Interactive comment on "Composition and sources of sedimentary organic matter in the deep Eastern Mediterranean Sea"

by R. Pedrosa-Pàmies et al.

Anonymous Referee #1

Received and published: 31 July 2015

In their manuscript, they applied multi proxies including lipid biomarkers, bulk elemental and isotopic compositions to evaluate the sources and distribution of organic matter (OM) in deep slopes and basins of the oligotrophic Eastern Mediterranean Sea. The manuscript is well written and clearly structured. The data are novel, and of relevance for the scientific communities focusing on organic geochemistry deep sea ecosystem. The interpretation of the data in this study is great. However, there are a few points of weakness identifiable in the manuscript listed below which needs to be addressed.

We would like to deeply thank the Referee for the time and effort provided to review our manuscript and for his/her constructive comments that greatly helped us improve its quality during the revision process. We have addressed the Reviewer's suggestions for corrections/modifications in the revised version of the manuscript, in which certain parts (mainly abstract and discussion) have been re-worked accordingly. Overall, we believe that the manuscript has been significantly improved. Please follow our detailed responses to Reviewer's #1 comments below.

General comments

1. The abstract is not informative enough (such as Page 2, Line 15-20) and needs rewritten.

Response: Corrected according to the Reviewer's suggestion. The abstract has been re-worked in order to be more informative.

2. I am wondering why you didn't check the fatty acid composition, which is also important to address the OM sources.

Response: We agree with the Reviewer's view that fatty acid is an important class of lipids in the marine environment. In this study though, we have focused on lipid compounds that can be ascribed to: (a) characteristic planktic sources/ primary producers (namely diatoms, coccolithophorids, dinoflagellates, and nanoplankton species), (b) terrestrial biomarkers deriving from land plant waxes and (c) anthropogenic OM. The extend of re-working of OM in the water column and underlying sediments that can be attributed to microorganisms, zooplankton and benthic invertebrates, with their specific biomarkers concentrations will be presented thoroughly in a future paper.

3. The authors excluded a few stations when the do correlations bud did not provide evidence why some certain stations could be excluded.

Response: We have excluded a few stations in the correlation analysis in three occasions: (1) %OC and %TN vs. %lithogenic (stations BF15, H07 and H12), (2) $\delta^{13}C$ vs. $CaCO_3$ (station Red3), and (3) TERNA and TERNOH vs. Sitosterol (stations H07 and H12). The stations excluded present values for the corresponding parameters clearly out of the interval confidence on the population value of Pearson's correlation and the general trend of all other stations. This is due to their singular and exceptional geochemical composition/characteristics which is/are

extensively discussed in section 5.2 of the BGD paper (e.g. pag. 9948 lines 13-22). Following the Reviewer's comment we have included in section 3.2.5 of the revised manuscript the aforementioned information that justifies our decision to exclude certain stations during correlation analysis.

Specific comments

1. Page 3 line 0-5 (P3L0-5), 'e.g.' or 'e.g.,'? Keep in consistent.

Response: Corrected according to the Reviewer's suggestion.

2. P3L0-5, I suggest include a reference.

Response: Following the Reviewer's suggestion we have added relevant references (Bouloubassi et al., 1997; Durrieu de Madron et al., 2000; Kaiser et al., 2014) that support that the deep sea receives inputs of organic particles from multiple sources, both autochthonous (e.g., primary production) and allochthonous (i.e. particulate matter from rivers, atmosphere and anthropogenic activities).

3. P15 section 4.4, would be nice to show a few typical chromatograms.

Response: Chromatograms of each eluted fraction containing the various compound classes have been thoroughly presented in several previous papers of the authors (e.g. Gogou et al., 1998; Parinos et al., 2013). We believe that it is beyond the scope of this study to present chromatograms, since this work is not focused only on biomarkers but contains many different parameters that correspond to numerous figures in the MS.

4. P18L0-5 (r = 0,65 and r = 0.72, respectively, p <0.05, : : :)

Response: Corrected according to the Reviewer's suggestion.

5. P20L20-25, why don't you normalize the TerNA, TerN-OH and Mar data to OC?

Response: ∑TerNa and ∑TerN-OH (p 9952 line 22 and p9959 line 11 of BGD paper, respectively) and ∑Mar (p9952 line 24 and p9959 line 22 of BGD paper) values have not been normalized to OC contents because in this section the correlation of these variables to OC is investigated. If the values are normalized to OC contents, the subsequent correlation to OC has no statistical meaning.

6. The authors need to focus more on explaining their own results instead of providing lots of background information, such as P21L10-15, 25-29; P22L15-20. 7. P22L20-25, this information has been suggested by various previous studies.

Response: Following the Reviewer's suggestion the text of the revised manuscript has been extensively re-worked in order to delete background information and highlight instead the results of the present study. We would like to thank the Reviewer for this suggestion/comment.

8. P27L24, Straits'?

Response: Corrected according to the Reviewer's suggestion.

9. P45 Table 1, the longitude for west Ionian Sea sediments need to be corrected.

Response: Corrected according to the Reviewer's suggestion.

Interactive comment on "Composition and sources of sedimentary organic matter in the deep Eastern Mediterranean Sea"

by R. Pedrosa-Pàmies et al.

T.T. Tesi (Referee)

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Received and published: 1 August 2015

In this study Pedrosa-Pamies et al have analyzed slope and deep surface sediments collected in the EMS. The analysis was carried out at bulk and molecular level with the overarching goal to characterize the sedimentary OC accumulating in EMS sediments. The paper presents a suite of biogeochemical parameters that, interpreted via multivariate analysis, were used to understand composition and provenance of the material. Pedrosa-Pamies et al have carried out a significant amount of work and the data presented here are of high quality. I strongly recommend this paper for publication in BG after addressing the following major and minor points.

We would like to deeply thank Dr. Tesi for the time and effort provided to review our manuscript and for his constructive comments that greatly helped us improve its quality. We have addressed his suggestions for corrections/modifications in the revised version of the manuscript, in which certain parts (Materials and methods, results, discussion, and Figures 6 and 8) have been re-worked accordingly. Please follow our detailed responses to Dr. Tesi's comments below.

Major points

Overall I found the text too wordy. The paper would gain fluency by making paragraphs shorter. Make sure that only the important information is conveyed and try to avoid redundant parts. Furthermore, sentences are a way too long, keep sentences to the point. To give you an example, among several, the potential contribution by IN has been presented at least three times in the discussion. While I agree on the presence of IN (likely ammonia within the mineral clay sheets), this repetition is clearly redundant and doesn't help the reader.

Response: Following the Reviewer's suggestion the revised text has been extensively re-worked making the paragraphs shorter, restructuring the text and deleting the redundant sentences. In order to avoid any repetitions, the discussion on the potential contribution by IN has been focused just in the section 5.2.1 of the revised manuscript.

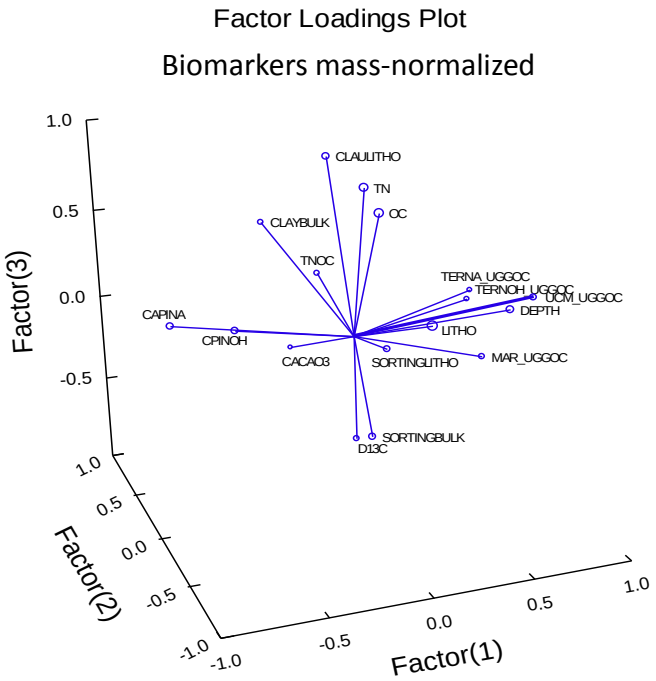
Presentation and discussion of the data is fragmented in some sections, especially where the parallel construction is missing. For example, figure 8b has nothing to do with figure 8a. Rather move it to fig 4. Also, as part of the parallel construction, the authors should show both CPIs, not only the n-alkanols.

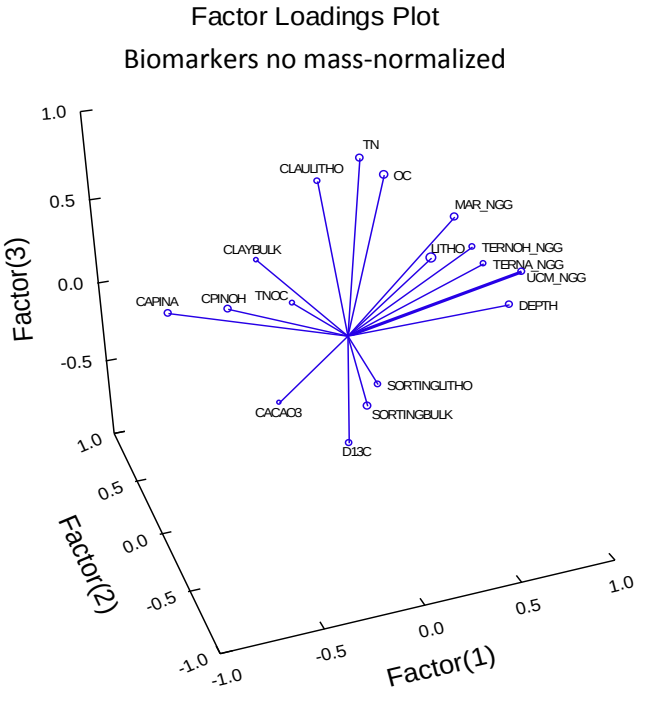
Response: The figures have been revised accordingly in order to avoid the fragmentation of the sections. Figure TN vs OC has been moved to figure 6 along with the TN/OC ratios vs $\delta^{13}C$. In addition, according to the Reviewer's suggestion the spatial distribution of CPI_{NA} has been added in the revised Figure 8.

Another major issue I see here is the unit used for the PCA. Specifically I'm referring to the mass-normalized biomarker data. By doing so, it's not a huge surprise so observed covariance between terrestrial and marine biomarkers. I question whether this is really informative, because essentially they all mirror changes in OC content that, as the authors

suggest, is driven by the surface area (grain size) of the mineral matrix. Have the authors considered presenting both sediment and OC normalized PCA results?

Response: The PCA was performed on standardized variables and with mas-normalized biomarker data. We have specified this in the text to be clear. In order to show the robustness of the methodology applied we have performed the PCA without mass-normalizated biomarkers data (see figure attached). If we compare the PCA with the mass-normalized biomarker data to the PCA without mass-normalizated biomarker data we can see that in both cases the same three main principal components are identified, accounting for 64.3% and 67.8, respectively. In addition, the factor scores on each PC display the same significant variability amongst the studied stations.





Also, the spatial variability of biomarkers concentrations normalized to OC content follows, with minor discrepancies, the trends observed for concentrations expressed per gram of sediment (ng g^{-1}). Therefore, we consider that the use of mass-normalized units of the biomarkers presented in the manuscript is appropriate and robust.

Additional points:

- I might have missed it but I do not see anywhere whether or not the TN/OC refers to the molar ratio. Make sure that the ratio is reported with the stoichiometry notation, as the Redfield ratio. If the ratio is indeed molar, make it explicit in the text. If not, tables, text and figures must be modified accordingly.

Response: The TN/OC ratios reported in this study are indeed in stoichiometry notation, as the Redfield ratio. We have put explicit in the text in order to avoid confusions.

- Page 9944, line 1. Please list all the solvents used to elute F1, F2, and F3 fractions as well as how the silica gel column was packed (e.g. if deactivated, pre-packed, etc). Explain how the quantification was performed and how the extraction efficiency was assessed. Finally, how was the UMC quantified? (not in the method)

Response: Following the suggestion of Reviewers #2, #3 and #4, all relevant analytical information regarding the determination of lipid biomarkers have been added accordingly in the materials and methods section 3.2.4 (Lipid biomarkers analysis and definitions of molecular indices) of the revised manuscript.

- Page 9954, line 15 and page 9962, line 23. For the direct comparison with organic material supplied by dense water cascading events from the Adriatic margin, I recommend Tesi et al., 2008 DSR and Turchetto et al., 2007 MARGEO. You would quickly realize that Ionian sediments are more depleted than the material supplied by the Adriatic. This could suggest that either the Adriatic sediments do not make it to the Ionian sector or there are further changes/dilution occurring during transport.

Response: We would like to thank the Reviewer for this comment. The studies by Tesi et al., 2008 and Turcheto et al., 2007 have been carefully consulted and we have improved sections 5.1 and 5.2.2 of the revised manuscript. We now better describe the sediment transport and deposition processes in relation to the organic material supplied by dense water cascading events from the Adriatic margin to the Ionian Sea. An important point that has been considered is that during energetic dense-water cascading events, lateral flux prevails over the vertical flux in the southern Adriatic Sea. In this circumstance, the lignin content doubles and OC content drops, suggesting increased contribution of soil-derived OC during dense water cascading events. Moreover, during such events there is a relatively elevated retention time of sediments on the inner shelf of the southern Adriatic Sea, allowing for significant microbial degradation and/or marine dilution of the terrestrial material that reaches the outer-shelf and shelf-break before arriving to the Ionian Sea (Otto and Simpson, 2006; Tesi et al., 2008).

- As far as the average composition of the African dust concerns, there is a great paper by Eglinton et al in G3, 2002. "Composition, age, and provenance of organic matter in NW African dust over the Atlantic Ocean". Re-elaborate the discussion to include these results in the discussion.

Response: The Eglinton et al. (2002) study has been carefully consulted during the preparation of the revised manuscript. An important point of this study is the description of OM in Saharan dust, which consists mainly of minute charcoal-like fragments of burnt vegetation, leaf wax-derived lipids absorbed on clays, and cuticular fragments, pollen grains, and fungal spores. Therefore depositions rich in Saharan dust particles contain carbon in amounts that might easily

reach 1% dry weight. This carbon pool, originated during vegetation fires and accumulated/stored in soils, is likely not to be very labile. We have included all this information in the revised version of the manuscript.

- What's the relationship between UCM and CPIs? Shouldn't they trace similar sources (petrogenic/oil sources). Please elaborate this in the text.

Response: As stated in page 9944, lines 4-9 of the BGD paper "the Carbon Preference Indices of long chain *n*-alkanes (CPI_{NA}) and *n*-alkanols ($CPI_{N\text{-}OH}$) have been used as indicators of terrestrial OM degradation with CPI values in fresh leaves being typically >4, although the occurrence of petroleum hydrocarbons bias (lower) CPI_{NA} values with increasing petroleum contribution, since petroleum products present CPI_{NA} values ~1". This petroleum bias is associated with the presence of non-degraded (fresh) fossil inputs that could potentially influence only the values of CPI_{NA}, since petroleum hydrocarbons (and UCM) are eluted in fraction F1 (aliphatic hydrocarbons) while *n*-alkanols in fraction F3 (alcohols/sterols). Aliphatic compounds of crude oil and petroleum products released in aquatic environments are subjected to degradation, with a prominent initial microbial preference for straight chain compounds (Wang et al., 1999). This leads to the gradual removal of major compounds that can be resolved by gas chromatography and the subsequent appearance of a UCM, consisting of branched alicyclic hydrocarbons, that is used as an indicator of the contribution from degraded petroleum products (i.e. chronic oil pollution; stated in section 3.2.4). Moreover, as stated in page 9956 - lines 16-17, of the BGD paper, the patterns of long-chain *n*-alkanes and *n*-alkanols with elevated CPI_{NA} and $CPI_{N\text{-}OH}$ values, respectively, indicate the presence of allochthonous natural (terrigenous) inputs from epicuticular higher plant waxes in the study area. Thus, although a prominent signal related to chronic oil pollution (degraded petroleum products) is abundant in the study area (presence of UCM), we assume no important bias associated with the presence of non-degraded (fresh) fossil inputs, and both CPIs trace natural (biogenic) terrestrial inputs. In the opposite case, we would expect significantly lower CPI_{NA} values, since *n*-alkane compounds of petroleum products present CPI_{NA} values ~1. The corresponding text has been re-worked during the preparation of the revised manuscript in order to include the above information and be clearer to the reader that the petroleum hydrocarbons bias on CPI_{NA} values is related to non-degraded (fresh) petroleum inputs.

-Page 9957, line 26 "inorganic IN", please correct. -Page 9935, line 18 "approach is hired", please modify.

Response: Corrected according to the Reviewer's suggestion. The sentence 'approach is hired' has been changed by 'approach is carried out'.

Interactive comment on "Composition and sources of sedimentary organic matter in the deep Eastern Mediterranean Sea"

by R. Pedrosa-Pàmies et al.

Anonymous Referee #3

Received and published: 6 August 2015

The manuscript by Pedrosa-Pàmies and corworkers describes grain-size distributions, elemental and selected lipid biomarker compositions of a series of surface sediments from the Eastern Mediterranean Sea. The goal is to use this multiparameter data set to address sedimentary organic matter (OM) sources and the physical processes, in particular the balance between settling and hydrodynamic sorting, that determine its distribution in the sediments. The manuscript addresses important factors related to the OM composition of the studied sediments, and in particular the inclusion of the grain-size analyses complements the geochemical measurements in providing novel insight into the potential effect of particle sorting during and shortly after sedimentation.

We would like to deeply thank the Referee for the time and effort provided to review our manuscript and for his/her constructive comments that greatly helped us improve its quality during the revision process. We have addressed the Reviewer's suggestions for corrections/modifications in the revised version of the manuscript, in which certain parts have been re-worked accordingly (Materials and Methods, Results and Discussion sections, Table 2). Please follow our detailed responses to Reviewer's #3 comments below.

General

At several places in the manuscript (e.g., line 7, p 9956), the authors tell us that the OM in the studied sediments is a mix of terrigenous and marine material ... "thus indicating that the composition of the OM: can be explained as a mixture of terrigenous (low TN/OC and d13C) and marine (high TN/OC and d 13C) derived materials." It would be very useful to be given some sense of the relative proportions of terrigenous vs marine OM. On p 9940 we see what the primary production rates are, and that _0.3% o this is exported below 2000m. Most of the terrigenous input comes from Aeolian transport, mainly of Sahara dust, that riverine inputs to these locations is low, the sedimentation rate is given. The discussion then goes on to talks about marine biogenic CaCO3 vs dust/terrigenous clays. But what is missing is some feeling of the relative amounts that each contributes to the overall sediment OM content.

Response: An overall positive relationship for molar TN/OC ratios and $\delta^{13}C$ values ($r=0.53$, $p<0.05$, excluding station Red3) becomes apparent (Fig. 6), thus indicating that the composition of the OM in the studied sediment samples can be explained as a mixture of terrigenous (low TN/OC and $\delta^{13}C$) and marine (high TN/OC and $\delta^{13}C$) derived materials. Stations can be grouped by the predominance of either terrestrial or marine OM, according to $\delta^{13}C$ and TN/OC values. Following the suggestion of the reviewer we have estimated the relative proportions of marine and terrestrial OC using a simple binary mixing model and assuming a marine $\delta^{13}C$ value of -20.4‰ and a terrestrial $\delta^{13}C$ value of -27.0‰ (Tesi et al., 2007):

marine OC = $(\delta^{13}C+27.0)/(-20.4+ 27.0)$

terrestrial OC = 1- marine OC

Values obtained are presented in the revised version of the manuscript (see Table 2).

This mixing model evidences a mixed contribution of autochthonous and allochthonous sources for the sedimentary OM. In general sediments from the west (Ionian Sea) are characterized by higher contributions of terrigenous OM relative to the other areas in the east (W Cretan Straits, Cretan Sea and NW Levantine Sea) (Figs. 3d-e). The considerable spread of the samples in the plot TN/OC vs $\delta^{13}C$ (Fig. 6b) suggest that some additional local factors probably exerted important influences on these bulk tracers of sedimentary OM. Therefore, we can use the simple two-end-member mixing model (between terrestrial and marine OC) to describe the relative contribution of marine and terrestrial sources of OC, taking into consideration however the probable limitations associated to the effect of degradation processes (discussed in the text) on OM preservation. The above information have been added accordingly in the revised version of the manuscript (Results but also Discussion sections, Table 2). We would like to thank the Reviewer for this comment.

Specific comments:

p 9938 line 16 - "complex topography with tenths of depressions" probably should be "complex topography with ten's of depressions"…

Response: Corrected according to the Reviewer's suggestion.

p 9941 line 23 – "freeze-dried and grounded sediments" probably should be "freezedried and ground sediments"…

Response: Corrected according to the Reviewer's suggestion.

p 9943 line 24 – how was the UCM measured? Response factors same as for the alkanes? How was the UCM integrated? This is important since the UCM seems to be about 10x more concentrated than the long-chain alkanes (extrapolated from Fig. 4).

Response: Following the suggestion of Reviewers #2, #3 and #4, all relevant analytical information regarding the determination of lipid biomarkers have been added accordingly in the materials and methods section 3.2.4 (Lipid biomarkers analysis and definitions of molecular indices) of the revised manuscript.

p 9944 line 16 – Usually concentrations of alkanols are higher than alkanes, but here the reverse is the case. Presumably some of this reflects the presence of petroleum alkanes as indicated by the UCM. Since _TerNA and _TerN-OH are used as composite concentrations of the terrestrial lipids, were the long-chain even-carbon numbered alkanes used in _TerNA corrected somehow for the contributions of the petroleum HC, as would be estimated by the abundances of even-carbon numbered alkanes?

Response: Indeed, in the present study the reported concentrations of TerNA are higher than the concentrations of TerN-OH. As stated in page 9956 - lines 16-17, of the BGD paper, the patterns of long-chain *n*-alkanes and *n*-alkanols with elevated CPI_{NA} and $CPI_{N\text{-}OH}$ values, respectively, indicate the presence of allochthonous natural (terrigenous) inputs from epicuticular higher plant waxes in the study area. Thus, although a prominent signal related to chronic oil pollution is abundant in the study area (presence of UCM), we assume there is no important bias on *n*-alkanes concentrations (and subsequently TerNA compounds) associated with the presence of non-degraded (fresh) fossil inputs. In the opposite case, we would expect significantly lower CPI_{NA} values, since *n*-alkane compounds of petroleum products present CPI_{NA} values ~1.

We believe that lower abundances of TerN-OH compared to TerNA can be related to the fact that the overall sedimentation rate in the deep areas of the open EMS is very low (i.e. 2-5 cm kyr^{-1}), and thus to the long residence time of the lipid compounds in the sediment, resulting in the enhanced degradation of ∑TerN-OH relatively to ∑TerNA. The latest are more resistant to degradation than their alcohol counterparts. This aspect is further considered in the revised version of the manuscript, in which the relative text on the use of the abundance ratio of ∑TerNA to ∑TerN-OH that is hired in the BGD paper as a proxy of the proportion of labile vs. refractory terrestrial components has been reworked accordingly.

p 9945 line 15 – here mass-normalized concentrations are used for PCA; elsewhere OC-normalized and "not normalized to OC" (e.g., p. 9952 line 24) are used. This is confusing!

Response: ∑TerNa and ∑TerN-OH (p 9952 line 22 and p9959 line 11 of BGD paper, respectively) and ∑Mar (p9952 line 24 and p9959 line 22 of BGD paper) values have not been normalized to OC contents because in this section the correlation of these variables to OC is investigated. If the values are normalized to OC contents, the subsequent correlation to OC has no statistical meaning.

p 9951 line25 – "PCA results mirror the composition of surface sediments"… Isn't this statement a given (obvious) since the PCA is based on the composition of the sediments?

Response: The Reviewer is correct. We have deleted the sentence due to the "PCA results mirror the composition of surface sediments" is obvious.

p 9953 line 22 – is the statement "This strongly suggests that the Sahara desert is the main source of lithogenics to the deep EMS" not a bit contradictory to the sentence on the next page (p 9954 line 9)"The high lithogenic contents found in most Ionian Sea stations points to fluvial inputs reaching this area from in the Adriatic Sea"? Perhaps this is a geographic distinction between regions, but it is unclear.

Response: Corrected according to the Reviewer's suggestion. The Sahara desert is the main source of lithogenics to the deep EMS, while the influence of terrigenous riverine/estuarine inputs in deep-sea surface sediments of the EMS is limited and localized. However, there are geographic distinctions between regions in the EMS, and for example in the north Ionian Sea, the relatively high lithogenic contents found points to fluvial inputs reaching the area from the Adriatic This paragraph has been modified to clarify its contents.

p 9957 line 4 – the Rampen et al reference does not seem to be the correct one for diols and keto-ols. Do you mean Rampen et al. (2012) Long chain 1,13- and 1,15-diols as a potential proxy for palaeotemperature reconstruction. Geochim. Cosmochim. Acta 84, 204–216, or one of the Rampen papers cited therein?

Response: The Reviewers is absolutely correct. This was a mistaken Mendeley import. The reference has been of course updated in the revised MS. We would like to thank the Reviewer for this comment.

p 9957 line 18 – PCA "provides"…; line 26 – should "inorganic IN" just be inorganic N"?

Response: Corrected according to the Reviewer's suggestion.

p 9958 line 24 – is 19% correct- it looks more like 0.19% in the figure.

Response: Corrected according the Reviewer's observation. The %TN vs. %OC values in surface sediments of the study area showed a strong linear correlation ($r=0.87$, $p<0.01$, Fig. 6a) with a regression equation as follows: %TN=0.089(%OC)+0.019. The x-intercepts of this

regression is on the N axis but close to zero, suggesting that although most of N measured is predominantly organic in origin, there is a constant fraction (0.019%) of IN (presumably as $NH4^+$ adsorbed on clays, mixed with the organic material. Considering that the %TN averages 0.06% then the 0.019% of the regression represents around 30% of inorganic N.

P 9961line 9 – the Wakeham et al. reference does not provide information about grain size, but rather particle density.

Response: The Reviewer is correct. We have replaced the reference of Wakeham et al., 2009 with the references of Bergamaschi et al., 1997. Bergasmachi et al., (1997) investigate the effect of grain size distribution and sediment surface area on organic matter content and composition in Peru Margin sediments.

Interactive comment on "Composition and sources of sedimentary organic matter in the deep Eastern Mediterranean Sea"

by R. Pedrosa-Pàmies et al.

Anonymous Referee #4

Received and published: 7 August 2015

Overview: The authors present an interesting study on the inorganic and organic composition of sediments collected from the Eastern Mediterranean Sea. The strength of this manuscript lies in the multi proxy approach the authors use to understand the source and transport of materials to the sediments collected. The manuscript is well written with data clearly presented.

We would like to deeply thank the Referee for the time and effort provided to review our manuscript and for his/her constructive comments that greatly helped us improve its quality during the revision process. We have addressed the Reviewer's suggestions for corrections/modifications in the revised version of the manuscript, in which certain parts have been re-worked accordingly (Materials and Methods, tables and Figures 5 and 7). Please follow our detailed responses to Reviewer's #4 comments below.

Overview

The major suggestion that will greatly improve the quality and impact of the manuscript is to put the findings into a larger more global context. Presently it is limited to the study location.

Response: According to the Reviewer's suggestion we have put the findings of our paper into a larger more global context. This aspect has been included in the discussion section 5.1 of the revised manuscript, which has been re-worked and developed accordingly in order to improve the quality and impact of the manuscript.

Additional Comments:

Methods

Please mention the QA/QC procedures for the lipid analysis.

Response: Following the suggestion of Reviewers #2, #3 and #4, all relevant analytical information regarding the determination of lipid biomarkers have been added accordingly in the materials and methods section 3.2.4 (Lipid biomarkers analysis and definitions of molecular indices) of the revised manuscript.

Figures and Tables

In all of the tables, please address the significant figures presented.

Response: Corrected according to the Reviewer's suggestion. There were some tables with mistakes related with the decimals of the values. All this has been corrected.

Figure 5: The PCA figure needs to be larger since it is hard to read in its current form.

Response: Corrected according to the Reviewer's suggestion. Figure 5a and 5b have been put side by side instead of one below the other.

Figure 7: In the caption please mention in the coloured symbols correlate to the axis.

Response: Corrected according to the Reviewer's suggestion. The sentence "Orange triangles and green circles correspond to molar TN/OC ratios and $\delta^{13}C$ values, respectively" has been added in the figure caption.

Composition and sources of sedimentary organic matter in the deep Eastern Mediterranean Sea

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Abstract

Surface sediments collected from deep slopes and basins (1018-4087 m depth) of the oligotrophic Eastern Mediterranean Sea have been analysed for bulk elemental and isotopic composition of organic carbon, total nitrogen and selected lipid biomarkers, jointly with grain size distribution and other geochemical proxies. The distribution and sources of sedimentary organic matter (OM) have been subsequently assessed and general environmental variables, such as water column depth and currentsphysical circulation patterns, have been examined as causative factors of deep-sea sediment characteristics. Lithogenic and biogenic carbonates are the dominant sedimentary fractions, while bothaccounting for up to 85.4% and 66.5% of the total weight, respectively. The low OC and TN contents in the surface sediments of the study area, that ranged from 0.15 to 1.15% and 0.06 to 0.11%, respectively, reflect the oligotrophic character of the EMS. Both bulk and molecular organic tracers reflect a mixed contribution from autochthonous and allochthonous sources for the sedimentary OM, as indicated by relatively degraded marine OM, terrestrial plant waxes and anthropogenic OM includinge.g., degraded petroleum by-products, respectively. Wide regional variations have been observed amongst the studied proxies, which reflect the multiple factors controlling sedimentation in the deep Eastern Mediterranean Sea. Our findings highlight the role of deep Eastern Mediterranean basins as depocentres of organic-rich fine-grained sediments (mean 5.4±2.4 μm), with OM accumulation and burial duebeing attributed to aggregation mechanisms and hydrodynamic sorting. A multi-proxy approach is hiredapplied aiming to investigate the biogeochemical composition of sediment samples, which sheds new light on the sources and transport mechanisms along with the impact of preservation vs. diagenetic processes on the composition of sedimentary OM in the deep basins of the oligotrophic Eastern Mediterranean Sea.

1 Introduction

The burial of organic matter (OM) in marine sediments constitutes the main link between "active“ pools of carbon in the oceans, atmosphere and landmasses, and carbon pools that cycle on much longer, geological, time scales (Burdige, 2007). Therefore, investigating the processes that control the composition of sedimentary OM that is buried in deep-sea sediments is crucial for understanding carbon cycling on a global scale.

The deep sea receives inputs of organic particles from multiple sources, both autochthonous (e.g. biogenic particulate matter from primary production in ocean surface waters) and allochthonous (i.e. land-sourced OM from soils, plant debris, riverine phytoplankton and man-made compounds transported by runoff and atmospheric deposition into the marine domain) (Bouloubassi et al., 1997; Durrieu de Madron et al., 2000; Kaiser et al., 2014). Consequently, sedimentary OM constitutes an heterogeneous and complex mixture of organic compounds with a wide range of chemical and physical properties (Mayer, 1994; Hedges and Oades, 1997; Hedges et al., 1997; Goñi et al., 1998). Due to the heterogeneity and complex nature of sedimentary OM sourcesTherefore, the combined use of bulk geochemical indicators such as total nitrogen (TN) to organic carbon (OC) ratios, stable isotopesisotope of OC and TN,($\delta^{13}C$), and molecular proxies such as lipid biomarkers is requiredcan aid to assessgain knowledge on the origin, delivery and preservation of OM in marine sediments (Bouloubassi et al., 1997; Meyers, 1997; Goñi et al., 2003; Volkman, 2006).

The biogeochemical composition of sediments in deep basins of the oligotrophic Eastern Mediterranean Sea (EMS), as well as the sources, transport and preservation of sedimentary OM, have been scarcely investigated so far. SomePrevious studies have shown that the composition of surficial sediments is principally controlled by the geochemical characteristics of the source areas, the prevailing metoceanic conditions on the adjacent shelves, the contribution of atmospheric aerosols and the dominant regional circulation (e.g., Weldeab et al., 2002; Ehrmann et al., 2007; Hamann et al., 2008). Nevertheless, the factors involved in the supply, distribution and fate of sedimentary OM are still poorly known. The reason for this lack of knowledge lies on the complex interactions amongst the

~~various physical, chemical and biological factors that altogether control OM cycling (Francois et al., 2002; Lutz et al., 2002; Danovaro et al., 2010).~~

In the present study, surface sediments collected from deep slopes and basins of the EMS have been analysed for physical and geochemical parameters such as grain size distribution, lithogenic, calcium carbonate ($CaCO_3$), opal, OC and TN contents, along with molar TN/OC ratios, stable isotopic ratios of OC ($\delta^{13}C$) and selected lipid biomarkers. Our main goal is to investigate the spatial distribution and main sources of sedimentary OM and to evaluate the impact of autochthonous vs. allochthonous contributions in the study area. We also examine whether and up to which point general environmental factors, such as ~~currents~~water mass circulation patterns and water column depth, could explain the observed deep-sea sediment geochemical properties.

2 Oceanographic setting

The EMS is a land-locked sea with a complex topography including shelves, slopes, ridges, seamounts, trenches and four main basins: the Adriatic Sea, the Ionian Sea, the Aegean Sea and the Levantine Sea (Fig. 1) (Amblàs et al., 2004; Medimap Group, 2007). The Ionian Sea to the west and the Levantine Sea to the east are longitudinally connected and cover most of the EMS area. They are also the ~~largest and~~ deepest basins ~~in~~of the EMS, with the maximum depth (5267 m) ~~achieved~~located at the Hellenic Trench, south of the Cretan Arc. The Aegean Sea and~~, especially,~~ the Adriatic Sea represent the northern extensions of the EMS. Both are relatively shallow, in particular the Adriatic Sea, which is dominated by a broad shelf and a slope sub-basin shallower than 1200 m. In the Aegean Sea, which has a particularly complex topography with ~~tenths~~tens of depressions, highs and islands, water depths up to 2500 m are found ~~in its southernmost part~~ north of the island of Crete (Amblàs et al., 2004; Medimap Group, 2007). The southern Aegean Sea~~, often referred to in the literature as the "~~ (Cretan Sea~~",~~) is the sea area comprised between the Cyclades Archipelago to the north and the island of Crete to the south, which also includes the western Cretan Straits.

The general circulation pattern ~~in~~of the EMS is anti-estuarine, which results from interactions ~~of~~between basin, sub-basin and mesoscale ~~flow~~flows (Bethoux, 1979). The EMS communicates with the Western Mediterranean Sea through the Sicily Strait, with an inflow of low-salinity Modified Atlantic Water (MAW) at the upper 100-150 m of the water column (Rabitti et al., 1994; Malanotte-Rizzoli et al., 1997). MAW flows in an easterly direction getting progressively saltier and warmer till transforming into Levantine Intermediate Water (LIW) into the Levantine Sea where it sinks to mid depths~~, largely in the Rhodes gyre~~ (Milliff and Robinson, 1992; Lascaratos et al., 1993).

The Eastern Mediterranean Deep Water (EMDW) is a relatively well oxygenated water mass, likely as a result of the formation and sinking of warm deep-water that ventilates the deepest levels in the EMS (Schlitzer et al., 1991; Roether and Well, 2001; Meador et al., 2010). Waters from the Adriatic Sea (Adriatic Deep Waters, ADW) have been ~~classically~~ considered as the main contributor of deep and bottom waters to the EMS (Malanotte-Rizzoli and Hecht, 1988). ~~ADW outflows over the sill of Otranto Strait and circulates along the deep western boundary of the Ionian Sea before entering into the Levantine Basin (Robinson et al., 1992).~~ Nevertheless, the Aegean Sea constitutes a sporadically significant contributor to EMDW through the Cretan Deep Water (CDW), as ~~shown during~~in the case of the Eastern Mediterranean Transient (EMT) anomaly in the 1990s ~~(Roether et al., 1996; Lascaratos et al., 1999; Theocharis et al., 1999)~~(Lascaratos et al., 1999; Theocharis et al., 1999). Additionally, the Aegean Sea constitutes a possible secondary source of intermediate waters to the adjacent Ionian and Levantine seas, through outflows across the Cretan Arc straits (Robinson et al., 2001).

Key factors that control the exchanges through the Cretan Arc straits are the thermohaline properties of water masses and mesoscale variability. For example, the Ierapetra anticyclonic gyre, which is located off the southeast corner of Crete (Ierapetra Basin), exhibits a strong seasonal signal that is linked to variations of the outflow across the eastern Cretan Arc straits (Theocharis et al., 1993; Larnicol et al., 2002). Actually, the several permanent and/or recurrent eddies in each of the EMS sub-basins enhance exchanges between continental shelf and slope waters (Robinson et al., 1992; Malanotte-Rizzoli et al., 1997; Millot and Taupier-Letage,

2005), which in turn influence primary productivity and the settling of OM to the deep-sea floor (Danovaro et al., 2010).

Thermohaline circulation and overall environmental conditions make the EMS one of the most ~~conspicuous~~ ultra-oligotrophic environments ~~in~~of the world ocean ~~(Psarra et al., 2000; Tselepides et al., 2000; Krom et al., 2005; Thingstad et al., 2005; Gogou et al., 2014). The EMS (except the Adriatic Sea) is characterized by very low concentrations of nutrients reflected by low overall chlorophyll-a concentrations and low levels of primary production. Within the EMS, the Ionian Sea and the Levantine Sea are the most nutrient-depleted basins (Bosc et al., 2004). Annual particulate~~(Psarra et al., 2000; Krom et al., 2005; Thingstad et al., 2005; Gogou et al., 2014a). Annual primary production in the EMS averages between 121 and 145 g C m^{-2} y^{-1} ~~(Bosc et al., 2004; Gogou et al., 2014).~~(Bosc et al., 2004; Gogou et al., 2014b). However, the fraction of primary production exported below 2000 m of water depth averaged 0.3% ~~(Gogou et al., 2014).~~

(Gogou et al., 2014b). The low autochthonous contribution to OM fluxes ~~to~~in the deep open EMS is counterbalanced by allochthonous inputs resulting from long-range atmospheric transport and deposition ~~of nutrients~~ by aerial dust (Jickells, 1995; Gogou et al., 1996; Tsapakis and Stephanou, 2005). ~~The Saharan dust flux, which follows a general westward direction, is a relevant contributor to~~ The overall sedimentation ~~in~~rate in the deep areas of the open EMS ~~(Guerzoni et al., 1997)~~is low (i.e. 2-5 cm kyr^{-1}) (Van Santvoort et al., 1996, 2002; Garcia-Orellana et al., 2009; Stavrakakis et al., 2013)~~. The Saharan dust spreads rather uniformly across the EMS (Rutten et al., 2000; Jickells et al., 2005). Riverine inputs have a rather minor influence on the open EMS sedimentation as they are small and localized (Weldeab et al., 2002; Statham and Hart, 2005; Garcia-Orellana et al., 2009). The overall sedimentation rate in the deep areas of the open EMS is low (i.e. 2-5 cm kyr^{-1}) (Van Santvoort et al., 1996, 2002; Garcia-Orellana et al., 2009; Stavrakakis et al., 2013)~~.

3 Materials and methods

3.1 Sampling

Short sediment cores were collected with a multicorer at 29 stations, ranging from 1018 to 4087 m water depth, during six oceanographic cruises in the Ionian Sea, the southern Aegean Sea (Cretan Sea) and the northwestern Levantine Sea from January 2007 to June 2012 (Fig. 1 and Table 1). ~~Only the undisturbed top centimetre of each sediment core is considered in this study, as our target is the most recent record of OM fluxes in the study area.~~

Once onboard, multicores were visually described and sliced at 1-cm intervals. Sub-samples collected for grain size, elemental and stable isotopic composition were stored in sealed plastic bags at 4ºC, while those collected for the analysis of lipid biomarkers were stored in pre-combusted aluminium foils at -20ºC. Only the undisturbed top centimetre of each sediment core is considered in this study.

3.2 Analytical procedures

3.2.1 Particle size characterization

The grain size distribution of sediment samples was determined using a Coulter LS230 Laser Diffraction Particle Size Analyzer, which measures sizes between 0.04 and 2000 µm. Prior to analysis, freeze-dried samples were oxidized with a 10% H_2O_2 (v/v) solution in order to remove OM. Each sample was then divided into two sub-samples, one of which was treated with 1M HCl to remove carbonates and thus obtain the grain size distribution of lithogenic (siliciclastic) particles. Subsequently, both bulk and lithogenic fractions were dispersed into 20 cm^3 of a 5% $NaPO_5$ (v/v) solution and mechanically shaken for 4 hours, and then introduced into the particle size analyzer after using a 2000 µm sieve to retain occasional coarse particles that might obstruct the flow circuit of the instrument.

The measured particle size spectrum is presented as % volume in a logarithmic scale, where volume is calculated from particle diameter, assuming spherical shapes. Results were recalculated to percentages of clay (<4 µm), silt (4-63 µm) and sand (63 µm-2 mm).

3.2.2 Elemental and stable isotopic analysis of carbon and nitrogen

For the determination of total carbon (TC), TN, OC contents and stable isotopic composition of OC ($\delta^{13}C$) freeze-dried and ~~grounded~~ground sediments were analysed using a Flash 1112 EA elemental analyser interfaced to a Delta C Finnigan MAT isotope ratio mass spectrometer. Samples analyzed for %OC and $\delta^{13}C$ were initially de-carbonated using repetitive additions of a 25% HCl (v/v) solution, separated by 60ºC drying steps, until no effervescence was observed (Nieuwenhuize et al., 1994). Stable isotope data are reported using the conventional per thousand $\delta^{13}C$ notation relative to the Pee Dee Belemnite standard. Uncertainties for elemental composition were lower than 0.1%, while uncertainty for $\delta^{13}C$ was lower than 0.05‰.

In consistency with published data in the Mediterranean Sea we assumed OM as twice the OC content (e.g., Heussner et al., 1996; Masqué et al., 2003). The inorganic carbon content was calculated from the difference between TC and OC measurements. Assuming all inorganic carbon is contained within calcium carbonate, $CaCO_3$ content was determined using the molecular ratio of 100/12.

~~Atomic~~Molar TN/OC ratios were also calculated. TN/OC is plotted in order to constrain the elemental ratios of N-depleted samples (i.e. TN/OC $\approx$ 0 rather than OC/TN ∞ 0) following Goñi et al. (2006), and to avoid the underestimation of the terrestrial-derived carbon fraction (Perdue and Koprivnjak, 2007).

3.2.3 Biogenic opal and lithogenic fraction analysis

The biogenic silica content was analysed using a two-step 2.5 h extraction with a 0.5M Na_2CO_3 solution, separated by centrifugation of the leachates. Si and Al contents of both leachates were analysed with a Perkin-Elmer Optima 3200RL Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES), correcting the Si content of the first leachate by the Si/Al ratio of the second one. All values are reported as opal ($SiO_2 \cdot 0.4H_2O$), a parameter defined by 2.4 times the weight percentage of biogenic Si content determined for each sample (Mortlock and Froelich, 1989). The opal detection limit, associated to the detection limit of the ICP-OES system, is approximately 0.2%.

The lithogenic fraction was estimated by subtracting the concentration of the major constituents from total dry weight (%lithogenic= 100 – [%OM + %$CaCO_3$ + %opal]). This fraction represents the residual component of particles such as quartz, feldspars, clay minerals and aluminosilicates (Mortlock and Froelich, 1989).

3.2.4. Lipid biomarkers analysis and definitions of molecular indices

~~Freeze-dried sediment samples were solvent-extracted three times by sonication with a dichloromethane: methanol mixture (4:1, v/v). Combined extracts were fractionated on a silica column (modified after Gogou et al., 1998) into three fractions, containing aliphatic hydrocarbons (F1), ketones (F2) and alcohols, sterols and diols (F3), respectively. Instrumental analysis of F1 and F3 fractions was carried out by Gas Chromatography-Mass Spectrometry (GC-MS) on an Agilent 7890 GC coupled to an Agilent 5975C Mass Selective Detector, while F2 fractions were analyzed on an Agilent 7890 GC equipped with a Flame Ionization Detector (FID). Details regarding the instrumental analysis are reported elsewhere (Gogou et al., 2007).~~

The analytical procedure followed for the determination of lipid biomarkers has been previously presented in detail (Gogou et al., 1998, 2000, 2007). Briefly, freeze-dried sediment samples were initially solvent-extracted three times by sonication with a dichloromethane: methanol mixture (4:1, v/v). Combined extracts were subsequently separated into different compound classes by column chromatography using silica gel that had been activated for 1 hour at 150 °C. The following solvent systems were used to elute different compound classes: (1) *n*-hexane (fraction F_1, aliphatic hydrocarbons), (2) dichloromethane/*n*-hexane (fraction F_2, carbonyl compounds) and (3) ethyl acetate/*n*-hexane (fraction F_3, alcohols, sterols).

F_1 and F_3 fractions were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) while F_2 fractions were analyzed by Gas Chromatography using Flame Ionization Detection (GC-FID). Hydroxyl-bearing compounds (fraction F_3) were derivatized to the corresponding trimethylsilyl ethers prior to GC-MS analysis using N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) for 1hour at 80^{o}C. Details regarding the GC instrumental parameters are presented elsewhere (Gogou et al., 2007; Parinos et al., 2013).

The individual lipids were identified by a combination of comparison of GC-retention times to authentic standards and comparison of their mass spectral data to those in the literature. Quantification was based on the GC-MS or GC-FID response and comparison of peak areas with those of known quantities of standards added prior to the extraction of the sediment samples ([$^{2}H_{50}$]*n*-tetracosane for *n*-alkanes, *n*-hexatriacontane for long-chain alkenones, 5α-androstan-3β-ol for sterols and heneicosanol for *n*-alkanols). The signal of the Unresolved Complex Mixture (UCM) of aliphatic hydrocarbons was defined by the chromatographic area (fraction F_1) between the solvent baseline and the curve defining the base of resolved peaks. UCM quantification was performed relatively to [$^{2}H_{50}$]*n*-tetracosane using the average response factor of *n*-alkanes.

Procedural blanks processed in parallel to the samples were found to be free of contamination. Reproducibility of the analytical method based on multiple extractions of sediments was better than 6% in all cases.

A range of selected lipid biomarkers are ~~reported~~considered in this study, namely long chain *n*-alkanes and *n*-alkanols, long-chain alkenones, long-chain diols & keto-ols and a suite of sterols, along with lipid biomarkers' indices, as proxies of organic matter sources and/or degradation. As OC can vary due to the supply of inorganic material (dilution effect) the concentrations of the reported lipid compounds were normalized to OC contents.

The sum of the concentrations of the most abundant high molecular weight *n*-alkanes and *n*-alkanols, which are major components of epicuticular higher plant waxes (Eglinton and Hamilton, 1967; Ohkouchi et al., 1997), are defined, respectively, as:

$$\sum \mathbf{TerNA} = \sum n\text{-}C_{27,29,31,33} \quad (1)$$

$$\sum \mathbf{TerN\text{-}OH} = \sum n\text{-}C_{24,26,28,30} \quad (2)$$

The sum of the concentrations of the considered lipid biomarkers having a clear marine (algal) origin (see Sect. 5.1.2) was calculated as follows:

$$\sum Mar=\sum(_{28}\Delta^{5,22E}+_{30}\Delta^{22E}+C_{30}\ diols\&keto\text{-}ols+\ alkenones) \quad (3)$$

The abundance of the Unresolved Complex Mixture (UCM) of aliphatic hydrocarbons, a commonly observed persistent contaminant mixture in marine sediments consisting of branched alicyclic hydrocarbons (Gough and Rowland, 1990), is used as an indicator of the contribution from degraded petroleum products, i.e. chronic oil pollution in the study area (Wang et al., 1999).

The Carbon Preference Indices of long chain *n*-alkanes (CPI_{NA}) and *n*-alkanols ($CPI_{N\text{-}OH}$) have been used as indicators of terrestrial OM degradation with CPI values in fresh leaves being typically >4~~, although the occurrence of petroleum hydrocarbons bias (lower) CPI_{NA} values with increasing petroleum contribution, since~~ (Collister et al., 1994). However, the abundance of non-degraded petroleum hydrocarbons could potentially bias (lower) CPI_{NA} values with increasing petroleum contribution, since *n*-alkane compounds of petroleum products present CPI_{NA} values ~1 (Wang et al., 1999). The indices were calculated, respectively, as:

$$CPI_{NA}=\sum([n\text{-}C_{25}] - [n\text{-}C_{33}]) / \sum([n\text{-}C_{26}] - [n\text{-}C_{34}]) \quad (4)$$

$$CPI_{N\text{-}OH}= \sum([n\text{-}C_{24}] - [n\text{-}C_{30}]) / \sum([n\text{-}C_{23}] - [n\text{-}C_{29}]) \quad (5)$$

Finally, the abundance ratio of ∑TerNA to ∑TerN-OH is used as a proxy of the proportion of ~~labile vs.~~ refractory vs. labile terrestrial components~~ because the former~~, since ∑TerNA are more resistant to degradation than their alcohol counterparts (Eglinton and Hamilton, 1967; Ohkouchi et al., 1997). The ratio is defined as:

$$[NA]/[N\text{-}OH]=[\sum TerNA] / [\sum TerN\text{-}OH] \quad (6)$$

3.2.5 Data analysis and presentation

Statistical treatment of grain size data was carried out using the GRADISTAT v. 8.0 software (Blott and Pye, 2001). Median diameter (D_{50}), sorting and skewness were calculated geometrically (in metric units) following the approach of Folk and Ward (1957), which is most appropriate when data are non-normally distributed, as in the case of polymodal sediments from the study area.

D_{50} was calculated as the average equivalent diameter, which is the diameter where 50% of the sediment sample has a larger equivalent diameter and the other 50% has a smaller equivalent diameter. Sorting (expressed by the standard deviation) indicates the fluctuation in the degree of kinetic energy and the depositional regime on grain size characteristics. Skewness measures the degree of asymmetry onto particle distribution. The skewness for a normal distribution is zero, and any symmetric data should have skewness near zero. Positive values indicate skewness towards the finer grain sizes (skewed left) ~~and~~while negative values indicate skewness towards the ~~coarse~~coarser grain sizes (skewed right). The results of grain size distribution analysis were hierarchically clustered (using IBM SPSS Statistics 18.0) according to the above statistical parameters (autoscaled prior to cluster analysis), in order to determine the similarity of samples within each station measuring the squared Euclidean distance.

~~Principal component analysis (PCA) was performed on grain size and elemental composition data (%clay and sorting of lithogenic and bulk fractions, lithogenic, $CaCO_3$, OC, TN contents), on bulk organic matter signatures (TN/OC ratios and $\delta^{13}C$) and on indices and mass-normalized concentrations of lipid biomarkers. Through linear combinations PCA assigns a loading value to each variable on each factor (principal component, PC), while the same assignment is given to scores, representing sample location. Factors determine the percentage of data variance explanation. A subroutine, the Varimax rotation, was applied to the first three factors in order to maximize or minimize loadings within each factor, and thus simplify the visual interpretation of PCA projections (Yunker et al., 2005). While loadings reflect the influence of variables on sample patterns, site scores reveal the distance from the origin to each sample point along each PCA axis. Correlation analysis was also performed using the same variables. This statistical technique allows identification of~~

~~the similarity amongst samples as well as the specificity of each individual compound in tracing OM (Fernandes et al., 1999; Goñi et al., 2000).~~

~~Spatial distributions~~Principal component analysis (PCA) was performed on standardized grain size and elemental composition data (%clay and sorting of lithogenic and bulk fractions, lithogenic, $CaCO_3$, OC and TN contents), on standardized bulk organic matter signatures (molar TN/OC ratios and $\delta^{13}C$) and on standardized indices and mass-normalized concentrations of lipid biomarkers. A subroutine, the Varimax rotation, was applied to the first three factors in order to maximize or minimize loadings within each factor, and thus simplify the visual interpretation of PCA projections. Correlation analysis was also performed using the same variables. In certain occasions during correlation analysis, the singular stations that were clearly out of the trend were excluded in order to strengthen the evident trends of the examined variables. These stations are explained in detail in the discussion section (see Sect. 5.2).

The spatial distribution of the various geochemical parameters' contents, bulk OM signatures and selected lipid biomarkers' concentrations/indices considered in this study were visualized using Ocean Data View (ODV) (Schlitzer, 2011).

4 Results

4.1 Grain size characteristics

The grain size composition (% clay, silt and sand) and the sedimentary parameters (D_{50}, sorting and skewness) are presented in Table 2, while the statistical dendrogram, type-averaged grain size spectrum and spatial distributions of grain size types are presented in Figure 2.

Silt- and clay-sized particles dominate the bulk sediment, accounting for up to 76.7% and 57.1% of the total weight, respectively (Table 2). The lowest values (<40%) for the silt fraction are found in the upper slope of the western Cretan Straits (station Red3) and the northwestern Levantine Sea (station BF19), while the highest values (>65%) correspond to the Ionian Sea (stations H12 and H03). The lowest clay contents (<20%) are also found in the upper slope of the western Cretan Straits (station Red3) but also in the northeastern Ionian Sea (station H12), while

~~top~~maximum values (>55%) are recorded at the northwestern Levantine Sea (station Red1.1 in Ierapetra Basin~~, an abyssal basin a maximum depth of 4420 m~~) and the western Cretan Straits (station H01). Sand contents show large variations, i.e. from 0 to 47.7% (station Red3 in the upper slope of western Cretan Straits), with values less than 2% in most of the stations (Table 2). ~~Rather~~Relatively high values (>10%) are also obtained in the northwestern Levantine Sea (stations Red2, BF19 and BF24). D_{50} values range between 3.5 and 56.6 μm (Table 2).

Sorting of bulk sediment ~~range~~ranges from 3.0 to 5.2 (Table 2). Most of the northwestern Levantine Sea and western Cretan Straits' stations are very poorly sorted and all stations within the southern Aegean Sea and most of the Ionian Sea are poorly sorted (Table 2 and Fig. 2a). Skewness values for the investigated samples range from −0.45 to 0.27 (Table 2), varying from a very clear negative skewness ~~in~~ in the upper slope of the western Cretan Straits (station Red3), to positive skewness in the northwestern Levantine Sea (stations Red2.1, BF19, BF22 and BF24).

The hierarchical cluster analysis of all bulk sediment samples resulted into seven grain-size types (Fig. 2a). Most of the samples group into cluster types I (n=11), II (n=6) and III (n=6), with grain size profiles almost symmetrical and poorly sorted, and a dominance of clay and silt fractions. Type V includes three very poorly sorted and positive skewed samples from the northwestern Levantine Sea, which consist mainly of clay and silt fractions. Types IV, VI and VII include only one sample each (Red2, H12 and Red3, respectively). Samples Red2 and Red3, dominated by coarse silt fractions (D_{50} 11.1 μm and 56.61 μm, respectively), are both very poorly sorted but with different types of skewed distributions (symmetrical and negatively skewed, respectively). Finally, sample H12, composed mostly of fine silt, is poorly sorted and slight positive skewness.

As in the bulk sediment, silt- and clay-sized particles dominate the lithogenic fraction, accounting for up to 73.5% and 50.8% of the total weight, respectively. The hierarchical cluster analysis of the lithogenic fraction identified six grain size types (clusters) (Fig. 2b). A majority of samples are highly similar (types I-V), with an average composition of 35.2±5.6% clay, 63.5±5.3% silt and 1.3±2.3% sand, a D_{50} of 6.6±1.3 μm and a bimodal or trimodal, symmetrical, poorly sorted grain size

distribution. Sample Red3 from the upper slope of western Cretan Straits is an exception, in which belongs to type VI. The composition of its lithogenic fraction is 10.3% clay, 34.6% silt and 55.1% sand, with a D_{50} of 78.1 μm and a bimodal, very poorly sorted and negatively skewed grain size distribution (Fig. 2b and Table 2).

4.2 Bulk geochemical sediment composition

The spatial variability of lithogenics, $CaCO_3$, OC and TN contents within the study area is presented in Figure 3a-c.

The lithogenics content in the analyzed surface sediments range between 32.5 and 85.4% (Fig. 3a). Higher percentages (>70%) are found in stations of the Ionian Sea (with the exception of station H02), while the lowest percentages (<40%) are found in the southern Aegean (stations Red4 and Red5) and northwestern Levantine seas (stations Her01 and BF19) (Table 2). The $CaCO_3$ contents also show a wide range of values throughout the study area, from 13.2 to 66.5% (Fig. 3b and Table 2). Stations in the western Ionian Sea (H04, BF27, H03, BF15, BF13 and H07) have the lowest $CaCO_3$ contents (<22%), whereas most stations in the southern Aegean and northwestern Levantine seas and in the western Cretan Straits have elevated $CaCO_3$ contents (>40%).

Opal contents are very low, ranging from below detection limits to a maximum of 0.24% in the southern Aegean and northwestern Levantine seas (stations Red5 and Red13) (Table 2). Since opal contents are very close to the detection limits, those values can be considered as negligible. Therefore inorganic geochemical fraction of the investigated deep EMS sediments consists only of lithogenic (terrigenous) and carbonate components.

OC contents in the studied samples range from 0.15 to 1.15%, with an average value of 0.47% (Table 2). The lowest values are recorded in the northeastern Ionian Sea, south of Otranto Strait (station H12), while the highest values are found ~~not too far~~ off the Gulf of Taranto (station H07), followed by ~~other~~ stations ~~also~~ in the Ionian Sea (stations BF27, H04 and H03). ~~However, the overall distribution of OC contents is rather patchy and does not seem to have any clear pattern, as stations with higher and lower contents appear close one to each other (Fig. 3c).~~ TN contents range from

0.01 to 0.11% with an average value of 0.06%. TN display a pattern similar to OC, also with the highest values recorded off the Gulf of Taranto (station H07) and the lowest south of Otranto Strait (station H12), both in the northern Ionian Sea.

4.3 Elemental and stable isotopic composition of sedimentary OM

The spatial distribution of molar TN/OC ratios and $\delta^{13}C$ within the study area is presented in Figure 3d-e.

Molar TN/OC ~~atomic~~ ratios of the sedimentary OM range from 0.08 to 0.16 (Fig. 3d and Table 2). The highest molar TN/OC ratios values (>0.14) are recorded in the southern Aegean (station Red8) and northwestern Levantine (stations Her01, BF22 and BF24) seas, whereas the lowest molar TN/OC ratios (<0.09) are recorded in stations from the northwestern Levantine Sea (station Red15.1), the western Cretan Straits (stations Red3 and Red3.1) and the northern Ionian Sea (stations H07 and H12). However, there is no clear spatial trend (Fig. 3d).

The spatial distribution of $\delta^{13}C$ values shows that relatively lower values are more common in the Ionian Sea than in the northwestern Levantine Sea, the southern Aegean Sea and the south Ionian Sea (Fig. 3e). $\delta^{13}C$ values range from -18.3 to -24.6‰ (Fig. 3e and Table 2), with stations from the Ionian Sea (stations H03, H07 and H12) yielding relatively depleted $\delta^{13}C$ values (<-24‰) and stations from the western Cretan Straits (station Red3) and the northwestern Levantine Sea (Ierapetra Basin, stations BF22, Red1.1 and Ier01) having relatively enriched $\delta^{13}C$ values (>-22‰).

4.4 Lipid biomarkers

The analysed sedimentary aliphatic hydrocarbons comprise of a series of resolved compounds, mainly *n*-alkanes, and a UCM (Parinos et al., 2013). The UCM dominate amongst aliphatic hydrocarbons in concentrations ranging between 0.50 and 6.64 mg g OC^{-1} (Fig. 4a and Table 3). Maximum concentrations (>5 mg g OC^{-1}) are recorded in the northwestern Levantine Sea (station Red2.1) followed by the deep central

Ionian Sea (station H03). The lowest UCM values (<1.0 mg g OC^{-1}) are obtained in the northern Ionian Sea (station H12) and in the western Cretan Straits (station H01), while rather low values are also recorded in the southern Aegean Sea and west of Crete.

The molecular profile of the *n*-alkanes is dominated by long chain homologues ($C_n \geq 24$), maximizing at *n*-C_{31}, with elevated CPI_{NA} values (4.9±1.6) (Table 3). ∑TerNA range between 40.8 and 483 µg g OC^{-1}, with an average value of 172 µg g OC^{-1} (Fig. 4b and Table 3). The station with the highest concentration (station Red2.1) is found in the northwestern Levantine Sea, while the stations with the lowest ones (<110 µg g OC^{-1}) are located in the northern Ionian Sea (stations H07 and H12) and in the southern Aegean Sea (station Red9). Furthermore, relatively elevated ∑TerNA concentrations (>210 µg g OC^{-1}) are recorded at the deep station of the western Cretan Straits' (station Red3.1) and the deep central Ionian Sea (stations H03 and H05).

The aliphatic alcohol fraction is dominated by a series of *n*-alkanols ranging from *n*-C_{22} to *n*-C_{30}, with maxima at *n*-C_{26}, and elevated $CPI_{N\text{-}OH}$ values (4.5±0.8) (Table 3). ∑TerN-OH range from 13.4 to 105 µg g OC^{-1}, with an average of 40.4 µg g OC^{-1}, displaying similar distribution with ∑TerNA (Fig. 4c and Table 3). The [NA]/[N-OH] ratios for the analysed sediments range between 2.9 and 6.9, with an average of 4.3±0.9 (Table 3).

Long-chain di- and tri-unsaturated C_{37} and C_{38} methyl ketones and C_{38} ethyl ketones, commonly referred to as long-chain alkenones, are present in all samples with total concentrations ranging from 3.41 to 30.5 µg g OC^{-1}, 13.0 µg g OC^{-1} on average. The major C_{27}-C_{30} sterols considered in this study, i.e. cholesterol (cholest-5-en-3β-ol; $_{27}\Delta^{5}$), brassicasterol (24-methylcholesta-5,22-dien-3β-ol; $_{28}\Delta^{5,22}$), β-sitosterol (24-ethylcholesta-5-en-3β-ol; $_{29}\Delta^{5}$) and dinosterol (4α,23,24-trimethyl-5α(H)-cholest-22(E)-en-3β-ol -$_{30}\Delta^{22}$), have total concentrations ranging between 10.3 and 62.4 µg g OC^{-1}, averaging 31.7 µg g OC^{-1}. Long-chain C_{30} *n*-alkan-1,15-diols and the corresponding C_{30} keto-ols are also found in concentrations ranging from 7.30 to 35.81 µg g OC^{-1}, with an average of 20.3 µg g OC^{-1} (Table 3).

∑Mar range between 18.2 to 72.6 µg g OC^{-1}, 43.6 µg g OC^{-1} on average (Fig. 4d and Table 3), displaying a generally increasing eastward trend with maximum

concentrations (>55 µg g OC^{-1}) recorded in the deep northwestern Levantine Sea (stations Red2.1, Her01, Ier01 and Red7). Elevated ∑Mar values are also recorded at stations Red3 in the upper slope of the western Cretan Straits, but also stations H04 and H05 in the deep Ionian Sea. The lowest values (<40 µg g OC^{-1}) are obtained in the southern Aegean Sea (stations Red8, Red9), the northern Ionian Sea (station H12) and the western Cretan Straits (station H01).

4.5 Multivariate analysis of geochemical parameters

~~Grain size, lithogenics, $CaCO_3$, OC and TN contents, TN/OC ratios, stable isotopic compositions ($\delta^{13}C$) and lipid biomarkers' concentrations and indices provide a robust database to assess the composition of sediments and the provenance of sedimentary OM in the investigated areas, which cover a large part of the EMS. The PCA allow the identification of similarities amongst samples, as well as the value of each individual proxy in tracing the composition of surface sediments of the deep EMS.~~

Three main principal components (PCs) are identified from PCA, accounting for 64.3% of the variation within the data set (23.8%, 22.8% and 17.7% for PC1, PC2 and PC3, respectively). PC1 is characterised by positive loadings for water depth, ∑TerNA, ∑TerN-OH, ∑Mar, UCM and negative loadings for CPI_{NA} and CPI_{N-OH}. The highest positive loadings on PC2 are associated to $\%CaCO_3$, %clay in the bulk sediment and TN/OC values, while negative loadings are associated to %lithogenics. Finally, the geochemical parameters with high positive loadings on PC3 are %OC, %TN, and %clay of the lithogenic fraction, while those with negative loadings are $\delta^{13}C$ and sorting of bulk sediment (Fig. 5a).

Factor scores on each PC display significant variability amongst the studied stations, both within the same area and from one area to another (Fig. 5b). High positive factor scores on PC1 are observed both in stations to the west (Ionian Sea) and east (western Cretan Straits and northwestern Levantine Sea). For PC2, an eastward increasing contribution of positive factor score values seems to exist, with the highest ones located in the southern Aegean Sea and the northwestern Levantine Sea. In

contrast, the prevalence on PC3 is recorded in stations of the Ionian Sea and in parts of the northwestern Levantine Sea (Ierapetra Basin).

~~PCA results mirror the composition of surface sediments. Indeed, the~~The contents of $CaCO_3$ show an increasing nort-south and west-east gradient (Figs. 3b and 5). In the southern Aegean Sea, the northwestern Levantine Sea and the western Cretan Straits' stations, $CaCO_3$ contents are positively correlated to %clay of the bulk sediment (r=0.48, p<0.05) and to alkenone concentrations (r=0.62, p<0.05). Lithogenic contents are higher in the north and west (Ionian Sea) while being significantly positively correlated to OC and TN contents (r=0.65 and r=0.72 ~~and~~, p<0.05, respectively, excluding stations BF15, H07 and H12 of the Ionian Sea). Furthermore, OC and TN contents of stations deeper than 2100 m show a significant positive correlation to water depth (r=0.54 and r=0.70, respectively, p<0.05). However, this is not highlighted by the PCA. A significant positive correlation is also observed for OC and TN contents in the analysed samples (r=0.87, p<0.0001) (Fig. 6a).

Surface sediments of the Ionian Sea show a significant (p<0.05) positive correlation of OC and TN contents ~~with~~to %clay (r=0.80 and r=0.73), and a negative correlation ~~with~~to %silt (r=-0.75 and r=-0.65) and D_{50} of the lithogenic fraction (r=-0.79 and r=-0.83). $\delta^{13}C$ values (excluding station Red3 of the western Cretan Straits) are significantly (p<0.05) and positively correlated to $CaCO_3$ contents (r=0.53), %clay of the bulk sediment (r=0.65) and molar TN/OC ratios (r=0.53), and negatively correlated to %OC (r=-0.46), %silt (r=-0.66) and D_{50} (r=-0.59) of the bulk sediment.

Terrestrial lipid ~~biomarker~~biomarkers concentrations (∑TerNA and ∑TerN-OH) display a significant positive correlation amongst them (r=0.95, p<0.0001), but also to %clay (both with r=-0.55, p<0.05) and D_{50} (r=0.62 and r=0.58, respectively, p<0.01) of the bulk lithogenic fraction. Moreover, ∑TerNA and ∑TerN-OH show a significant positive correlation (p<0.05) to β-Sitosterol ($_{29}\Delta^5$) (r=0.71 and r=0.56, respectively, excluding stations H07 and H12 of the Ionian Sea). ∑TerNA and ∑TerN-OH (not normalized to OC contents) are also significantly correlated to OC (r=0.81 and r=0.76, respectively, p<0.001), again excluding stations H07 and H12 of the Ionian Sea. ~~Moreover,~~ ∑Mar (not normalized to OC contents) display a significant positive correlation with OC (r=0.7, p<0.001), ~~with~~while a significant positive correlation

(r>0.65, p<0.005 in all cases) ~~also found~~is evident amongst the concentration of cholesterol ($_{27}\Delta^{5}$) and marine algal markers ($_{28}\Delta^{5,22E}$, $_{30}\Delta^{22E}$, C_{30} diols&keto-ols and alkenones; see Sect. 5.2.1).

5 Discussion

5.1 Sources of sedimentary material in the deep Eastern Mediterranean Sea

~~Clearly the surface sediments of the deep EMS mostly consist of lithogenics and carbonates, have low OC contents and opal is nearly absent (Table 2). The range of lithogenics, carbonates and opal contents recorded in our samples are in agreement to those previously reported in the Eastern Mediterranean Sea (Emelyanov and Shimkus, 1986; Bethoux, 1989; Cros, 1995; Kemp et al., 1999; Rutten et al., 2000; Struck et al., 2001). The OC contents are also comparable to those for the Eastern Mediterranean Sea (0.23-0.99%, Bianchi et al., 2003; 0.30-0.82%, Gogou et al., 2000; 0.25-1.73%, Polymenakou et al., 2006) as well as the western Mediterranean Sea (0.8-1.6%, Kaiser et al., 2014; 0.47-1.53%, Masqué et al., 2003; 0.23-1.85%, Roussiez et al., 2006).~~

Clearly, the surface sediments of the deep EMS mostly consist of lithogenics and carbonates, have low OC contents while opal is nearly absent (Table 2). The range of lithogenics, carbonates and opal contents recorded in the investigated samples are similar to those previously reported for the Eastern Mediterranean Sea (Emelyanov and Shimkus, 1986; Bethoux, 1989; Cros, 1995; Kemp et al., 1999; Rutten et al., 2000; Struck et al., 2001). OC contents reach values slightly above 1% and are also comparable to those found in the Eastern Mediterranean Sea (0.56-1.51%, Danovaro et al., 1993; 0.23-0.99%, Bianchi et al., 2003; 0.30-0.82%, Gogou et al., 2000; 0.25-1.73%, Polymenakou et al., 2006), and relatively lower than those found in the Western Mediterranean Sea (0.80-1.60%, Kaiser et al., 2014; 0.47-1.53%, Masqué et al., 2003; 0.23-1.85%, Roussiez et al., 2006). Values found are comparable to the typical hemipelagic sediments found in continental slopes (Rullkötter, 2006) and slightly higher than those in deep basin areas (Seiter et al., 2004).

5.1.1 Lithogenics and carbonate

~~Generally speaking, lithogenics can be supplied from different sources through aeolian and riverine transport, discharge and deposition. Several studies have highlighted that deposition of mineral aerosol particles may have a profound influence on the geochemistry and sedimentology of the open Mediterranean Sea (Buat-Menard et al., 1989; Rutten et al., 2000; Guerzoni and Molinaroli, 2005). The grain size of the lithogenic fraction found in the studied sediments is very similar to Saharan dust particles, which mainly consist of clayey silts and silty clays, with particle~~The grain size of the lithogenic fraction found in the studied sediments is very similar to that of Saharan dust particles, which mainly consist of clayey silts and silty clays with diameters ranging from 0.5 to 60 µm (D_{50} ~5 µm) and two main modes at 3-4 µm and 60 µm ~~(Guerzoni and Molinaroli, 2005~~(Ratmeyer et al., 1999; Guerzoni and Molinaroli, 2005 and references therein). This strongly suggests that the Sahara desert is the main source of lithogenics to the deep EMS. ~~Such a view~~This is further supported by observations pointing to Saharan dust transported by southerlies blowing over the great North African desert as the main lithogenic input to the EMS (Guerzoni et al., 1999; Weldeab et al., 2002). The Saharan dust spreads rather uniformly across the EMS (Rutten et al., 2000; Jickells et al., 2005). ~~(Guerzoni et al., 1999; Rutten et al., 2000; Weldeab et al., 2002; Jickells et al., 2005). Furthermore~~Furthermore, but to a lesser extent, volcanic ash deposition into the EMS represents another external source of fine-grained particles (<5-50 µm) (Kelepertsis et al., 2003). Mount Etna, located on the island of Sicily ~~(Italy) in the central Mediterranean Sea~~, generates volcanic ash plumes that are transported by the wind ~~hundreds of kilometers over the Mediterranean Sea~~ reaching as far as Greece and Libya (Olgun et al., 2013 and references therein).

~~In contrast to the atmospheric deposition, the influence of terrigenous riverine/estuarine inputs in deep-sea surface sediments of the EMS is limited and localized (Statham and Hart, 2005; Garcia-Orellana et al., 2009). The high lithogenic contents found in most~~Riverine inputs have a rather minor influence onto the open EMS sedimentation as they are small and localized (Weldeab et al., 2002; Statham and Hart, 2005). The relatively higher lithogenic contents found in most of the Ionian Sea stations (Fig. 3a and Table 2) points to fluvial inputs reaching the area from the

Adriatic Sea~~ and local rivers.~~. The main source of riverine inputs is the Po River, opening into the northernmost end of the Adriatic Sea, ~~but~~although inputs from ~~some~~ smaller rivers draining the Apennines ~~can~~could be also relevant (Weldeab et al., 2002). In the Ionian Sea, river-sourced particles are carried by both surface and deep currents flowing southwards along the Italian Peninsula as part of the overall anticlockwise circulation in the Adriatic Sea (Orlic et al., 1992). It should be noted that dense water formation takes place seasonally in the ~~northern~~ Adriatic Sea ~~(and also in the southern),~~, which triggers episodes of fast~~-~~-flowing, sediment-loaded dense ~~water~~ near-bottom currents that cascade into the deeper Meso Adriatic depression before passing through the Otranto Strait, subsequently spreading into the Ionian Sea where their particle load settles to the bottom ~~(Zocolotti and Salusti, 1987; Manca et al., 2002; Vilibic, 2003; Trincardi et al., 2007a, b; Canals et al., 2009).~~(e.g., Zoccolotti and Salusti, 1987; Manca et al., 2002; Canals et al., 2009).

The grain-size variability of the carbonate particles recorded in the studied sediment samples is indicative of calcareous skeletons of primary producers. While the abundance of particles <8 μm is attributable to coccoliths, which is the most abundant primary producer in the EMS (Emelyanov and Shimkus, 1986), coarser carbonate particles mostly correspond to shells and fragments of calcareous dinoflagellates and planktonic foraminifers, in agreement with Ziveri et al. (2000) and Frenz et al. (2005). ~~Despite~~Although part of the carbonate fraction might also have a terrestrial provenance as transported, for instance, with Saharan dust (Chester et al., 1977; Correggiari et al., 1989; Rutten et al., 2000), this does not seem to be the case with ~~our~~the investigated samples. Like other aeolian particles, aeolian carbonates are typically ~~are~~ better sorted than those formed *in situ*, as ~~usually~~ shown by a well-sorted unimodal distribution due to gravitational settling during atmospheric transport (Skonieczny et al., 2013). The predominance of very poorly sorted grain-size distributions within the bulk sediment samples (Fig. 2a) and the highly variable $CaCO_3$ contents (Fig. 3b) in ~~our~~the investigated samples, suggests that even within such a highly oligotrophic environment biogenic carbonates are the main source of $CaCO_3$ in the deep EMS.

5.1.2 Sources of sedimentary organic matter

Bulk geochemical proxies such as elemental (TN/OC) and stable isotopic ratios of OC ($\delta^{13}C$) have been widely used to assess the sources of OM in marine sediments~~,~~ ~~by taking advantage of the distinct signatures of marine and terrestrially sourced OM~~ (Meyers, 1994; Goñi et al., 2003; Hu et al., 2006). Sedimentary molar TN/OC ratios and $\delta^{13}C$ values determined in this study are consistent with values previously reported for surface sediments of the deep EMS (Tesi et al., 2007b; Meyers and Arnaboldi, 2008; Carlier et al., 2010; Goudeau et al., 2013).

Marine-derived OM is characterized by high TN contents yielding TN/OC ratio values >0.12, while vascular plants are N-depleted ~~due to the predominance of nitrogen-free biomolecules, thus~~ yielding TN/OC ratio values <0.08 ~~(Redfield et al., 1963; Hedges and Oades, 1997)~~(Redfield et al., 1963; Hedges and Oades, 1997). $\delta^{13}C$ values in marine algae from low- to mid- latitude temperate seas vary from -18‰ to -22‰ (Goericke and Fry, 1994; Meyers, 1994; Harmelin-Vivien et al., 2008), whereas most terrestrial OM inputs from C3 plants show depleted $\delta^{13}C$ values ranging from -25‰ to -28‰ (Hedges et al., 1997).

~~δ^{13}C~~In order to constrain the origin of sedimentary OM and assess the spatial variability in its marine-to-terrestrial blend molar TN/OC ratios were plotted against $\delta^{13}C$ values. Plots show that the elemental and isotopic composition of sedimentary OM fall out of the typical compositional ranges of the potential sources (Fig. 6b). Excluding station Red3, located in the upper slope of western Cretan Straits, an overall positive relationship for molar TN/OC ratios and $\delta^{13}C$ values ($r=0.53$, $p<0.05$) becomes apparent (Fig. 6b), thus indicating that the composition of the OM in the studied sediment samples could be explained as a mixture of terrigenous (low TN/OC and $\delta^{13}C$) and marine (high TN/OC and $\delta^{13}C$) derived materials.

Additionally, the relative contribution of the marine vs. terrestrial sources of OC over the study area has been evaluated by means of a simple $\delta^{13}C$-based binary mixing model (Table 2), where a marine $\delta^{13}C$ value of -20.4‰ and a terrestrial $\delta^{13}C$ value of -27.0‰ (Tesi et al., 2007a) are assumed, considering that the contribution of C4 vascular plants ($\delta^{13}C$ from -12 to -15‰) can be considered negligible throughout the study area (e.g., Collatz et al., 1998).

As evident in Table 2, sediments from the Ionian Sea are characterized by elevated contributions of terrestrial OC (OC_{terr}), reaching up to 64.2%. In contrast, W Cretan Straits, Cretan Sea and NW Levantine Sea stations show low OC_{terr} contributions and marine OC (OC_{mar}) peaks of 87.7% (see also section 5.2). The elevated OC_{terr} values recorded in the Ionian Sea suggest that terrigenous OM entering the Adriatic Sea escapes towards the deep Ionian basins. Indeed, during energetic dense shelf water cascading events, lateral flux prevails over the vertical flux in the southern Adriatic Sea and the contribution of soil-derived OC increases up to ~60% (Turchetto et al., 2007; Tesi et al., 2008). Despite the relatively high OC_{terr} found preserved in the deep Ionian Sea, values are lower than those recorded in areas impacted by extreme events such as storms that enhance the export of organic matter from the shelf to the deep environment, for example in the western Mediterranean (up to 78% of OC_{terr}) (Pedrosa-Pàmies et al., 2013) and the East China Sea (up to 90%) (Selvaraj et al., 2015).

~~values in marine algae from low- to mid- latitude temperate seas vary from -18‰ to -22‰ (Goericke and Fry, 1994; Meyers, 1994; Harmelin-Vivien et al., 2008), whereas most terrestrial OM inputs from C3 plants show depleted $\delta^{13}C$ values ranging from -25‰ to -28‰ (Hedges et al., 1997). The contribution of C4 vascular plants can be considered negligible throughout the study area because C4 plants are generally absent in the Mediterranean climate (e.g., Teeri and Stowe, 1976; Collatz et al., 1998). The $\delta^{13}C$ range obtained in this study also provides evidence of absence of C4 plants in the EMS.~~

~~Sedimentary TN/OC ratios and $\delta^{13}C$ values determined in this study are consistent with previously reported values for surface sediments of the deep EMS (Tesi et al., 2007; Meyers and Arnaboldi, 2008; Carlier et al., 2010; Goudeau et al., 2013). In order to constrain the origin of sedimentary OM and assess the spatial variability in its marine-to-terrestrial blend we plotted TN/OC ratios against stable isotope signatures ($\delta^{13}C$) (Fig. 6). Plots show that elemental and isotopic composition of sedimentary OM fall out of the typical compositional ranges of the potential sources. Excluding station Red3 from the upper slope of western Cretan Straits, an overall positive relationship for TN/OC ratios and $\delta^{13}C$ values ($r=0.53$, $p<0.05$) becomes apparent (Fig. 6), thus indicating that the composition of the OM in the studied~~

~~sediment samples can be explained as a mixture of terrigenous (low TN/OC and $\delta^{13}C$) and marine (high TN/OC and $\delta^{13}C$) derived materials.~~

Lipid biomarkers have often been used as molecular proxies to identify specific biological precursors of sedimentary OM (Meyers, 1997; Volkman, 2006). The concentrations of the sedimentary lipid biomarkers ~~reported~~determined in this study are fairly comparable to those previously reported in areas devoid of significant fluvial influence both in the Eastern and Western Mediterranean basins (Grimalt and Albaigés, 1990; Gogou et al., 2000; Gogou and Stephanou, 2004; Kaiser et al., 2014).

The patterns of long-chain *n*-alkanes and *n*-alkanols with elevated CPI_{NA} and $CPI_{N\text{-}OH}$ values (Sect. 4.4; Table 3), respectively, indicate the presence of allochthonous natural (terrigenous) inputs from epicuticular higher plant waxes (Eglinton and Hamilton, 1967). ~~Terrestrial plant waxes are major components of EMS aerosols (Gogou et al., 1996), which are highly relevant vectors for the transport of terrestrial OM into the open EMS~~Saharan dust is probably the main vector for the transport of small charcoal-like fragments of burnt vegetation, leaf wax-derived lipids absorbed on clays, and cuticular fragments into the open EMS, given the relatively minor direct influence of riverine inputs ~~(Gogou et al., 2000).~~ (Gogou et al., 1996; Eglinton et al., 2002).

Lipid biomarkers preserved in the surface sediments of the study area also highlight the contribution from autochthonous marine OM derived from *in situ* phytoplankton production. ~~Brassicasterol~~More specifically, the abundance of brassicasterol ($_{28}\Delta^{5,22E}$) ~~is~~reveals the ~~major sterol in many~~presence of diatoms and prymnesiophytes, while dinosterol ($_{30}\Delta^{22E}$) is a major compound in dinoflagellates ~~and is commonly used as source-specific biomarker for these algae~~ (Volkman, 1986). The presence of long-chain alkenones reflects the productivity from algal species of the *Prymnesiophyte* class, e.g.~~.~~, *Emiliania huxleyii* (Marlowe et al., 1984), which constitute the dominant primary producers across the Mediterranean Sea (Ziveri et al., 2000; Triantaphyllou, 2004). ~~Regarding the long-chain C_{30} *n*-alkan-1,15-diols and the corresponding C_{30} keto-ols, although their major sources remain unknown, microalgae of the genus Nannochloropsis (class *Eustigmatophyceae*) are potential sources, while C_{30} keto-ols might result from oxidation of the corresponding C_{30} diols (Volkman, 1986; Volkman~~

~~et al., 1999; Rampen et al., 2007). Cholesterol ($_{27}\Delta^5$) is mainly considered as a biomarker for consumer organisms and a proxy for~~Regarding the long-chain C_{30} *n*-alkan-1,15-diols and the corresponding C_{30} keto-ols, although their major sources remain unknown, microalgae of the genus Nannochloropsis (class *Eustigmatophyceae*) are potential sources, while C_{30} keto-ols might result from oxidation of the corresponding C_{30} diols (Volkman, 1986; Volkman et al., 1999; Rampen et al., 2012).

In addition, while the abundance of cholesterol ($_{27}\Delta^5$) highlights the existence of marine consumer organisms such as zooplankton and benthic animals (Grice et al., 1998), ~~while~~ β-~~Sitosterol~~sitosterol ($_{29}\Delta^5$) may derive from both terrigenous and marine sources (Volkman, 1986). In the study area however, the positive correlation between ∑TerNA (and ∑TerN-OH) and β-~~Sitosterol~~sitosterol argues for a dominant terrestrial origin for this compound.

~~Aside from natural sources, the abundance of UCM in the investigated sediments indicates a contribution of anthropogenic OM resulting from degraded petroleum hydrocarbons. Two main pathways have been identified for the introduction of petroleum hydrocarbons in the deep EMS, which are direct discharges from merchant shipping and oil transportation (UNEP, 2010) and atmospheric transport and deposition (Gogou et al., 1996; Castro-Jiménez et al., 2012; Parinos et al., 2013).~~

Aside from natural sources, the abundance of UCM indicates a contribution of anthropogenic OM resulting in chronic oil pollution of the investigated sediments (Parinos et al., 2013). UCM levels recorded in the deep EMS are comparable to those reported for surface sediments in unpolluted coastal and/or open-sea areas and are at least one order of magnitude lower than those reported for coastal areas subjected to enhanced anthropogenic inputs (Gogou et al., 2000; Parinos et al., 2013; Kaiser et al., 2014; Romero et al., 2015; and references therein). Two main pathways have been identified for the introduction of petroleum hydrocarbons into the deep EMS, which are direct discharges from merchant shipping and oil transportation

(UNEP, 2010) and atmospheric transport and deposition(Gogou et al., 1996; Castro-Jiménez et al., 2012; Parinos et al., 2013).

5.2 Regional variability and oceanographic control on the geochemical composition of deep Eastern Mediterranean Sea surface sediments

The PCA ~~provide~~provides a robust overview of the variables and processes controlling the geochemical composition of the investigated deep-sea surface sediments (Fig. 5).

The significant positive loadings of ∑TerNA, ∑TerN-OH, ∑Mar, UCM and depth on PC1 are indicative of a considerable contribution from both natural (marine and terrestrial) and anthropogenic (degraded petroleum products) OM preserved in deep-sea surface sediments of the EMS. ~~The negative PC1 loading of CPI_{N-OH} ratios on PC1 indicates that the terrestrial OM is relatively altered, while the negative PC1 loading of CPI_{NA} ratios is indicative of an enhanced contribution of petroleum products. Furthermore, the non-zero intercept of the TN to OC ratio values suggests that inorganic IN is present (see section 5.2.1).~~Moreover, the negative PC1 loadings of CPI_{NA} and CPI_{N-OH} ratios vs. depth indicate that the terrestrial OM is relatively altered with increasing water column depth. Although the negative PC1 loading of CPI_{NA} ratio could be also indicative of an enhanced contribution from non degraded petroleum inputs, the patterns of aliphatic hydrocarbons for the investigated sediment samples indicate no important bias associated to non degraded petroleum products on CPI_{NA} ratio values (Parinos et al., 2013). Overall, PC1 represents the degradation processes and fate of the sedimentary OM in the study area.

The second PC separates samples with high carbonate contents, molar TN/OC ratios and enhanced contribution of clay-sized particles from those with high lithogenic contents. Therefore, samples with positive loadings ~~of~~on PC2 are enriched in fine marine carbonate particles, while those with negative loadings are enriched in lithogenic particles (see section 5.2.2).

Finally, PC3 separates samples with high contents of OC, TN and clays from those with high values of $\delta^{13}C$. Consequently, positive loadings on PC3 are associated to sediments with an enhanced contribution of OC-rich fine particles, thus pointing to

hydrodynamic processes that control grain size sorting and remobilization/deposition of sedimentary material with different OC contents (see section 5.2.2).

5.2.1 Processes modulating the biogeochemical signal of the sedimentary organic matter

~~The quantity of OC and TN buried in marine sediments depends on the rate of OM supply, the degree to which this fraction is diluted by other sediment components and the degree of preservation of the deposited material (Calvert and Pedersen, 1992). The low OC and TN contents in the surface sediments of the study area reflects~~The low OC and TN contents in the surface sediments of the study area reflect the oligotrophic character of the EMS (e.g., Krom et al., 2003). ~~However, it should be taken also into account that~~In the studied sediments some processes may have further pushed TN to OC ratios towards low values (Fig. ~~8a~~6a). These include the preferential degradation of N-rich proteinaceous components of algal OM during early diagenesis (Meyers et al., 1996; Meyers, 1997; Hopmans et al., 2004) and the enrichment of OC relative to TN due to the input of petroleum residues (Friligos et al., 1998). Furthermore, a significant contribution of inorganic N, presumably as $NH4^+$ adsorbed on clays (Müller, 1977; Meyers, 1997), is inferred from the positive intercept on the N axis at around ~~19~~0.02% (Fig. ~~8a~~6a).

~~We assume that the diagenetic~~Although isotopic fractionation ~~during sinking and burial of OM in the study area~~specifically associated with early diagenesis is ~~minor since previous studies Mediterranean sea have shown that~~negligible and the isotopic composition of sedimentary OM is fairly conservative~~, reflecting the isotopic signatures of the sources.~~ ~~(e.g., Di Leonardo et al., 2009). However, isotopic signatures can be potentially shifted by inputs of anthropogenic OM. δ^{13}C values for crude oil and petroleum products are around~~(e.g., Di Leonardo et al., 2009 and references therein), δ^{13}C values can be potentially shifted by microbial rearrangements (Lehmann et al., 2002) and inputs of anthropogenic OM. δ^{13}C values for crude oil and petroleum products are in the order of -28.5‰ and -28.9‰, respectively (Rumolo et al., 2011 and references therein). In the study area, the ~~negative PC1 loadings of the CPI_{NA} ratio values together with the~~ positive PC1

loadings of depth and UCM indicate an enhanced contribution of degraded petroleum products with increasing water depth. This points to an enrichment of the sediments in degraded petroleum hydrocarbons in the deep Ionian Sea and western Cretan ~~Straits~~Straits' stations H03 and Red3.1 where such an isotopic shift is observed (Figs. 3e and 7), in addition to maximum concentrations of UCM along with relatively low molar TN/OC ratios (<0.11) (Table 2, Figs. 3d and 4a).

Lipid biomarkers provide further information on the natural sources of sedimentary OM. The significant positive correlation of ∑TerNA and ∑TerN-OH concentrations (not normalized to OC) to OC contents suggests a close association of terrestrial OM to OC, while the significant positive correlation of ∑TerNA and ∑TerN-OH to %clay suggests that the transport and accumulation of terrestrial OM is associated to fine particles (see section 5.2.2). ~~Furthermore, the~~The relatively uniform spatial distribution of ~~[NA]/[N-OH]~~CPI_{NA} and $CPI_{N\text{-}OH}$ ~~ratios~~ratio values (Fig. 8~~),~~) together with the negative PC1 loadings of CPI_{NA} and $CPI_{N\text{-}OH}$ ratios *vs.* depth (Fig. 5), are overall indicative of ~~an existent but non intensive~~ the reworking of the terrestrial OM accumulated in ~~the~~ deep EMS~~, which is~~ basins. Moreover, the elevated values of the [NA]/[N-OH] ratio in the study area (Fig.8; Table 3) are indicative of the enhanced degradation of ∑TerN-OH relatively to ∑TerNA. The above are rather consistent with ~~its~~the long-range atmospheric transport, and long residence time in the water column and into the sediments of the terrestrial OM, and the fact that ∑TerNA are more resistant to degradation than their alcohol counterparts (Gogou and Stephanou, 2004). Moreover, the relatively elevated retention time of terrestrial OC in the inner shelf of the Adriatic Sea before being conveyed to the Ionian Sea by dense shelf water cascading events, allows for its significant microbial degradation or marine dilution (Tesi et al., 2008).

~~On the contrary, while~~While a significant positive correlation is observed for ∑Mar concentrations (not normalized to OC contents) and OC, indicating that the latter exerts an important control on the distribution of algal markers' concentrations in the study area, no significant correlation is observed between ∑Mar and grain size. These correlations together with the deviation trend observed for molar TN/OC ratios from the classical Redfield ratio (16/106) with increasing water depth, which is more evident for the deep Ionian Sea stations (Fig. ~~8a~~6a), probably reflect the preferential

degradation processes during the transport and deposition of marine labile sedimentary OM, that probably also masks the association of marine OM to fine particles. The observations above, jointly with the presence of cholesterol ($_{27}\Delta^5$) and its significant positive correlation with the concentrations of marine algal markers, are altogether indicative of the re-working of algal OM by zooplankton ~~that produces faecal pellets rapidly sinking in the water column and by~~and benthic invertebrates (Volkman et al., 1990; Gogou and Stephanou, 2004).

5.2.2 Sediment transport and deposition ~~and~~ processes

The second and third PCs of the PCA ~~allowed us to determine~~highlight the main processes that affect sediment dispersal and deposition~~.~~ in the study area. These relate to pelagic settling of marine skeletons from surface waters (corresponding to PC2~~) from surface waters~~), and ~~to the~~ hydrodynamic sorting of organic-rich fine sediment by bottom currents (corresponding to PC3).

Particulate matter exported from the upper layers of the water column in the EMS is primarily composed of biogenic particles and atmospheric dust, which while settling to the seabed are able to transfer OC, other nutrient elements, and OC-associated organic pollutants (e.g., Stavrakakis et al., 2000, 2013; Theodosi et al., 2013). In the deep EMS, the distribution of pelagic carbonates (second PC) seems to be mainly influenced by planktonic contributions. In the study area, the phytoplankton biomass and primary production are relatively higher in ~~the cyclonic~~ regions ~~where the nutricline ascends to the base~~ of ~~the euphotic zone~~cyclonic water mass circulation. The Rhodes cold-core gyre, situated in the southeast of the Rhodes Island (NW Levantine Sea), is the most prominent dynamic feature in the EMS and is the main source area of the LIW. In this cyclonic gyre, which is enhanced during winter period, dense water masses from deeper layers tend to upwell at its centre, feeding the upper layers with nutrient-rich ~~masses~~waters (Salihoğlu et al., 1990). Therefore, this gyre plays an important role in the productivity of the Levantine Sea.

The third PC separated samples with high OC, TN and clay contents, which is indicative of a close OM-mineral association. This is in agreement with the high OC contents found in the fine-grained sediment samples from the deeper stations

representing an essentially quiet environment (Figs. 2, 3 and 7). This is in contrast ~~with~~to the lower OC contents observed in coarser samples (D_{50} >14 μm) from shallower depths where currents up to 20 cm s^{-1} occur commonly (Kontoyiannis et al., 2005; Ursella et al., 2014). Fine-grained particles have high capacity for OM adsorption due to their large specific surface area, and thus enhanced OM contents relatively to coarse-grained particles (Mayer, 1994; Hedges and Keil, 1995). Physical processes such as hydrodynamic sorting remobilize and transport sedimentary material with different OC contents, with the OC-rich finest ones easily reaching the deep EMS. A similar situation has been reported in ~~other land-locked seas or marginal settings~~active sedimentary environments such as the submarine canyons in the Western Mediterranean Sea (Pedrosa-Pàmies et al., 2013), the northwestern Gulf of Mexico (Goñi et al., 1998)~~, or the Eel River margin (Wakeham et al., 2009). In short, the deep EMS behaves as a sink~~ and the Peru Margin (Bergamaschi et al., 1997). However, none of these studies reported such OM-mineral associations at depths beyond 4000m. This indicates that this organic-mineral interaction is maintained from the shallow to high depths, which constitute the final sedimentary sink. In short, the deep EMS behaves as a depocenter for OM-rich fine particles.

~~Grain-size provides additional information on sediment sources, transport mechanisms and depositional processes that affect sedimentary particles including their OM load (Folk and Ward, 1957; Hedges and Keil, 1995; Sun et al., 2002; Wakeham et al., 2009). What we found, as a general pattern, in the EMS is that bulk sediments show a poorer sorting than the lithogenic fraction (Fig. 2), which is caused by~~Moreover, in the EMS these bulk sediments show a poorer sorting than the lithogenic fraction (Fig. 2). This could be related to the presence of coarse biogenic carbonate particles in bulk samples or the effective hydrodynamic sorting linked to the prevailing depositional conditions in such deep low-energy environments (Friedman, 1969).

The poor sorting and positive skewness found in grain-size types I, II, IV and V of the bulk sediment samples (Fig. 2a) in the southern Aegean Sea and the northwestern Levantine Sea, is explained by the prevalence of pelagic biogenic sedimentation, as shown by the high positive score values observed on PC2 (Fig. 5b). Accordingly, high percentages of $CaCO_3$ have been measured in stations of the southern Aegean

Sea, the northwestern Levantine Sea and western Cretan ~~Straits'~~Straits, which correlate ~~with~~to %clay fraction of the bulk sediment samples and the concentrations of alkenones (Table 3). This links to the formation of clay-carbonate concretions that have been reported in particularly large amounts in the southern Aegean Sea (Emelyanov and Shimkus, 1986). Vertical mixing and upward transport of nutrients in the eddies and gyres, such as the Rhodes gyre, may trigger ~~first~~ primary production and ~~then~~subsequently the sinking and dominance of pelagic biogenic particles over particles from other sources in the northwestern Levantine Sea (Siokou-Frangou et al., 1999). The $\%OC_{mar}$ and the ∑Mar distribution ~~is~~are indicative in that respect as ~~it shows~~they show a general eastward increasing trend with peak concentrations in deep basins of the northwestern Levantine Sea.

Surface sediments in the Ierapetra Basin (stations Red15, Red1.1 and Ier01) also show positive scores ~~in~~on PC3 (Fig. 5b), which point to an influence of hydrodynamic sorting processes. The relatively high OC content in these stations (Fig. 7), along with the elevated values of the associated natural and anthropogenic lipid concentrations (Table 3), suggests that the Hellenic Trench is a sink of OC associated to fine particles transferred by the active outflows of the Cretan Straits, besides the pelagic sedimentation related to the well-known semi-permanent Ierapetra anticyclone (Larnicol et al., 2002; Taupier-Letage, 2008).

Sediments with grain size types I-III of the bulk sediment samples (Fig. 2a) in the Ionian Sea show lower $CaCO_3$ contents due to the dilution by lithogenic components, with station H02 being the only exception ~~of station H02~~. High positive score values on PC3 (Fig. 5b), and the significant positive correlation for OC and TN contents ~~with~~to %clay of the lithogenic fraction, further suggest ~~again~~ a significant influence of hydrodynamic sorting processes, which largely determine a differential distribution of OM in surface sediments according to grain size. In this area, the Otranto Strait may act as a preferential conduit by funnelling ~~sedimentary material and associated OM~~fine OC-rich particles from the Adriatic Sea towards the deep basins of the adjacent Ionian Sea, which may eventually reach the Levantine Sea~~. Cascading of North Adriatic dense water and subsequent propagation and outflow through the Otranto Strait~~ (Bensi et al., 2013)~~ may feed the deep Ionian Sea with fine OC-rich particles. Our Ionian samples off the southern mouth of the Adriatic Sea present~~

~~relatively~~. The enhanced contributions of ~~terrestrial OM as indicated by low $\delta^{13}C$ values (Fig. 3e~~OC_{terr} (Table 2) and terrestrial biomarkers concentrations (Figs. 4b-c and Table 3~~). This~~) of the Ionian samples off the southern mouth of the Adriatic Sea, probably also reflect the preferential degradation of labile marine OM in deep Ionian Sea basins due to slower sedimentation rates and longer residence time of ~~organic matter occurring in these sites.~~OM. Low OC content (Fig. 3c), poor sorting, very negatively skewed, high %sand of grain size type VI (Fig. 2a) at the shallower station H12 just south of Otranto Strait supports winnowing of fine OC-rich particles due to episodic events of high current speed exiting the Adriatic Sea (Bignami et al., 1991; Gacic et al., 1996; Poulos et al., 1999).

Finally, station Red3 from the upper slope of western Cretan Straits representing grain size type VII of the bulk sediment samples (Fig. 2a) shows the highest contents of sand (47.7%), which is poorly sorted. This is in agreement with the occurrence of the topographically restricted deep outflow of the western Cretan Straits. ~~In these~~These straits~~, a seasonal signal is~~ are characterized by ~~intensification in the~~maximum outflow speeds during winter and minimum speeds during fall (Kontoyiannis et al., 2005). The turbulent, fluctuating outflow current should normally trigger sediment resuspension and induce selective transport, thus leaving coarse OC-poor particles in the upper slope of the western Cretan Straits (negative factor scores of PC2 and PC3) and carrying fine OC-rich particles to the lower slope. A similar pattern has been also observed in ~~some~~other submarine canyon settings of the Mediterranean Sea, such as the Cap de Creus Canyon (Sanchez-Vidal et al., 2008) and the Blanes Canyon (Pedrosa-Pàmies et al., 2013). The top $\delta^{13}C$ values found in the upper slope (Fig. 7 and Tables 2-3) indicates high contribution of marine OC, which however is not supported by the lipid biomarkers results. Winnowing of fine particles loaded with terrestrial OC, thus shifting the isotopic signal of the remaining coarse particles towards high and more marine values seems to be the most plausible explanation.

6 Conclusions

Surface sediments collected from deep basins of the oligotrophic EMS were investigated using a multi-proxy approach that involved elemental composition, grain

size, stable isotopes and selected lipid biomarkers' analyses resulting in a robust database to determine sediment sources, the degradation and preservation state of OM, and ~~transport and depositional~~ processes that affect sediment dispersal and deposition. The PCA analysis helped to identify the main controlling factors of the observed geochemical variability in the investigated sediments. Such factors are sediment sources in terms of allochthonous *vs.* autochthonous, a highly variable physiography, the thermohaline structure, and the regional and local circulation, leading to hydrodynamic sorting and regulating particle settling ~~and~~ /deposition~~,~~ and OM preservation state.

Surface sediments of the investigated part of the EMS mostly consist of airborne lithogenic particles and biogenic carbonate particles ~~derived~~, the latter deriving from primary production ~~in~~into surface waters. Sedimentary OM appears in rather low contents (0.15 – 1.15% OC), ~~as derived~~with bulk and molecular organic tracers reflecting a mixed contribution from both natural (autochthonous and allochthonous) and anthropogenic sources~~, namely marine algae, terrestrial plants and degraded petroleum products~~. Samples from locations in the Ionian Sea and the western Cretan Straits that are under the direct influence of the Adriatic ~~Sea outflow of~~ dense waters outflow through the Otranto Strait and of currents exiting the southern Aegean Sea, respectively, are appreciably sorted. Current regime impacted not only grain size but also OC loadings ~~in~~within each ~~region within~~subregion of the study area, with winnowing of fine OC-rich particles to the deepest EMS. In contrast, coarse OC-poor particles tend to occur in upper slope settings. While OC associated to fine particles was relatively non-degraded terrestrial OM, marine OM was found to be mostly degraded and reworked during transport processes and before reaching the deep seafloor.

The spatial variability in the yields of sedimentary OC and lipid biomarkers presented in this study highlights the heterogeneous nature of the particle load exported to the deep basins of the Eastern Mediterranean Sea. Such variability must be taken into account during the development of quantitative carbon budgets for this area.

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Tables

Table 1. Location, depth and collection date of ~~surface sediments~~sediment samples.

Sample Code	Latitude (N)	Longitude (E)	Water depth (m)	Date of collection	Physiographic regions
Ionian Sea					
North					
H12	39.30	19.30	1450	Jan-07	Otranto Valley
H07	39.~~107~~11	17.75	1866	Jan-07	Taranto Valley
Central					
BF27	38.22	16.63	1264	juny-09	Calabrian Slope
BF13	37.66	16.56	2012	juny-09	Calabrian Arc
BF15	36.20	16.35	3335	juny-09	Ionian Basin
H04	35.92	16.00	3750	Jan-07	Ionian Basin
West					
H02	35.75	21.00	3008	Jan-07	Ionian Basin
H05	37.50	18.50	3154	Jan-07	Ionian Basin
H03	35.70	18.50	4087	Jan-07	Ionian Basin
S. Aegean Sea (Cretan Sea)					
Red5	35.68	25.10	1018	May-10	Cretan Trough
Red9	36.00	23.89	1200	May-11	Cretan Trough
Red4	35.76	25.10	1615	May-10	Cretan Trough
Red8	36.07	25.28	1715	May-11	Cretan Trough
W Cretan Straits					
H01	35.70	23.00	2117	Jan-07	Kithira Strait
Red3	35.40	23.40	2976	May-10	Antikithira Strait
Red3.1	35.30	23.32	3317	May-10	Antikithira Strait
Red7	34.60	24.15	3589	May-11	Ptolemy Strait
NW Levantine Sea					
Ierapetra Basin					
Red13	34.95	25.93	1101	juny-12	Cretan-Rhodes Ridge
BF19	34.51	25.76	1200	juny-09	Hellenic Trench
BF22	34.48	25.87	2015	juny-09	Hellenic Trench
Red15.1	34.61	25.92	2428	juny-12	Hellenic Trench
Red1.1	34.40	26.25	3568	juny-12	Hellenic Trench
Ier01	34.44	26.19	3626	Jan-07	Hellenic Trench
Open Sea					
Rho02	35.62	27.~~7~~70	1305	Jan-07	Rhodes Strait
Her01	33.92	27.74	2680	Jan-07	EM Ridge
Red2	33.74	26.15	2717	May-10	EM Ridge
Red2.1	33.71	26.34	2720	May-10	EM Ridge
BF24	34.15	25.57	2902	juny-09	Pliny Trench
Her03	33.67	29.00	3090	Jan-07	Herodotus Basin

January 2007 samples were collected during the M71 (Leg 3) cruise onboard the *R/V* Meteor (University of Hamburg, Germany), June 2009 samples during the Biofun1 cruise onboard the *R/V* Sarmiento de Gamboa (CSIC-UB, Spain), and May 2010, 2011 and June 2012 samples during the ReDEco cruises onboard the *R/V* Aegaeo (HCMR, Greece).

Table 2. Bulk composition and sedimentological parameters of the investigated surface sediments.

Sample Code	$Clay_{bulk}$ (% ,<4 µm)	$Silt_{bulk}$ (%, 4-63 µm)	$Sand_{bulk}$ (%, 63 µm-2 mm)	$Sorting_{bulk}$	$Sorting_{litho}$	$Skewnes_{bulk}$	$D_{50\ bulk}$ (µm)	Lithogenic (%)	$CaCO_3$ (%)	Opal (%)	OC (%)	TN/OC	$\delta^{13}C$ (‰)	OC_{mar} (%)	OC_{terr} (%)
Ionian Sea															
North															
H12	18.1	76.7	5.24	3.47	3.31	-0.13	14.6	71.2	28.5	0.03	0.15	0.08	-24.2	42.3	57.7
H07	41.2	58.8	0.00	3.01	4.12	-0.07	5.34	75.7	22.0		1.15	0.08	-24.4	40.2	59.8
Central															
BF27	52.8	46.1	1.04	3.38	2.83	-0.04	3.97	80.8	17.8	0.16	0.64	0.12	-23.0	60.0	40.0
BF13	50.8	48.1	1.08	3.41	2.92	-0.05	4.17	76.7	22.0	0.21	0.58	0.12	-22.9	62.7	37.3
BF15	39.1	57.0	3.98	4.01	2.91	0.03	5.88	77.9	21.6		0.28	0.14	-22.5	68.8	31.2
H04	41.6	58.4	0.04	4.69	3.53	-0.23	5.52	85.4	13.2	0.04	0.65	0.13	-23.6	50.9	49.1
West															
H02	53.3	46.7	0.00	2.99	6.16	-0.07	3.92	47.7	51.3	0.04	0.45	0.110	-22.5	68.6	31.4
H05	41.6	58.4	0.00	2.98	3.48	-0.01	5.34	60.7	38.2		0.57	0.11	-23.7	50.2	49.8
H03	34.5	65.5	0.08	3.11	3.49	-0.04	7.03	77.6	21.0	0.11	0.63	0.110	-24.6	35.8	64.2
S. Aegean Sea (Cretan Sea)															
Red5	54.0	46.0	0.00	3.32	3.61	-0.01	3.88	32.5	66.5	0.24	0.39	0.110	-22.4	69.2	30.8
Red9	50.1	49.9	0.00	3.24	3.28	-0.01	4.23	46.6	52.2	0.15	0.55	0.12	-22.6	67.4	32.6
Red4	52.6	47.4	0.00	3.26	3.58	-0.06	4.00	39.3	59.8	0.09	0.42	0.12	-22.2	73.0	27.0
Red8	53.1	46.9	0.00	3.12	3.36	-0.03	3.97	44.0	55.3	0.08	0.33	0.15	-22.0	75.5	24.5
W Cretan Straits															
H01	55.1	44.9	0.00	4.74	4.77	-0.11	3.65	42.8	56.6		0.29	0.12	-22.6	66.5	33.5
Red3	14.5	37.9	47.7	5.23	4.54	-0.45	56.6	59.2	39.9	0.15	0.37	0.08	-18.3		
Red3.1	37.7	61.5	0.88	4.32	3.82	-0.07	6.74	55.7	43.0	0.12	0.58	0.09	-22.9	62.4	37.6
Red7	36.0	63.5	0.59	3.55	3.57	-0.01	6.37	61.4	37.5	0.07	0.51	0.12	-22.7	64.7	35.3
NW Levantine Sea															
Ierapetra Basin															
Red13	50.1	49.3	0.66	4.84	3.07	-0.15	4.23	59.1	39.8	0.22	0.46	0.11	-22.3	71.1	28.9
BF19	51.1	38.5	10.4	4.98	3.43	0.27	4.12	39.4	59.9		0.34	0.14	-22.6	67.3	32.7
BF22	47.5	44.0	8.53	4.71	3.34	0.20	4.56	57.7	41.7		0.26	0.15	-21.2	87.7	12.3
Red15.1	47.5	51.8	0.73	4.60	2.77	-0.03	4.59	51.8	46.9	0.880	0.61	0.08	-23.3	56.1	43.9
Red1.1	57.1	42.8	0.15	3.73	2.61	-0.13	3.53	51.8	47.1	0.05	0.54	0.110	-21.5	83.8	16.2
Ier01	49.1	50.4	0.00	3.84	2.67	0.03	4.35	55.6	43.3	0.06	0.52	0.12	-21.7	80.2	19.8
Open Sea															
Rho02	43.0	55.9	1.11	4.43	3.25	-0.14	5.24	58.4	40.6	0.16	0.47	0.12	-22.7	65.2	34.8
Her01	48.2	51.8	0.00	3.88	4.89	0.04	4.44	35.8	63.4	0.13	0.31	0.15	-22.7	65.5	34.5
Red2	32.4	53.2	14.4	4.95	3.85	-0.01	11.1	45.0	53.9	0.07	0.5	0.09	-24.0	46.2	53.8
Red2.1	48.7	51.1	0.21	4.30	3.92	0.11	4.42	44.2	55.0	0.10	0.37	0.11	-22.4	70.5	29.5
BF24	43.1	45.0	11.9	5.25	3.51	0.20	5.34	55.0	44.3	0.11	0.29	0.16	-22.3	70.6	29.4
Her03	39.8	60.2	0.00	4.05	3.20	-0.19	5.81	48.2	50.7	0.11	0.49	0.11	-22.4	70.2	29.8

*empty cell = not determined

1535 **Table 3.** Concentrations (OC-normalized) and indices of the considered lipid biomarkers.

Station	∑TerNA[a] (µg g^{-1} OC)	∑TerN-OH (µg g^{-1} OC)	∑Mar (µg g^{-1} OC)	∑Alkenones[b] (µg g^{-1} OC)	∑C_{30} diols&keto-ols[c] (µg g^{-1} OC)	∑Sterols[d] (µg g^{-1} OC)	$_{27}\Delta^{5}$ (µg g^{-1} OC)	$_{28}\Delta^{5,22}$ (µg g^{-1} OC)	$_{29}\Delta^{5}$ (µg g^{-1} OC)	$_{30}\Delta^{22}$ (µg g^{-1} OC)	CPI_{NA}[a]	$CPI_{N\text{-}OH}$	[NA]/ [N-OH]
Ionian Sea													
North													
H12	54.9	19.0	29.4	6.75	14.7	62.4	29.7	3.22	24.8	4.72	4.14	4.00	2.90
H07	40.8	13.4	34.5	5.97	14.6	35.6	6.77	5.52	14.9	8.37	4.39	4.14	3.03
Central													
BF27													
BF13													
BF15													
H04	169	52.1	54.1	12.3	21.5	59.6	10.6	8.57	28.6	11.7	4.04	5.95	3.24
West													
H02	176	35.2	34.2	8.14	19.7	17.1	3.67	2.36	7.06	3.96	3.57	3.73	5.00
H05	211	42.8	47.2	12.5	25.0	24.2	4.12	3.43	10.4	6.28	4.07	3.63	4.93
H03	214	37.0	35.7	8.77	17.4	25.2	6.04	3.65	9.62	5.92	2.80	4.08	5.78
S. Aegean Sea (Cretan Sea)													
Red5	206	50.7	45.3	20.1	15.9	40.1	10.8	4.74	20.0	4.51	5.07	4.89	4.06
Red9	101	14.7	22.2	9.85	7.30	17.7	3.77	2.66	8.83	2.42	7.25	5.12	6.88
Red4	196	48.4	41.0	17.4	14.8	38.6	11.5	4.63	18.3	4.15	5.36	5.21	4.05
Red8	127	29.4	35.5	16.8	12.3	26.3	5.62	3.23	14.2	3.20	6.40	4.97	4.32
W Cretan Straits													
H01	127	26.2	18.2	3.41	11.3	10.3	2.22	1.35	4.55	2.22	6.64	6.13	4.84
Red3	120	30.4	70.1	21.2	28.1	34.4	7.85	9.33	5.79	11.4	2.90	4.27	3.93
Red3.1	218	50.0	29.0	10.8	11.8	20.7	3.87	3.15	10.4	3.330	3.63	4.02	4.37
Red7	184	43.7	59.2	30.5	19.4	28.6	6.17	3.61	13.1	5.69	3.99	4.63	4.21
NW Levantine Sea													
Ierapetra Basin													
Red13	156	36.8	38.8	14.1	16.1	34.5	10.202	4.97	15.8	3.60	7.95	5.82	4.24
BF19													
BF22													
Red15.1	126	28.3	32.6	11.5	14.1	21.3	4.20	3.21	10.1	3.88	5.26	5.03	4.44
Red1.1	166	38.6	36.9	14.1	14.7	23.9	5.14	3.67	10.7	4.39	6.07	4.79	4.30
Ier01	206	44.4	59.0	11.1	35.0	29.8	4.94	4.69	11.9	8.30	6.37	3.68	4.63
Open Sea													
Rho02	166	49.9	51.2	5.92	33.2	30.2	5.56	4.90	12.6	7.17	6.88	4.68	3.33
Her01	195	52.2	66.3	14.2	35.8	46.5	11.3	7.59	18.9	8.71	4.43	3.70	3.74
Red2													
Red2.1	483	105	72.6	23.6	35.5	47.8	7.86	6.54	26.4	6.97	1.93	4.23	4.59
BF24													
Her03	157	39.7	45.7	7.95	29.5	22.2	4.57	3.05	9.39	5.23	3.69	3.49	3.96

*empty cell = not determined

[a] reported by Parinos et al., 2013

[b] Sum of the concentrations of C37:3M, C37:2M, C36:2FAME, C38:3Et, C38:3M, C38:2Et, C38:2M (the corresponding unsaturated homologues are indicated with the number of their carbon atoms (n) and the number of double bonds (x)-(Cn:x); M: methyl; Et: Ethyl; FAME: Fatty acid methyl ester).

[c] Sum of the concentrations of long-chain C_{30} *n*-alkan-1,15-diols and C_{30} keto-ols

[d] Sum of the major C_{27}-C_{30} sterols considered in this study i.e., cholesterol (cholest-5-en-3β-ol; $_{27}\Delta^{5}$), brassicasterol (24-methylcholesta-5,22-dien-3β-ol; $_{28}\Delta^{5,22}$), β-sitosterol (24-ethylcholesta-5-en-3β-ol; $_{29}\Delta^{5}$) and dinosterol (4α,23,24-trimethyl-5α(H)-cholest-22(E)-en-3β-ol $_{-30}\Delta^{22}$)

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Figure captions

Fig. 1. (a) Location of sampling sites across the open Eastern Mediterranean Sea (see also Table 1). The map was produced using GEBCO Digital Atlas (IOC, IHO and BODC, 2003). (b) Plot of longitude vs. water depth of sampling stations.

Fig. 2. Statistical dendrogram of type-averaged grain-size profiles and geographical distribution of grain-size compositional types for a) the lithogenic fraction and b) the bulk fraction of the investigated sediments.

Fig. 3. Spatial distribution of (a) lithogenics, (b) $CaCO_3$ contents, (c) OC contents, (d) molar TN/OC ratios, and (e) ~~and~~ $\delta^{13}C$ values in surface sediments of the deep Eastern Mediterranean Sea.

Fig. 4. Spatial distributions of the OC-normalized concentrations of (a) Unresolved Complex Mixture (UCM), (b) ∑TerNA, (c) ∑TerN-OH and (d) ∑Mar in surface sediments of the deep Eastern Mediterranean Sea. Abbreviations of lipid biomarkers are defined in the text.

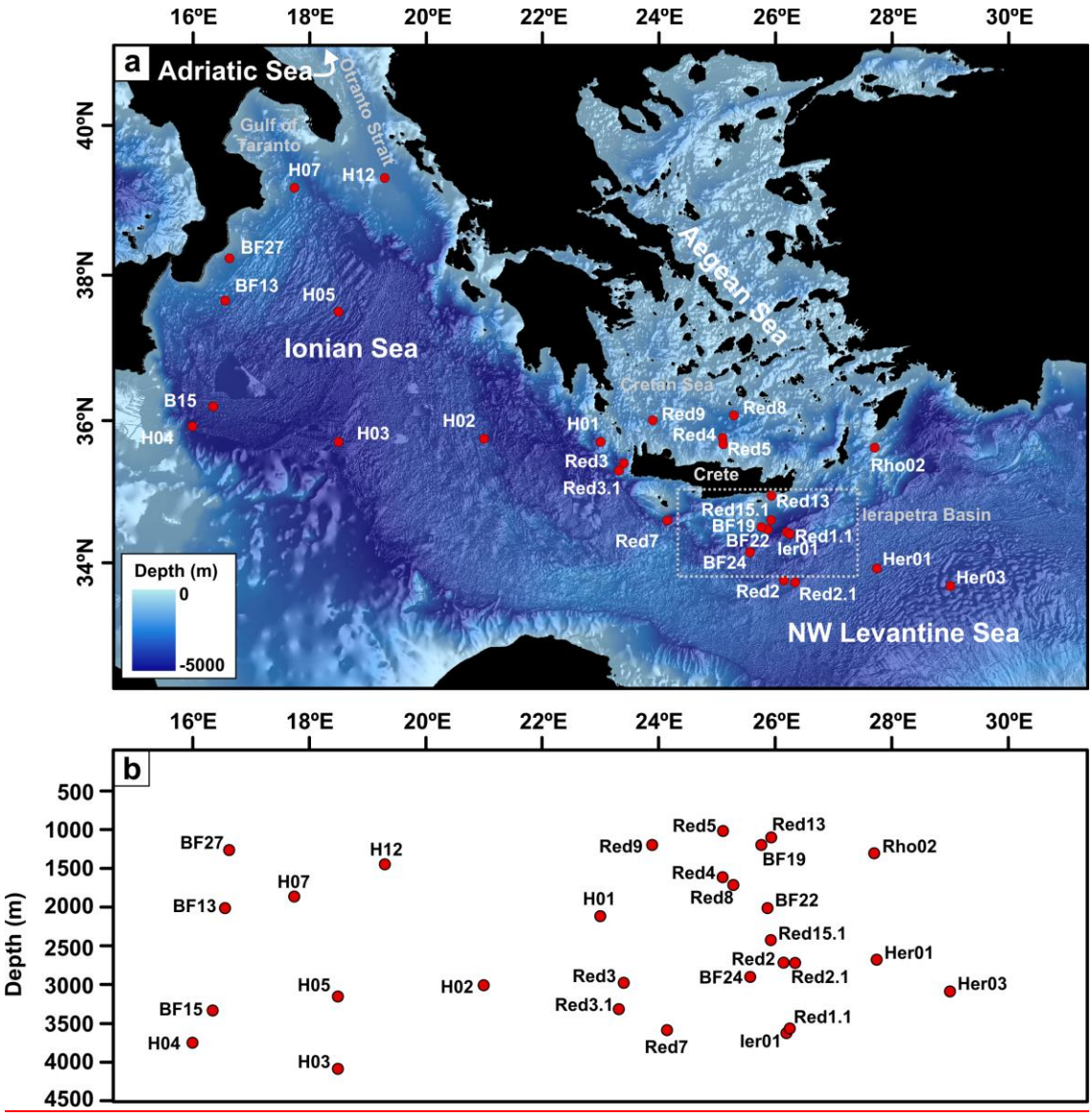
Fig. 5. (a) Scatter plot of the factor loadings of the three principal components obtained in the Principal Component Analysis, and (b) plot of the scores found at each station. Abbreviations of lipid biomarkers are defined in the text.

Fig. 6. ~~Plot of TN/OC atomic ratio vs.~~ (a) Co-plot of the weight percent content of nitrogen (TN) vs. organic carbon (OC) for the deep-sea surface sediments analysed. The linear fit of the data is shown (dotted line) along with the Redfield ratio N_{16}/C_{106} associated with the fresh marine phytoplankton (0.17 wt. /wt.). (b) Plot of molar TN/OC ratios vs. $\delta^{13}C$, in surface sediments of the deep Eastern Mediterranean Sea. The compositional ranges of organic matter sources illustrated in plots (boxes) derive from previously published studies (see section 5.1).

Fig. 7. Distribution of OC content and bulk sediment tracers (TN/OC and $\delta^{13}C$) in surface sediments of the deep Eastern Mediterranean Sea. The histogram reflects a spatially variable mixture of marine and terrestrial sources for sedimentary OM. Orange triangles and green circles correspond to molar TN/OC ratios and $\delta^{13}C$ values, respectively.

Fig. 8. ~~(a) Co-plot of the weight percent content of nitrogen (TN) vs. organic carbon (OC) for the deep-sea surface sediments analysed. The linear fit of the data is shown (dotted line) along with the Redfield ratio N_{16}/C_{106} associated with the fresh marine phytoplankton (0.17 wt. /wt.).~~ Spatial distribution of lipid biomarker indices (~~b~~a) [NA]/[N-OH~~]~~], (b) CPI_{NA} and (c) $CPI_{N\text{-}OH}$. Abbreviations of lipid biomarker indices are defined in the text.

1575 **1.**



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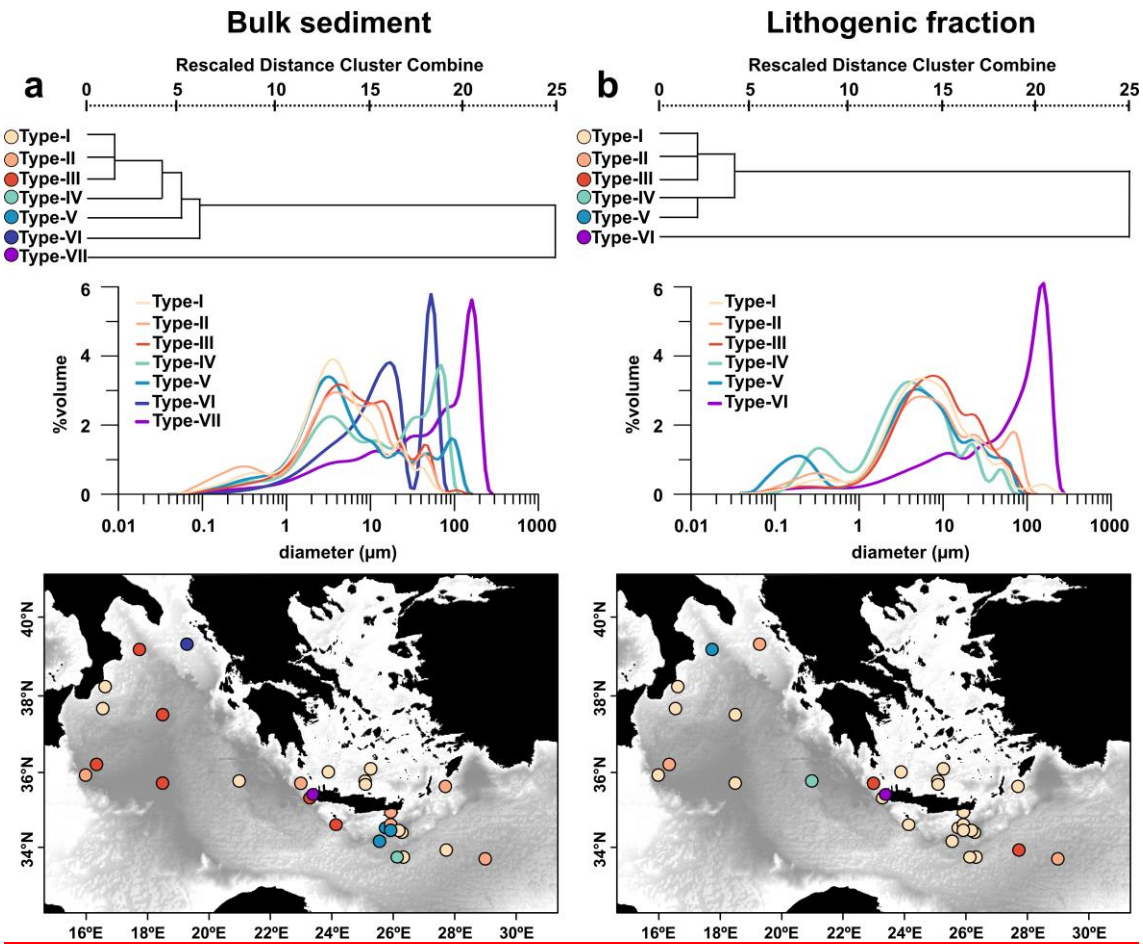
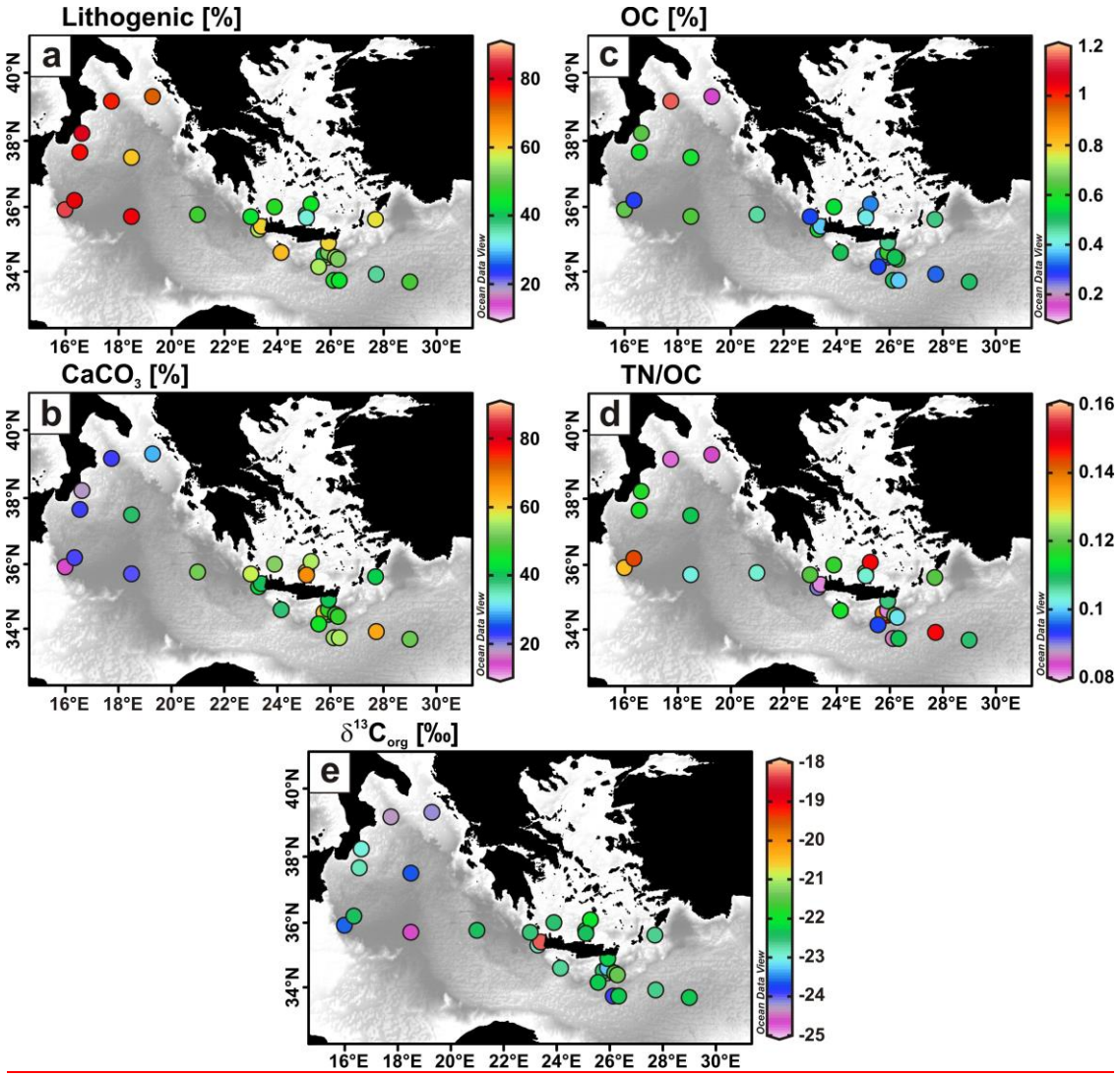
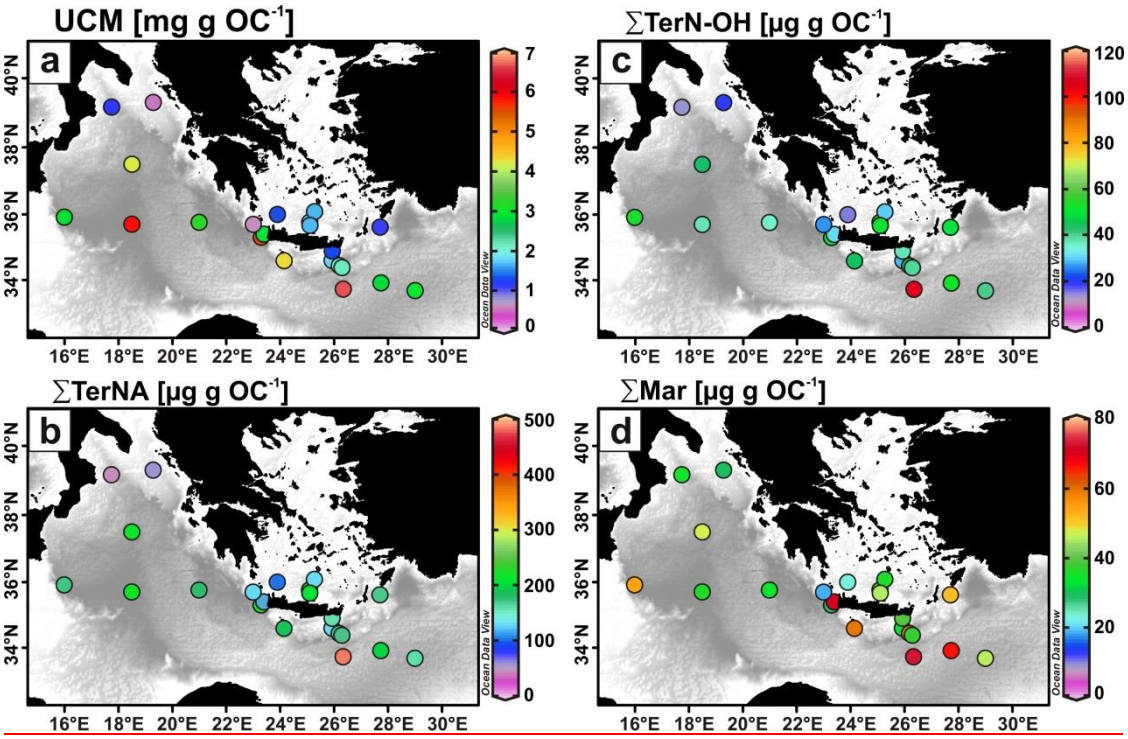
2.


Bulk sediment
Lithogenic fraction
a
b
Rescaled Distance Cluster Combine
0
5
10
15
20
25
Type-I
Type-II
Type-III
Type-IV
Type-V
Type-VI
Type-VII
%volume
diameter (µm)
0.01
0.1
1
10
100
1000
40°N
38°N
36°N
34°N
16°E
18°E
20°E
22°E
24°E
26°E
28°E
30°E

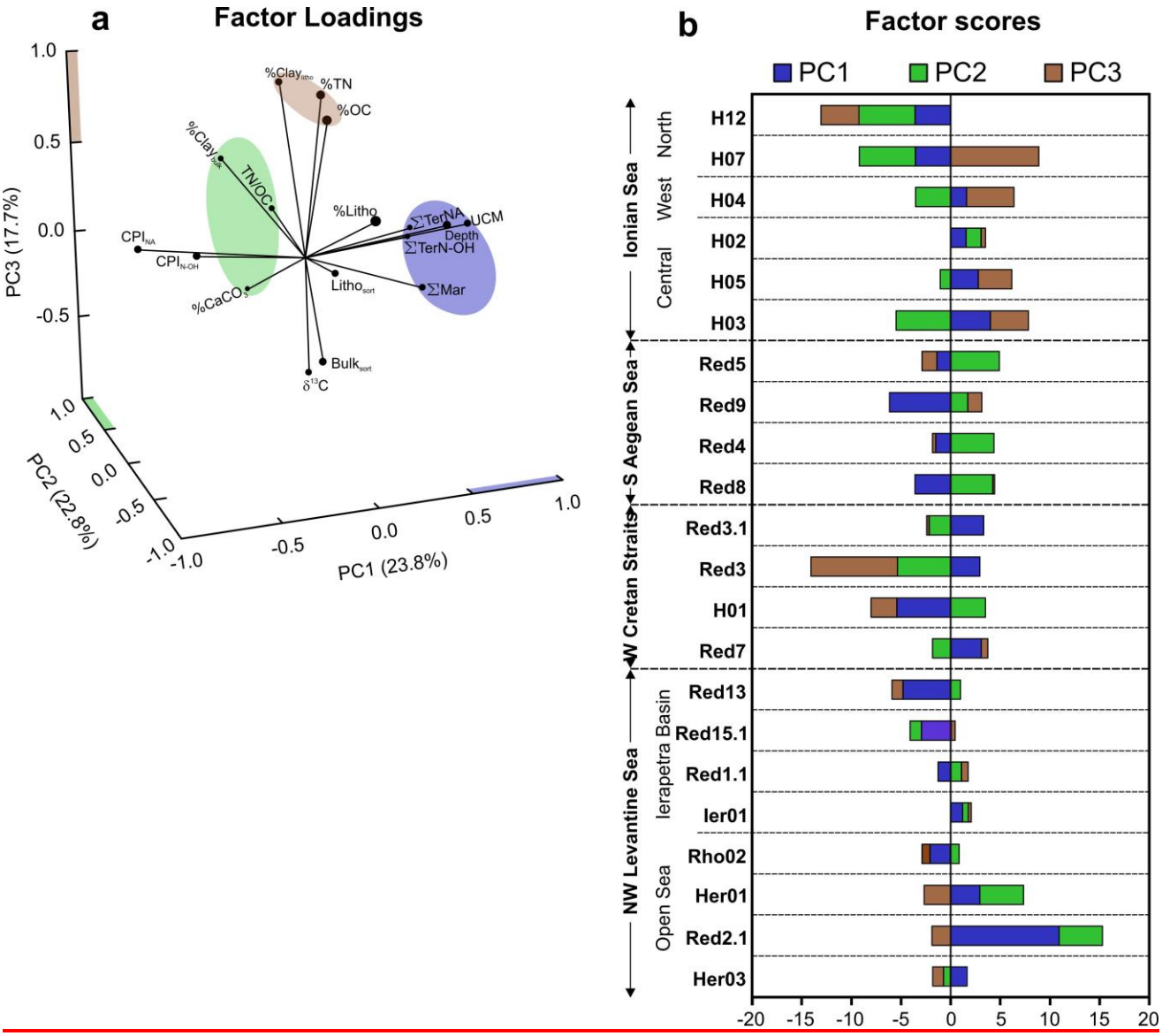
3.


Lithogenic [%]
a
40°N
38°N
36°N
34°N
16°E 18°E 20°E 22°E 24°E 26°E 28°E 30°E
80
60
40
20
Ocean Data View
OC [%]
c
1.2
1
0.8
0.6
0.4
0.2
CaCO3 [%]
b
TN/OC
d
0.16
0.14
0.12
0.1
0.08
δ13Corg [‰]
e
-18
-19
-20
-21
-22
-23
-24
-25

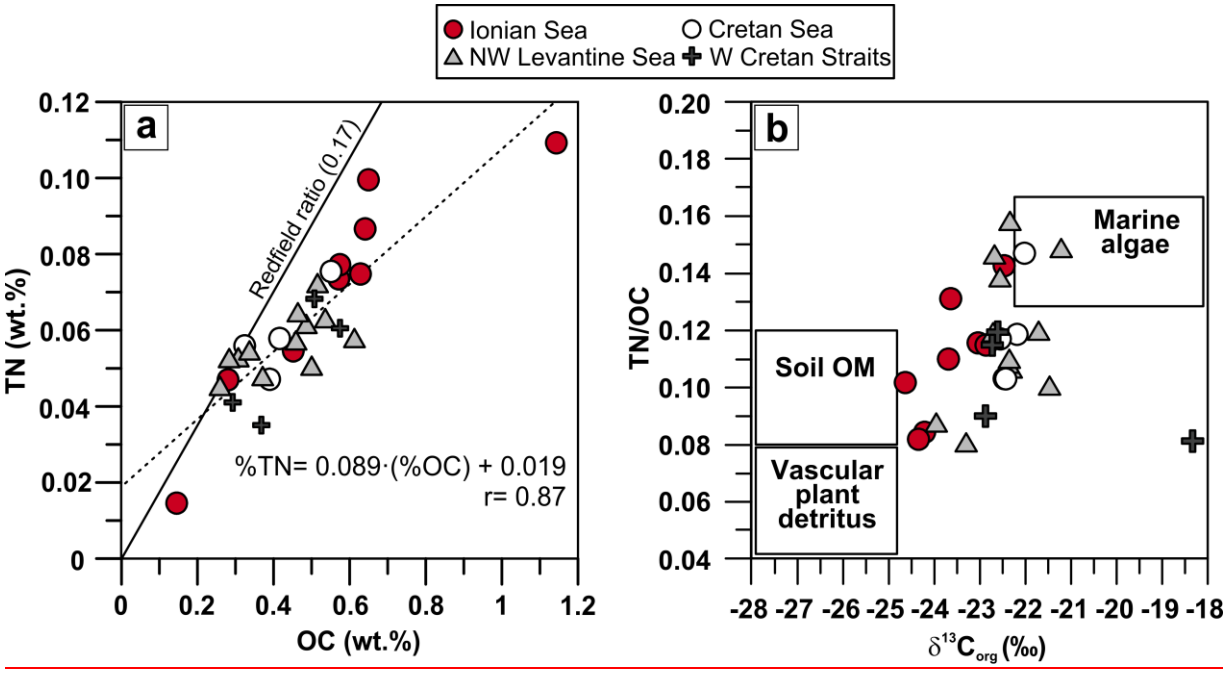
4.


UCM [mg g OC-1]
a
∑TerN-OH [µg g OC-1]
c
∑TerNA [µg g OC-1]
b
∑Mar [µg g OC-1]
d
40°N
38°N
36°N
34°N
16°E 18°E 20°E 22°E 24°E 26°E 28°E 30°E
Ocean Data View
0 1 2 3 4 5 6 7
0 20 40 60 80 100 120
0 100 200 300 400 500
0 20 40 60 80

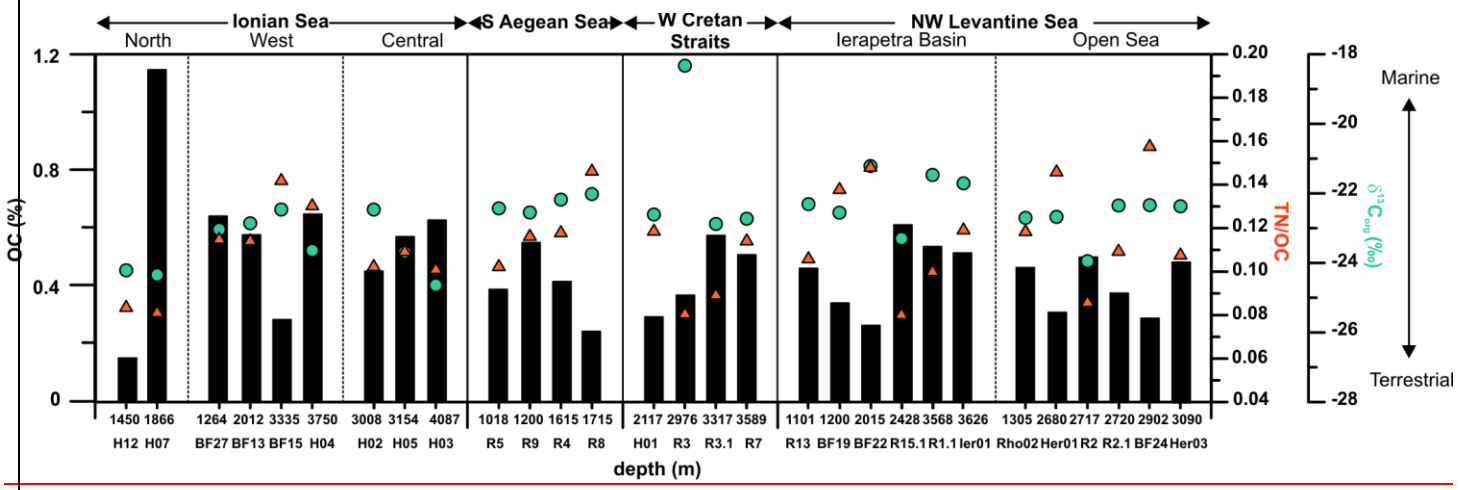
5.


a
Factor Loadings
%Clay_litho
%TN
%OC
%Clay_bulk
TN/OC
%Litho
∑TerNA
UCM
Depth
∑TerN-OH
CPI_NA
CPI_N-OH
%CaCO3
Litho_sort
∑Mar
Bulk_sort
δ13C
PC3 (17.7%)
PC2 (22.8%)
PC1 (23.8%)
b
Factor scores
PC1
PC2
PC3
Ionian Sea
North
West
Central
S Aegean Sea
W Cretan Straits
NW Levantine Sea
Ierapetra Basin
Open Sea
H12
H07
H04
H02
H05
H03
Red5
Red9
Red4
Red8
Red3.1
Red3
H01
Red7
Red13
Red15.1
Red1.1
Ier01
Rho02
Her01
Red2.1
Her03

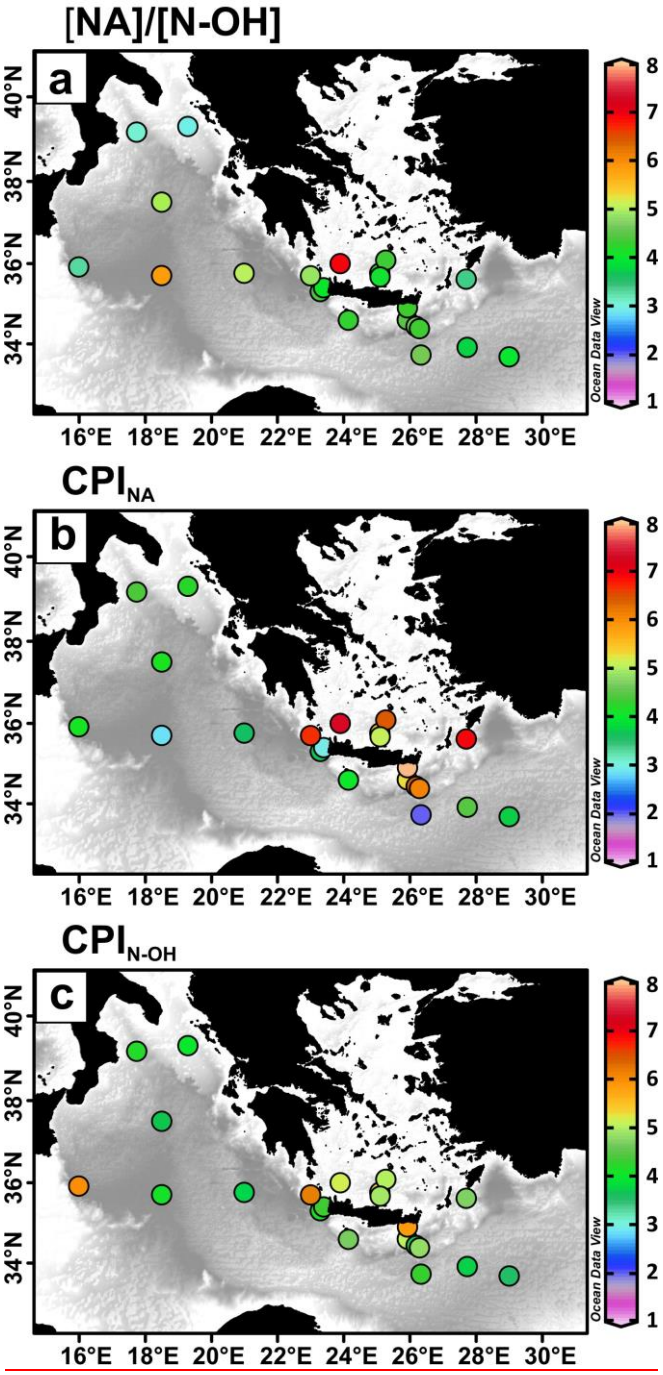
6.


Ionian Sea
Cretan Sea
NW Levantine Sea
W Cretan Straits
a
Redfield ratio (0.17)
%TN= 0.089·(%OC) + 0.019
r= 0.87
TN (wt.%)
OC (wt.%)
b
Marine algae
Soil OM
Vascular plant detritus
TN/OC
δ13Corg (‰)

7.


Ionian Sea
North
West
Central
S Aegean Sea
W Cretan Straits
NW Levantine Sea
Ierapetra Basin
Open Sea
OC (%)
TN/OC
$\delta^{13}C_{org}$ (‰)
Marine
Terrestrial
1450 1866
H12 H07
1264 2012 3335 3750
BF27 BF13 BF15 H04
3008 3154 4087
H02 H05 H03
1018 1200 1615 1715
R5 R9 R4 R8
2117 2976 3317 3589
H01 R3 R3.1 R7
1101 1200 2015 2428 3568 3626
R13 BF19 BF22 R15.1 R1.1 Ier01
1305 2680 2717 2720 2902 3090
Rho02 Her01 R2 R2.1 BF24 Her03
depth (m)

8.


[NA]/[N-OH]
a
CPI$_{NA}$
b
CPI$_{N-OH}$
c
40°N
38°N
36°N
34°N
16°E 18°E 20°E 22°E 24°E 26°E 28°E 30°E
8 7 6 5 4 3 2 1
Ocean Data View