.

Response: The appropriate corrections have been applied to the revised manuscript. As suggested by the reviewer Table 1 has been revised.

- Here are some trace metals related work in the MED that I found helpful: Saharan dust in sediment traps (Ternon et al., 2010) and anthropogenic trace metals in MED
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surface sediments (Angelidis et al., 2011) and some of my own: atmospheric metal inputs box model including a literature review of atmospheric trace metal inputs to the MED (Heimbürger et al., 2011) and composition of MED aerosols (Heimbürger et al., 2010a).

Response: We would like to thank the reviewer for the references provided. Ternon et al., 2010 and Heimbürger et al., 2011 have been included in the references list of the revised manuscript.

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