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Discussions

Interactive comment on "Occurrence, sources and transport pathways of natural and anthropogenic hydrocarbons in deep-sea sediments of the Eastern Mediterranean Sea" *by* C. Parinos et al.

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We regret the fact that during the preparation of the revised manuscript re-arrangements in the structure of the final text resulted in a disorder of the numeration of sections and figures in relation to those referred to in our originally submitted responses to reviewers. Please find attached below the original responses with corrected section/figures reference numbers. The original response text is of course maintained in all cases.

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We would like to thank both reviewers for the time and effort provided to review

our manuscript and for their constructive comments that greatly helped us improve it during the revision process. We have addressed their suggestions for corrections/modifications in the revised version of the manuscript, in which certain parts (abstract, introduction, oceanographic setting, results and discussion, conclusions, Tables 2-3-5, Figures 3 and 8) have been re-worked accordingly. Overall, we believe that the manuscript has been significantly improved. Please see our detailed responses to reviewer's comments below.

Reviewer #2: Anonymous - This is a nice and important manuscript reporting and discussing the occurrence of a number of families of hydrocarbons in the Eastern Mediterranean Sediments. The manuscript is generally well written, but the discussion could be improved in some sections. Especifically, the authors do not account for the different processes affecting the transport of hydrocarbons, and modifying the pattern of hydrocarbons during transport. I suggest that the manuscript can be accepted after the moderate modifications noted below.

Response: We appreciate the reviewer's positive opinion about the importance of the manuscript and its qualities. We also appreciate his/her comments for improving some sections, mainly by taking into account processes that may affect the transport of hydrocarbons and modify their patterns. Since this issue has been also raised by reviewer 1 we re-worked the manuscript by combining the remarks and recommendations of both reviewers (please see also our reply to reviewer 1).

Specific comments - Since the authors aim at providing new knowledge and clues about the "pathways" affecting hydrocarbons, my impression is that the literature covered is not comprehensive. One cannot study pathways without assessing or considering what happens in the water column. I would consider previous work by Tsapakis et al. EST, 2006, Berrojalbiz et al. GBC 2011 and references there in, among others, in addition to the papers cited by the authors.

- The discussion on sources is superficial, in part because the authors do not take

into consideration the modifications of the hydrocarbon profiles during their transport in the water column. Several studies have shown the modification of the abundance of ligher PAHs and alkanes (Lipiatou et al. Mar. Chem. 1993, Dachs et al. EST 1997, Dachs et al. Mar. Chem 1999). In addition, the relative abundance of vertical fluxes is different depending on the chemical. For example, sources of phenanthrene to the water column (atmospheric) are orders of magnitude higher than their vertical flux in the water column (and reflected in the sediment) (See Tsapakis et al. 2006). Then, it is erroneous, or precipitate, when the authors state that pyrolytic sources of PAHs dominate. It may depend on the compound. I suggest discussing the potential modifications of the pattern of PAHs, alkanes and other hydrocarbons during transport, and then making statements about potential sources. Distribution of hydrocarbons at surface waters for this region can be found in the literature in some cases, and for the other compounds may not be significantly different than in other parts of the Mediterranean or other oligotrophic seas.

Response: Following the comments/suggestions of both reviewers, we introduced in Sect. 5.2 of the revised version of the manuscript, focusing on sources of aliphatic and polycyclic aromatic hydrocarbons in the study area, an extended discussion regarding the differences in physico-chemical properties and particle associations of individual hydrocarbon classes and how they affect their dispersion pathways, their relative stability in the marine environment and preservation in marine sediments. Therein, a relative mention to the stability of long chain plant wax n-alkanes over planktonic hydrocarbons in the marine environment (Prahl and Carpenter, 1984) and also aliphatic compounds of crude oil and petroleum products released in aquatic environments which are subjected to rapid degradation (Wang et al., 1999), has been introduced. PAHs transportation, decomposition and biodegradation in the environment which are related to the size and stability of their carrier particle phase (Yunker et al., 2002 and references therein) is also thoroughly discussed. A specific mention is made to the selective preservation of PAHs deriving from pyrolytic/combustion sources which, being strongly associated to fine combustion particles (soot and/or char black carbon), are

protected from degradation during transport from initial sources through the water column and in marine sediments (Bouloubassi et al., 2006; Dachs and Eisenreich 2000; Dachs et al., 2002; Gustafsson et al., 1997; Yunker et al., 2002). We further discuss on the selective degradation (bacterial and by zooplankton) of low-MW labile compounds such as phenanthrene and its methyl derivatives, which has been proposed as an important factor affecting their concentrations in the water column (Berrojalbiz et al. 2009, 2011), and may result in their substantial depletion during downward transport. Indeed, atmospheric inputs reported in the Western and Eastern Mediterranean Sea are two orders of magnitude higher than settling fluxes (Castro-Jiménez et al., 2012; Dachs et al., 1997; Deyme et al., 2011; Tsapakis et al., 2006). The selective preservation of terrestrial n-alkanes, UCM and pyrolytic PAHs in the marine environment/sediments has been taken into account in the Results and Discussion sections when discussing the hydrocarbons spatial distribution and results of cluster analysis performed (Sect. 5.3), in order to better understand the contribution of anthropogenic vs. natural hydrocarbons inputs (Sect. 5.3) and the driving parameters of the hydrocarbons characteristics in the study area (Sect. 5.4).

- The authors discuss some spatial patterns of the concentrations as ng g-1. It is also shown that these concentrations are correlated with the OC content. Which is the spatial variability of the concentrations normalized by organic carbon? This could give more information than the sediment normalized concentrations. Also, I wonder if the concentrations normalized by OC increase with depth, and with the estimated post deposition time. As OC is reminarilized, the concentrations of some compounds, such as some heavy PAHs may increase since they are more persistent. Generally speaking, I think that post depositional processes could be better assessed with this data set, than what is done in its present version.

Response: We agree with the reviewer's suggestion. In the revised manuscript concentrations are presented both in ng g-1 and normalized to OC content of sediments (Tables 2-3; Fig. 3-4 of the revised manuscript) and discussed accordingly in Sections

4.3 and 5.3 and 5.4. The spatial variability of concentrations normalized to organic carbon content follows, with minor discrepancies, the trends observed for concentrations expressed per gram of sediment (ng g-1), that is they increase with depth in the case of aliphatic hydrocarbons but not for PAHs, in agreement with the observed trends for absolute ng g-1 concentrations. Observed variations between absolute and OC normalized concentrations are discussed in detail in both Results and Discussion sections of the revised manuscript (Sect. 4.3, 5.3 and 5.4).

- In addition, chemicals such as phenanthrene can indeed originate from fossil fuels, but there are a number of reports suggesting it could have a biogenic marine or terrestrial source (Nizzetto et al. EST 2008, Cabrerizo et al. EST 2011). Taking into account the short half-lives of phenanthrene in the environment, it is difficult to justify its environmental occurrence only from anthropogenic sources.

Response: We agree with the reviewer on the possible biogenic marine or terrestrial origin of phenanthrene in the environment suggested for surface waters of the Atlantic Ocean by Nizzetto et al. EST (2008) and soils by Cabrerizo et al. EST (2011). A relevant reference has been included in the introduction section of the revised manuscript, where the possible biogenic contribution of individual PAH compounds is mentioned. In our study, the postulated elevated contribution of anthropogenic (fossil) compounds within the phenanthrene series is assessed using a combination of criteria such as the high abundance of alkylated homologues over the unsubstituted compound, not only within the phenanthrene series (PAH isomeric ratio: C0/C0+C1 Phe) but also within pyrene and chrysene series, evidenced in the molecular profile of each individual sample (see also PAHs cluster analysis - cluster I). Furthermore, information derived from aliphatic hydrocarbons fraction characteristics (hopanes/ UCM/ light diesel/ heavy oil residues abundance) of corresponding samples also point to dominant anthropogenic sources. Accordingly, we use the total sum of phenanthrenes (ΣPhe) as representative of mostly petrogenic sourses (Sections 5.2.2 and 5.3 of the originally submitted manuscript). Furthermore, we agree with the point stated in Cabrerizo et al. (2011):

"in order to quantify the magnitude of the biogenic contribution a specific approach focusing on bacterial production of PAHs and isotopic characterization is essential", but this is beyond the scopus of our study.

- I suggest to perform a principal component analysis of the data set, and see if the authors obtain new information.

Response: We would like to thank the reviewer for this suggestion. We had considered including PCA analysis in the original submitted manuscript. However, one of the first requirements for stable results from a PCA (or factor analysis) is the availability of a sufficient number of samples for the number of variables studied (Reimann C. et al., 2008. Statistical data analysis explained, John Wiley & Sons Ltd, 211-231). Different rules have been suggested (Le Maitre, 1982), e.g., $n > p2 + 3p + 1$ (where n is the number of samples and p the number of variables). If more tolerant rules are used, e.g., $n > p2$, or $n > 9p$, or just $n > 8p$, the number of samples investigated is still rather low compared to the number of variables. Thus, we believe that PCA analysis is not suitable for our data set and was not included in the submitted manuscript. For that reason we performed cluster analysis instead, in order to highlight relationships between stations having common n-alkanes/PAHs molecular profile characteristics, which were further discussed/considered in the results and discussion sections.

- Maybe Canyons play an important role, as it has been suggested before, but it is difficult to me to quantify the importance of this process, since dense shelf water transport occurs intermittently and other transport processes occur all the time.

Response: We agree with the reviewer's comment. However, it is not the purpose of this study to quantify processes occurring in deep canyon settings since the low number of stations in the canyons' sites does not permit such an approach. Based on a combination of our results and data presented by Hatzianestis and Sklivagou (2001) regarding the high relative abundance of petrogenic PAHs in surface sediments of the central Aegean Sea, we suggest that the general cyclonic circulation of the Aegean

Sea and the net outflow, in the upper 400m of depth, towards the EMS observed in the western Cretan straits (Kontoyiannis et al., 1999, 2005) likely contribute to the transfer of petrogenic hydrocarbons from central Aegean Sea towards the western Cretan straits and that this transfer may be enhanced during periods of deep water formation in the Aegean Sea, when dense water outflows through the eastern and especially the western Cretan strait canyons. The fact that the station located within the canyon straits (RED3.1) shows a c.a. two-fold increase in OC content compared to the neighbouring station (RED3) located in the upper slope of the adjacent margin might indicate the role of western Cretan straits deep canyons in enhancing the transport of fine grained and OC rich sediment (Etcheber et al., 1999; Pusceddu et al., 2010; Sanchez-Vidal et al., 2008) and associated hydrocarbons. The latter is reflected in the observed elevated values (almost 2-fold) of TAHC, UCM, NA, TPAH25 concentrations and corresponding OC normalized concentrations. We have reworked the corresponding text presented in section 5.4 of the revised manuscript in order to make it clearer.

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