

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.

C. Parinos et al.

ksparinos@hcmr.gr

Received and published: 17 July 2013

We regret the fact that during the preparation of the revised manuscript rearrangements 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.

We would like to thank both reviewers for the time and effort provided to review
C9500

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 #1: Anonymous

- General comments: This paper presents the biomarkers compositions of surface sediments from deep basins of EMS, which is related to relevant scientific questions within the scopes of BG. The dataset is qualified and well presented. The results fill in the blank of limited hydrocarbons data in deep basin of the EMS. They found the deep basins and canyons of the EMS act as traps of both natural and anthropogenic hydrocarbons.

- However, the results are missing some important background information such as the grain size, water masses distribution, marine shipping routines, atmospheric inputs variation, bottom oxygen content etc. The discussion seems quite weak more like a comparison study within subregions, lack of detailed discussion with factors on distribution of hydrocarbons, especially selective preservation of biomarkers in the deep basin and impact on the sedimentary record.

Response: We are happy with the reviewer's positive appreciation on the quality and good presentation of the data, as well on the fact that this work does, indeed, fill the gap of hydrocarbons data in deep basins of the EMS and the role of the latter in trapping hydrocarbons. Following the helpful comments of both reviewers, an extended discussion regarding the modification of hydrocarbons patterns during their transport in the water column and the selective preservation of studied compounds in marine sediments has been included in the revised version of our manuscript (please follow our

detailed response to specific comment no. 3 below). Information about water masses characteristics were included in the "Oceanographic Setting" section of the originally submitted manuscript and also in sections dealing with the potential control of water masses on the distribution of hydrocarbons in the study area (Sect. 5.3.1, 5.3.2 and 5.3.3 of the BGD paper). In the revised version of the manuscript, this issue is discussed in a synthetic way in Section 5.4, which focuses on the driving parameters of hydrocarbon characteristics in the study area. Marine shipping routes and, most importantly, likely oil spills distribution in the study area are presented in a new Figure (Fig. 6, in the revised MS). Information regarding atmospheric inputs and bottom oxygen content have been included in corresponding sections of the revised manuscript focusing on sources of hydrocarbons in the study area (Sect. 5.2) and oceanographic setting (Sect. 2). In this study we report the first sedimentary hydrocarbon data set in deep EMS basins covering a wide area including the Ionian, Cretan and NW Levantine basins and thus comparisons amongst these sub-regions are essential in order to understand the distribution of hydrocarbons and the factors controlling their regional patterns. We believe that the manuscript has been improved in that aspect in response to the comments and suggestions of both reviewers.

Specific comments - 1. The title should be modified, because I was not convinced well with the transport pathways of hydrocarbons in this manuscript.

Response: Following the comments of both reviewers we have further considered and discussed transport pathways in the revised version. We thus believe that the title of the manuscript is now justified.

- 2. Abstract: the significant correlation with TOC might be contributed to grain size control, please make it clear; how the mesoscale variability of water masses impact the regional characteristics, please make a detailed explanation in discussion part.

Response: The abstract has been re-worked in response to both reviewers' comments. The relative discussion regarding water masses' control on the distribution

C9502

of hydrocarbons in the study area is included in the corresponding section of the revised manuscript (Sect 5.4), focusing on driving parameters of hydrocarbon mixtures' characteristics in the study area. Regarding grain size data please follow the response to the specific comment regarding Section 5 (Results) below.

- 3. Introduction: Add one paragraph of selective preservation of organic matter in deep sediments, how the record will be impacted.

Response: A short paragraph has been added in the introduction of the revised manuscript, stating that different sources and physico-chemical properties of individual hydrocarbons classes may also determine their dispersion pathways and fate in the marine environment (including preservation in marine sediments). Furthermore, following the suggestions of both reviewers, Sect. 5.2 of the revised version deals with: a) differences in physico-chemical properties and particle associations of individual hydrocarbons classes and how these may affect their dispersion pathways and relative stability in the marine environment, and b) factors affecting preservation of these chemical species in marine sediments. The likely selective preservation of terrestrial n-alkanes, UCM, and pyrolytic PAHs in the marine environment is also considered in the Result & Discussion sections in view of their spatial distributions (Sect. 4.3) and regional characteristics (Sect. 5.3), in order to understand its potential impact on the surface sediment record (Sect. 5.3 and Sect. 5.4).

- 4. Materials and methods: Figure 1 should illustrate the mesoscale variability of water masses, the marine shipping routine, and atmospheric inputs variations.

Response: Although we understand the utility for presenting the information requested by the reviewer, we believe that this is impossible to be done in a single figure, as suggested, for the sake of clarity of the Figure 1. However, marine shipping routes and likely oil spills distribution are presented in a new Figure (Fig. 6 in the revised version), while also, specific water masses control on the possible transfer of petrogenic hydrocarbons from central Aegean Sea towards the western Cretan straits is

C9503

presented in the revised Fig. 8 of the original submitted BGD paper (now Fig. 10 in the revised version of the manuscript). Information regarding atmospheric inputs variation has been included in Section 2 but also 5.2. of the revised manuscript that focuses on the sources of hydrocarbons reaching the study area.

- 5. Results: Consider to add grain size data, or SA data for the further discussion. Less information available about hopanes series.

Response: Following the reviewer's suggestion, grain size data have been considered in the corresponding section of the revised manuscript focusing on the driving parameters of hydrocarbon mixtures' characteristics in the study area (Sect. 5.4). In order to assess the main processes driving hydrocarbon's distribution, correlation analysis (Table 4 of the revised manuscript) was performed for absolute and OC normalized hydrocarbon concentrations, organic carbon (OC) content, water column depth, and also grain size data of collected sediments. However, in our data set there is no significant correlation between concentrations of aliphatic and polycyclic aromatic hydrocarbons and grain size distribution of collected sediments. This implies that hydrocarbon phase associations may not be similar among various source-materials and/or different regions in the study area. However, extreme caution should be exercised when considering interpolations in wide geographical areas, since the overall low density of available stations may not allow the appreciation of occurring variations. In spite of that, no significant correlations between concentrations of aliphatic and polycyclic aromatic hydrocarbons and grain size were evident even when limiting the data set to specific regions (Ionian Sea, Cretan Sea, northwestern Levantine Sea; data not shown). We agree with the reviewer's comment about the lack of information on hopane series. Accordingly, we have added it in Section 5.2.2 of the revised manuscript. The presence of C₂₉-C₃₅ 17 α (H), 21 β (H)-hopanes in all samples with extended C₃₁-C₃₅, homologues appearing as pairs of the C₂₂ diastereoisomers (22S and 22R), with a 22S/22S+22R ratio close to 0.6, is used as a geochemical marker supporting the information derived from n-alkanes profile and UCM regarding the presence of petrogenic

C9504

hydrocarbons. Hopane series data also highlighted the minor importance of bacterial sources, evidenced by the presence of hopenes (hop-17(21)-ene, hop-13(18)-ene and 17 β (H)-hop-22(29)-ene). In addition, we added in Section 5.2.2 of the revised version a relevant reference regarding the overall resilience of hopane compounds to biodegradation and their use as indicators of oil spill sources even in highly weathered oils.

- 5.1 Hydrocarbon levels: The comparison between shelf and deep basin of EMS should be emphasized here, the potential link or contrasting behavior will be helpful to further discussion; why not include hopanes series for the comparison.

Response: We have added such comparisons for the Mediterranean Sea and other settings, receiving enhanced or low anthropogenic inputs (see Section 5.1 of the revised manuscript). Hopanes are used as a geochemical marker supportive of petrogenic hydrocarbons presence and indicative of minor importance of bacterial sources in the study area (see our detailed response above), and thus we don't believe that they need to be included in the comparison. It must be considered also that quantitative hopane data in relevant studies in the Mediterranean are scarce since they are mostly used as qualitative indicators of petrogenic inputs, and thus a direct comparison is not applicable.

- 5.2 Sources: Considering the selective preservation of biomarkers in the sediments, source specified should also consider the potential impact.

Response: Addressing the comments of both reviewers, in Sect. 5.2 of the revised version of the manuscript an extended discussion is introduced regarding the preservation of aliphatic and polycyclic aromatic hydrocarbons in marine sediments, in order to assess the relative contribution of anthropogenic/natural hydrocarbon inputs (Sect. 5.3 and 5.4) and their sources.

- 5.3 Regional: Part of the discussion should moved to results part, and here focused on how the water masses etc control the distribution of hydrocarbons. Please specify the atmospheric inputs and marine ship activities among those regions.

C9505

Response: Both results and discussion parts has been extensively re-worked. In the “regional characteristics” section of the revised manuscript (Sect. 5.3) we present a synthesis of the data interpretation with regard to the complementary information (e.g. molecular profiles, marine shipping routes/oil spills, spatial distribution of concentrations and cluster analysis for aliphatic and polycyclic aromatic hydrocarbons, preservation aspects, atmospheric inputs) discussed in Sections 4.2, 4.3 and 5.2, in order to assess the regional characteristics of hydrocarbons mixtures in the study area. The likely water masses’ control on the distribution of hydrocarbons is presented in a synthetic way at Sect. 5.4 focusing on the driving parameters of hydrocarbon mixtures’ characteristics.

- 5.4 Drives: This should be most important part of discussion, please develop it according the above suggestions.

Response: The paragraph referring to drivers of hydrocarbons’ distribution in deep-sea sediments of the Eastern Mediterranean Sea has been extensively re-worked and developed in the revised version of the manuscript in response to both reviewers’ suggestions. In its revised form the paragraph also considers grain size data (please follow our specific response to reviewer’s comment No. 5 above) and water masses control on the distribution of hydrocarbons in the study area.

- 7 Conclusion: please consider as summary instead of conclusion here.

Response: The conclusions part has been extensively re-worked and re-written in the revised version of the manuscript taking into account both reviewers’ comments.

- Figures and Tables: Table 2 please specify the abbreviations of parameters

Response: Table 2 (and also Table 3) have been corrected according to the reviewer’s suggestion and include abbreviations of studied parameters in their revised form.

Interactive comment on Biogeosciences Discuss., 9, 17999, 2012.