Occurrence, sources and transport pathways of natural and anthropogenic hydrocarbons in deep-sea sediments of the eastern Mediterranean Sea

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Abstract. Surface sediments collected from deep basins (1018–4087 m depth) of the eastern Mediterranean Sea (Ionian Sea, southern Aegean Sea and northwestern Levantine Sea) were analyzed for aliphatic and polycyclic aromatic hydrocarbons as tracers of natural and anthropogenic inputs. Concentrations of total aliphatic hydrocarbons, n-alkanes and the unresolved complex mixture (UCM) of aliphatic hydrocarbons as tracers of natural and anthropogenic inputs. Concentrations of total aliphatic hydrocarbons, n-alkanes and the unresolved complex mixture (UCM) of aliphatic hydrocarbons varied significantly, ranging from 1.34 to 49.2 µg g⁻¹, 145 to 4810 ng g⁻¹ and 0.73 to 36.7 µg g⁻¹, respectively, while concentrations of total polycyclic aromatic hydrocarbons (PAHs) ranged between 11.6 and 223 ng g⁻¹. Molecular profiles of determined hydrocarbons reflect a mixed contribution from both natural and anthropogenic sources in deep-sea sediments of the eastern Mediterranean Sea, i.e., terrestrial plant waxes, degraded petroleum products, unburned fossil fuels and combustion of grass, wood and coal. Hydrocarbon mixtures display significant variability amongst sub-regions, reflecting differences in the relative importance of inputs from various sources and phase associations/transport pathways of individual hydrocarbons that impact on their overall distribution and fate. Hydrocarbon concentrations correlated significantly with the organic carbon content of sediments, indicating that the latter exerts an important control on their transport and ultimate accumulation in deep basins. Additionally, water masses’ circulation characteristics also seem to influence the regional features and distribution patterns of hydrocarbons. Our findings highlight the role of deep basins/canyons as repositories of both natural and anthropogenic chemical species.

1 Introduction

Hydrocarbons are ubiquitous components of the organic material introduced into coastal and open sites of the world’s oceans. They enter the marine environment through both atmospheric (dry/wet deposition, gas exchange across the air–water interface) and aquatic pathways (direct discharges, continental run-offs, off-shelf export) the relative importance of which largely depends on the geographical setting of a given area. Although they may derive from natural sources, both marine and terrestrial, a large proportion of hydrocarbons is related to various anthropogenic activities that result in the formation and release of hazardous organic pollutants. On account of their wide variety of sources, hydrocarbons occur as complex mixtures in the marine environment (Bouloubassi et al., 1997; Gogou et al., 2000; Prahl and Carpenter, 1984; Tolosa et al., 1996; Unkler et al., 2002).

Due to their hydrophobic nature, hydrocarbons in the marine realm tend to associate with particles resulting in their...
downward transport through the water column and final accumulation in sediments (Bouloubassi et al., 2006; Dachs et al., 2002; Deyme et al., 2011; Parinos et al., 2013; Prahl and Carpenter, 1979; Tsapakis et al., 2006). The sources and physico-chemical properties of individual compounds determine their phase associations, dispersion pathways, pre- and post-deposition fate in the marine environment and their ultimate preservation in marine sediments (Dachs and Eisenreich, 2000; Simo et al., 1997; Wang et al., 1999; Yunker et al., 2002; and references therein).

Aliphatic hydrocarbons derive from natural sources such as terrestrial plant waxes, marine phytoplankton and bacteria (Brassell et al., 1978), while they are also major components of petroleum products (Wang et al., 1999). The unresolved complex mixture (UCM) of aliphatic hydrocarbons, a commonly observed contaminant mixture in marine sediments consisting of branched alicyclic hydrocarbons (Gough and Rowland, 1990), has been proven as toxic to sediment-dwelling organisms (Scarlett et al., 2007). Polycyclic aromatic hydrocarbons (PAHs) are an important and ubiquitous class of environmental contaminants. They have been classified as priority pollutants by national and international environmental agencies (e.g., EPA-US, EEA-EU) since certain homologues are highly carcinogenic and mutagenic, exhibiting tendency to bioaccumulate in aquatic organisms (Samanta et al., 2002). PAHs' formation and release in the environment is related to various anthropogenic activities including pyrolysis/combustion of organic material (biomass burning, incomplete combustion of fossil fuels) and release of petroleum products (Neff, 1979; Simoneit, 1984; Yunker et al., 2002; and references therein). PAHs of biogenic origin may also occur in environmental samples. Such evidence has been reported for perylene, retene (Laflamme and Hites, 1978; Wakeham et al., 1980) and phenanthrene (Cabrerizo et al., 2011; Nizzetto et al., 2008).

The eastern Mediterranean Sea (EMS), and especially its coastal area, is a region under intense anthropogenic pressure resulting in pollutant discharges (EEA, 2006). The open EMS, being an important region of merchant shipping and oil transportation, receives substantial amounts of petroleum discharges, mainly along shipping routes (REMPEC, 2008; UNEP, 2010). Atmospheric deposition is another important pathway for the introduction of hydrocarbons into the EMS (Castro-Jiménez et al., 2012; Gogou et al., 1996; Tsapakis and Stefanou, 2005) including significant inputs of Saharan dust (Jickells et al., 2005), especially during dust storm events, that contain both natural and anthropogenic hydrocarbons (Ladj et al., 2010).

Aliphatic hydrocarbons and PAHs have been investigated over the last decades in surficial sediments of the EMS, primarily in coastal or shallow basin sites in the Aegean Sea, southern Italy, the coast of Egypt and the Adriatic Sea (Aboul-Kassim and Simoneit, 1995; Alebic-Juretic, 2011; Botsou and Hatzianestis, 2012; Cardellicchio et al., 2007; Gogou et al., 2000; Gonul and Kucuksezgin, 2012; Guzzella and De Paolis, 1994; Marcomini et al., 1986; Nemr et al., 2007; Sklivagou et al., 2008; Yilmaz et al., 1998). However, there is an important lack of data regarding their occurrence in deep basins, which might represent a long-term sink for hydrocarbons. To fill this gap we report here the first data set on sedimentary aliphatic and polycyclic aromatic hydrocarbons in deep EMS basins (1018–4087 m depth). The aim of this study is to assess their occurrence, major sources and transport pathways and to evaluate the role of deep EMS basins as their repository.

2 Oceanographic setting

The EMS is a semi-enclosed basin that connects with the western Mediterranean Sea through the Strait of Sicily. It includes four major sub-basins: the Ionian and Levantine basins, the Adriatic Sea and the Aegean Sea.

EMS presents a complex circulation pattern, with water masses' distribution being influenced by both large-scale and mesoscale variability. As a concentration basin, it is characterized by an antiestuarine circulation that transforms surface Atlantic Waters (AW), entering through the Strait of Sicily at the upper 100–200 m of the water column, into Levantine Intermediate Waters (LIW) in the eastern part of the region (Rhodes gyre), which leave the basin as a westward current through the Strait of Sicily at depths between 200 and 500 m. Intermediate water masses are also formed occasionally in the southern Aegean Sea (Cretan Intermediate Water – CIW), with characteristics similar to those of LIW, which feed the EMS through the Cretan Arc straits. Mesoscale variability, creating permanent and transient eddies/gyres, enhances exchanges between continental shelf waters and slope waters (Malanotte-Rizzoli et al., 1997; Millot and Taupier-Letage, 2005; Robinson et al., 1992).

Deep-water layers of the EMS originate mainly in the Adriatic Sea and are exported by means of bottom-arrested currents towards the abyssal layers of the Ionian Basin, flowing in an eastward path all the way towards the eastern Levantine Basin. The Aegean Sea also contributes to deep-water formation, and may even become more effective than the Adriatic as a deep-water source, as in the case of the Eastern Mediterranean Transient (EMT) during the early 1990s (Roether et al., 1996; Theocharis et al., 1999). The water column of the EMS is well oxygenated. The oxygen minimum found at depths of about 1000 to 2000 m is equivalent to 70–75% of saturation, while in deeper layers ventilation is enhanced by deep-water formation (Meador et al., 2010; Schlitzer et al., 1991).

Mean sedimentation rates in deep EMS basins are low and generally do not exceed 5 cm kyr⁻¹, mainly due to its oligotrophic character and the minor influence from riverine inputs (Garcia-Orellana et al., 2009). Thus, aeolian transport is of major importance for the delivery of land-derived natural and anthropogenic material to the open marine sites of
the EMS. Atmospheric circulation patterns are characterized by winds of dominant north-northeast direction (central and eastern Europe and Balkans) from May to September, while from October to April the prevalence of north-northwest sector is less pronounced. Especially in March/April and in October/November winds from the north-northwest, south-southwest (Africa) and west sectors (marine influence) are roughly equally distributed. This leads to complex aerosol dynamics, with large anthropogenic and natural emissions and intensive interaction between aerosols and gaseous pollutants, resulting in a variation of deposition modes (dry vs. wet) and composition of background aerosols in open EMS areas (Gogou et al., 1996; Lee et al., 2010; Mihalopoulos et al., 1997; Mandalakis et al., 2009; Polymenakou et al., 2008; Tsapakis and Stefanou, 2005, 2007; and references therein).

3 Materials and methods

3.1 Sampling

Sediment cores were collected with a multicorer at 22 stations in deep basins (1018–4087 m depth) of the Ionian Sea, Cretan Sea (southern Aegean Sea) and northwestern Levantine Sea during four oceanographic cruises conducted between January 2007 and June 2012 (Fig. 1, Table 1). January 2007 samples were collected during the M71 Leg. 3 cruise of the R/V Meteor (University of Hamburg, Germany), while May 2010, 2011 and June 2012 samples were collected during corresponding cruises of the R/V Aegaeo (HCMR, Greece). The undisturbed top centimeter (1 cm) of each core was recovered, wrapped in pre-combusted (450 °C, 6 h) aluminum foil and stored at −20 °C till further analysis.

3.2 Methods

For the analysis of organic carbon (OC) content, freeze-dried and grounded sediment samples were initially de-carbonated using repetitive additions of HCl (25 %, v/v), separated by 60 °C drying steps, until no effervescence was observed. Organic carbon was then determined by combustion in an oxygen atmosphere and the produced carbon dioxide was quantitatively measured using a Flash 1112 elemental analyzer.

For the analysis of aliphatic and polycyclic aromatic hydrocarbons freeze-dried sediments were spiked with a mixture of perdeuterated internal standards ([2H5]n-tetracosane, [2H10]phenantheine, [2H10]pyrene, [2H12]chrysene, [3H12]perylene and [2H12]benzo[g,h,i]perylene) and solvent extracted three times by sonication with a dichloromethane:methanol mixture (4 : 1, v/v). Combined extracts were fractionated on a silica column, applying a modified protocol after Gogou et al. (1998). Aliphatic hydrocarbons were eluted with 6 mL n-hexane and PAHs with 10 mL n-hexane/toluene (9 : 1, v/v). Both fractions were concentrated by vacuum rotary evaporation, transferred to a 1.5 mL amber vial and excess solvent was evaporated under a gentle nitrogen stream.

Instrumental analysis was carried out by gas chromatography mass spectrometry (GC-MS) on an Agilent 7890 GC, equipped with an HP-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm phase film), coupled to an Agilent 5975C MSD. For the analysis of aliphatic hydrocarbons the MSD operated in full scan mode and the GC oven temperature was initially held at 60 °C for 2 min, brought to 80 °C at a rate of 25 °C·min⁻¹, then to 300 °C at a rate of 5 °C·min⁻¹ and finally held at 300 °C for 35 min. PAHs were analyzed using a selected ion monitoring (SIM) acquisition program. The oven temperature program was the same as in the case of aliphatic hydrocarbons but with a 300 °C final isothermal of 6 min. Helium was used as carrier gas at a flow of 1.1 mL·min⁻¹.

Standard solutions of the targeted compounds, purchased from Dr. Ehrenstorfer GmbH, were spiked with the internal standards and run on each injection set in order to derive relative response factors (RRFs) of the analytes. The precision of the analytical method used for PAHs determination was evaluated by analyzing the standard reference material SRM 1941b – NIST USA (organics in marine sediment). The determined values ranged between 93 and 106 % of the certified values, while in terms of repeatability the relative standard deviation was below 5 %. Procedural blanks processed were found to be free of contamination.

Cluster analysis (joining clustering method) was applied to group stations with similar n-alkane or PAH profiles, using the relative homologues’ concentrations for the total sum of compounds monitored, respectively, as starting data.

Table 1. Location and characteristics of sampling sites.

<table>
<thead>
<tr>
<th>Station</th>
<th>Location</th>
<th>Water depth (m)</th>
<th>Sampling date</th>
<th>Organic carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RED1.2</td>
<td>33°42.81’</td>
<td>26°20.45’</td>
<td>May 2010</td>
<td>0.37</td>
</tr>
<tr>
<td>RED3</td>
<td>35°24.14’</td>
<td>23°24.10’</td>
<td>May 2010</td>
<td>0.37</td>
</tr>
<tr>
<td>RED1.1</td>
<td>35°18.17’</td>
<td>23°18.92’</td>
<td>May 2010</td>
<td>0.58</td>
</tr>
<tr>
<td>RED4</td>
<td>35°45.71’</td>
<td>25°06.00’</td>
<td>May 2010</td>
<td>0.42</td>
</tr>
<tr>
<td>RED5</td>
<td>35°40.57’</td>
<td>25°06.12’</td>
<td>May 2010</td>
<td>0.39</td>
</tr>
<tr>
<td>RED7</td>
<td>34°36.11’</td>
<td>24°08.73’</td>
<td>May 2011</td>
<td>0.51</td>
</tr>
<tr>
<td>RED8</td>
<td>36°04.47’</td>
<td>25°17.07’</td>
<td>May 2011</td>
<td>0.33</td>
</tr>
<tr>
<td>RED9</td>
<td>36°00.03’</td>
<td>23°53.55’</td>
<td>May 2011</td>
<td>0.40</td>
</tr>
<tr>
<td>RED11</td>
<td>34°24.13’</td>
<td>26°14.67’</td>
<td>June 2012</td>
<td>0.54</td>
</tr>
<tr>
<td>RED15.1</td>
<td>34°36.55’</td>
<td>25°55.49’</td>
<td>June 2012</td>
<td>0.62</td>
</tr>
<tr>
<td>RED13</td>
<td>34°57.01’</td>
<td>25°54.90’</td>
<td>June 2012</td>
<td>0.46</td>
</tr>
<tr>
<td>H01</td>
<td>35°45.00’</td>
<td>23°00.00’</td>
<td>Jan 2007</td>
<td>0.29</td>
</tr>
<tr>
<td>H02</td>
<td>35°45.00’</td>
<td>21°00.00’</td>
<td>Jan 2007</td>
<td>0.45</td>
</tr>
<tr>
<td>H03</td>
<td>35°45.00’</td>
<td>18°30.00’</td>
<td>Jan 2007</td>
<td>0.63</td>
</tr>
<tr>
<td>H04</td>
<td>35°55.00’</td>
<td>16°00.00’</td>
<td>Jan 2007</td>
<td>0.65</td>
</tr>
<tr>
<td>H05</td>
<td>37°30.00’</td>
<td>18°30.00’</td>
<td>Jan 2007</td>
<td>0.57</td>
</tr>
<tr>
<td>H07</td>
<td>39°10.00’</td>
<td>17°45.00’</td>
<td>Jan 2007</td>
<td>1.15</td>
</tr>
<tr>
<td>H12</td>
<td>38°50.00’</td>
<td>19°45.00’</td>
<td>Jan 2007</td>
<td>0.15</td>
</tr>
<tr>
<td>HER01</td>
<td>33°55.44’</td>
<td>27°44.45’</td>
<td>Jan 2007</td>
<td>0.31</td>
</tr>
<tr>
<td>HER03</td>
<td>33°40.00’</td>
<td>29°00.00’</td>
<td>Jan 2007</td>
<td>0.49</td>
</tr>
<tr>
<td>H091</td>
<td>34°26.54’</td>
<td>26°11.51’</td>
<td>Jan 2007</td>
<td>0.52</td>
</tr>
<tr>
<td>Rho02</td>
<td>35°37.12’</td>
<td>27°42.03’</td>
<td>Jan 2007</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Ward’s method was used for amalgamation of clusters while distances between objects were measured as Euclidean distances.

Spatial distributions of concentrations and characteristic parameters of aliphatic and polycyclic aromatic hydrocarbons were visualized using Ocean Data View – ODV (Schlitzer, 2011).

4 Results

4.1 Organic carbon

Organic carbon (OC) contents ranged from 0.15 to 1.15 % (Table 1). These values are comparable to those reported for the open northwestern Mediterranean Sea (0.38–1.47 %, Bouloubassi et al., 1997; 0.23–1.85 %, Roussiez et al., 2006; 0.7–1.5 %, Tolosa et al., 1996) and the open Cretan Sea (0.30–0.82 %; Gogou et al., 2000). Maximum values are found off the Gulf of Taranto (station H07), followed by deep Ionian Sea basins (stations H04 and H03), while minimum values are found in the northeastern Ionian Sea (station H12).

4.2 Molecular profile of hydrocarbons

Sedimentary aliphatic hydrocarbons comprised of a series of resolved compounds, mainly \( n \)-alkanes (NA), and a UCM. \( C_{12} \) to \( C_{42} \) \( n \)-alkanes were the main resolved constituents, representing on average 56 % of their total sum. Their molecular profile (Fig. 2a) was dominated by long-chain homologues (\( C_n \geq 24 \)) maximizing at \( n-C_{31} \) with an elevated odd/even carbon preference index \( (CPI_{24-35} = 4.86 \) on average, Table 2). NA with \( C_n > 35 \) constituted a large fraction at some stations (> 30 %), while \( C_n \leq 23 \) NA without odd/even carbon preference \( (CPI_{14-23} \sim 1) \) were also abundant in others (∼ 15 % on average). A UCM, present as a unimodal hump centered around \( n-C_{30} \), was the major component of aliphatic hydrocarbons accounting for up to 81 % of their total sum (69 % on average).

Twenty-five PAHs comprising parent (unsubstituted) compounds with 3–6 rings and alkyl-substituted homologues were determined. A typical PAH molecular profile is presented in Fig. 2b. Phenanthrene and its alkylated homologues dominated amongst low-MW PAHs (3 rings). Their sum, referred to hereafter as \( \Sigma \)Phe, accounted for 23 ± 6 % of total PAHs. High-MW parent compounds (≥ 4 rings) were dominated by benzo[ghi]perylene, indeno[1,2,3-cd]pyrene and, to a lesser degree, chrysene. Their sum, referred to hereafter as \( \Sigma \)COMB, excluding perylene which may have natural sources (Venkatesan, 1988), represents 55 ± 8 % of total PAHs.
Fig. 2. Molecular profile of n-alkanes (A) and PAHs (B) in deep-sea sediments of the study area. Individual compound abundances are normalized as percentage of the total sum of NA or PAHs (TPAH$_{25}$), respectively, and presented along with min–max deviation lines. NA homologues are assigned with their number of carbon atoms. PAH abbreviations: fluorene (Fl), dibenzothiophene (DBT), methyl dibenzothiophenes (C$_1$-DBT), dimethyl dibenzothiophenes (C$_2$-DBT), phenanthrene (Phe), methylphenanthrenes (C$_1$-Phe), dimethylphenanthrenes (C$_2$-Phe), trimethylphenanthrenes (C$_3$-Phe), anthracene (Anth), fluoranthene (Flth), pyrene (Pyr), methylpyrenes (C$_1$-Pyr), dimethylpyrenes (C$_2$-Pyr), retene (Ret), benz[a]anthracene (BaA), chrysene/triphenylene (Chry/Tri), methylchrysenes (C$_1$-Chry), dimethylchrysenes (C$_2$-Chry), benzo[b/j/k]fluoranthenes (BFlths), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Per), indeno[1,2,3-cd]pyrene (IndP), benzo[ghi]perylene (BgP) and dibenz[a,h]anthracene (DBA).

Table 2. Concentrations (per dry weight and OC-normalized) and characteristic parameters of aliphatic hydrocarbons determined in deep-sea sediments of the eastern Mediterranean Sea.

<table>
<thead>
<tr>
<th>Station</th>
<th>TAHC ($\mu$g g$^{-1}$)</th>
<th>UCM ($\mu$g g$^{-1}$)</th>
<th>NA (ng g$^{-1}$)</th>
<th>Ter.NA (ng g$^{-1}$)</th>
<th>TAHC (mg g$^{-1}$ OC)</th>
<th>UCM (mg g$^{-1}$ OC)</th>
<th>NA (µg g$^{-1}$ OC)</th>
<th>Ter.NA (µg g$^{-1}$ OC)</th>
<th>CPI$_{24-35}$</th>
<th>UCM/TrEs</th>
<th>Pr/Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>RED2.1</td>
<td>37.5</td>
<td>24.8</td>
<td>4810</td>
<td>1800</td>
<td>10.0</td>
<td>6.64</td>
<td>1290</td>
<td>483</td>
<td>1.93</td>
<td>3.2</td>
<td>0.61</td>
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<td>RED3</td>
<td>16.2</td>
<td>10.8</td>
<td>1680</td>
<td>442</td>
<td>4.39</td>
<td>2.93</td>
<td>455</td>
<td>120</td>
<td>5.36</td>
<td>2.3</td>
<td>0.57</td>
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<tr>
<td>RED3.1</td>
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<td>31.7</td>
<td>3820</td>
<td>1260</td>
<td>7.49</td>
<td>4.27</td>
<td>473</td>
<td>184</td>
<td>3.99</td>
<td>4.1</td>
<td>n.d</td>
</tr>
<tr>
<td>RED4</td>
<td>13.0</td>
<td>7.75</td>
<td>1790</td>
<td>819</td>
<td>3.11</td>
<td>1.86</td>
<td>428</td>
<td>196</td>
<td>7.25</td>
<td>4.5</td>
<td>n.d</td>
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<tr>
<td>RED5</td>
<td>11.6</td>
<td>6.41</td>
<td>1660</td>
<td>805</td>
<td>2.96</td>
<td>1.64</td>
<td>424</td>
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<td>938</td>
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<td>473</td>
<td>184</td>
<td>3.99</td>
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<td>681</td>
<td>414</td>
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<td>1.43</td>
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<td>H01</td>
<td>3.23</td>
<td>1.71</td>
<td>550</td>
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<td>0.58</td>
<td>187</td>
<td>127</td>
<td>6.64</td>
<td>1.8</td>
<td>n.d</td>
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<td>H02</td>
<td>20.1</td>
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<td>2160</td>
<td>800</td>
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<td>3.19</td>
<td>476</td>
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<td>3.57</td>
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<td>740</td>
<td>214</td>
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<td>4.7</td>
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<td>2.79</td>
<td>471</td>
<td>195</td>
<td>4.43</td>
<td>3.7</td>
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<td>166</td>
<td>6.88</td>
<td>2.6</td>
<td>n.d</td>
</tr>
</tbody>
</table>

TAHC: total aliphatic hydrocarbons (sum of total resolved compounds and UCM); UCM: unresolved complex mixture; NA: n-alkanes; Ter.NA: sum of terrestrial n-alkanes (n-C$_{27}$, n-C$_{29}$, n-C$_{31}$ and n-C$_{33}$); CPI$_{24-35}$: carbon preference index in the carbon range n-C$_{24}$ to n-C$_{35}$; UCM/TrEs: relative abundance of UCM compared to total resolved aliphatic hydrocarbons (TrEs); Pr: pristane; Ph: phytane; n.d: not detected.

4.3 Concentrations and spatial distribution of hydrocarbons

Concentrations of total aliphatic hydrocarbons (TAHC: sum of resolved compounds and UCM), UCM and NA in the study area are presented in Table 2. TAHC and UCM concentrations varied significantly, ranging from 1.34 to 49.2 µg g$^{-1}$ (average 18.4 µg g$^{-1}$) and from 0.73 to 36.7 µg g$^{-1}$ (average 13.1 µg g$^{-1}$), respectively, while NA concentrations ranged between 145 and 4810 ng g$^{-1}$, averaging 1890 ng g$^{-1}$. Normalized to OC content, TAHC, UCM and NA concentrations ranged from 0.91 to 10.0 mg g$^{-1}$ OC (average 3.75 mg g$^{-1}$ OC), 0.50 to 6.64 mg g$^{-1}$ OC (average 2.63 mg g$^{-1}$ OC) and 86.9 to 1290 µg g$^{-1}$ OC (average 398 µg g$^{-1}$ OC), respectively.

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Spatial distributions of absolute (per dry weight) and OC-normalized TAHC, UCM and NA concentrations in the study area are illustrated in Fig. 3. The highest TAHC levels were recorded in central Ionian Sea deep basins (average 31.4 µg g⁻¹ or 5.38 mg g⁻¹ OC), followed by deep northwestern Levantine basins (average 19.3 µg g⁻¹ or 4.40 mg g⁻¹ OC), while lower values were recorded at Cretan Sea stations (average 9.69 µg g⁻¹ or 2.51 mg g⁻¹ OC). In deep basins of the Ionian Sea and the northwestern Levantine Sea, TAHC, UCM and NA absolute and OC-normalized concentrations display generally a common increasing westward trend, with maximum concentrations recorded at station H03 in the central Ionian Sea and station RED2.1 located in the northwestern Levantine Sea. An almost twofold increase is observed in the concentrations of aliphatic hydrocarbons at the deep station of the western Cretan Straits’ canyons (RED3.1) in comparison to the neighboring RED3 located in the upper slope of the adjacent margin. Minimum TAHC, UCM and NA absolute and OC-normalized concentrations were recorded at station H12 in the northeastern Ionian Sea (Table 2).

Table 3 summarizes concentrations of PAHs in the study area. TPAH₂⁵ refers to the total sum of compounds monitored, while ∑PAH₁₃ refers to the sum of 13 parent compounds mostly considered in environmental studies, i.e., Fl, Phe, Anth, Flth, Pyr, BaA, Chry, BFlths, BeP, BaP, IndP, BgP and DBA (for abbreviations, see Fig. 2). TPAH₂⁵ and ∑PAH₁₃ concentrations ranged from 11.6 to 223 ng g⁻¹ (average 63.6 ng g⁻¹) and from 5.90 to 130 ng g⁻¹ (average 38.3 ng g⁻¹), respectively. The concentrations of ∑COMB ranged from 5.08 to 118 ng g⁻¹ (average 33.9 ng g⁻¹), while ∑Phe ranged between 2.74 and 38.3 ng g⁻¹, averaging 15.0 ng g⁻¹. Normalized to OC content, TPAH₂⁵, ∑COMB and ∑Phe concentrations ranged from 3.92 to 38.8 µg g⁻¹ OC (average 12.8 µg g⁻¹ OC), 1.73 to 20.6 µg g⁻¹ OC (average 6.90 µg g⁻¹ OC) and 0.80 to 7.28 µg g⁻¹ OC (average 3.01 µg g⁻¹ OC), respectively.

Spatial distributions of absolute (per dry weight) and OC-normalized TPAH₂⁵, ∑Phe and ∑COMB concentrations in the study area are illustrated in Fig. 4. The highest TPAH₂⁵ levels were recorded at central Ionian Sea deep stations (average 118 ng g⁻¹ or 20.0 µg g⁻¹ OC), while lower concentrations were recorded at both northwestern Levantine deep basins (average 49.5 ng g⁻¹ or 10.1 µg g⁻¹ OC) and Cretan Sea stations (average 41.9 ng g⁻¹ or 9.28 µg g⁻¹ OC). TPAH₂⁵ absolute and OC-normalized concentrations display, as in the case of sedimentary aliphatic hydrocarbons, a common increasing westward trend, with maximum
5 Discussion

5.1 Aliphatic and polycyclic aromatic hydrocarbons levels

Concentrations of total aliphatic hydrocarbons in the investigated deep basins of the EMS are comparable to those reported for surface sediments in unpolluted to moderately polluted coastal and/or open-sea areas in the Mediterranean, such as the Cretan Sea (Gogou et al., 2000), the north Aegean Sea (Hatzianestis et al., 1998), the open northwestern Mediterranean Sea (Tolosa et al., 1996), and in other sites worldwide, e.g., the East China Sea (Bouloubassi et al., 2001), the open Black Sea (Wakeham, 1996) and southern New England (Venkatesan et al., 1987). They are at least one order of magnitude lower than those reported for coastal areas subjected to enhanced urban and/or fluvial inputs such as Saronikos Gulf, Greece (Sklavougou et al., 2008); the coastal area off Barcelona, Spain (Tolosa et al., 1996); the Danube estuary, Black Sea (Readman et al., 2002; Wakeham, 1996); and the coastal area off Alexandria, Egypt (Aboul-Kassim and Simoneit, 1995).

Table 3. Concentrations (per dry weight and OC-normalized), characteristic parameters and source-specific diagnostic ratios of polycyclic aromatic hydrocarbons (PAHs) determined in deep-sea sediments of the eastern Mediterranean Sea.

<table>
<thead>
<tr>
<th>Station</th>
<th>TPAH&lt;sub&gt;25&lt;/sub&gt; (ng g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>∑PAH&lt;sub&gt;13&lt;/sub&gt; (ng g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>∑COMB (ng g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>∑Phe (ng g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>TPAH&lt;sub&gt;5&lt;/sub&gt; (ng g&lt;sup&gt;-1&lt;/sup&gt; OC)</th>
<th>∑COMB (ng g&lt;sup&gt;-1&lt;/sup&gt; OC)</th>
<th>∑Phe (µg g&lt;sup&gt;-1&lt;/sup&gt; OC)</th>
<th>C&lt;sub&gt;Phe&lt;/sub&gt;/(C&lt;sub&gt;Phe&lt;/sub&gt; + C&lt;sub&gt;COMB&lt;/sub&gt;)</th>
<th>Fih&lt;sub&gt;th&lt;/sub&gt;/ (Fih&lt;sub&gt;th&lt;/sub&gt; + Pyr)</th>
<th>BaA/ (BaA + Chry)</th>
<th>IndP/ (IndP + BgP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RED2.1</td>
<td>59.7</td>
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<td>31.0</td>
<td>17.4</td>
<td>16.0</td>
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<td>0.37</td>
<td>0.53</td>
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<td>28.0</td>
<td>13.2</td>
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</table>

TPAH<sub>25</sub>: total sum of polycyclic aromatic hydrocarbons; ∑PAH<sub>13</sub>: sum of 13 parent compounds mainly considered in marine pollution studies (i.e., Fl, Phe, Anth, Fih<sub>th</sub>, Pyr, BaA, Chry, BF<sub>th</sub>s, Bp, B<i>B</i>, IndP, B<i>B</i>gP and DBA); ∑COMB: sum of high MW parent compounds (≥ 4 rings) excluding perylene; ∑Phe: sum of Phe, C<sub>1</sub>-Phe, C<sub>2</sub>-Phe and C<sub>3</sub>-Phe; abbreviations of PAH compounds are presented in Fig. 2.
Fig. 4. Spatial contour maps of TPAH\textsubscript{25}, \(\sum\)Phe and \(\sum\)COMB absolute (per dry weight) and their OC-normalized concentrations in deep-sea sediments across the eastern Mediterranean Sea. TPAH\textsubscript{25}, \(\sum\)Phe and \(\sum\)COMB are defined in the text.

and thus should be considered when interpreting hydrocarbon profile characteristics.

5.2.1 Natural sources

Natural inputs in deep EMS surficial sediments are of dominant terrestrial origin as evidenced by the pattern of C\textsubscript{24}–C\textsubscript{35} n-alkanes with elevated odd/even carbon preference (Fig. 2a, Table 2) characteristic of epicuticular plant waxes (Eglinton and Hamilton, 1967). The sum of major terrestrial n-alkanes (n-C\textsubscript{27}, n-C\textsubscript{29}, n-C\textsubscript{31} and n-C\textsubscript{33}), referred to hereafter as Ter.NA, averaged 50 % of total NA (Table 2), showing the importance of natural terrestrial inputs throughout the study area. Terrestrial plant n-alkanes are major components of eastern Mediterranean aerosols (Gogou et al., 1996), with the latter constituting major vehicles for the transport of terrestrial organic matter in deep-sea sediments of the EMS (Gogou et al., 2000; Gogou and Stephanou, 2004) due to the minor influence from riverine inputs (see Sect. 2).

The low abundance of C\textsubscript{15}, C\textsubscript{17} and C\textsubscript{19} n-alkanes (< 5 % of NA) reflects a minor contribution from marine (planktonic) sources in the study area. This is consistent with the overall ultra-oligotrophic character of the eastern Mediterranean Sea (Krom et al., 2003) and the labile character of short-chain planktonic hydrocarbons, relative to the refractory long-chain terrestrial n-alkanes, which may also contribute to enhancement of terrestrial fingerprints (Prahl and Carpenter, 1984; Prahl et al., 1997). Bacterial sources, evidenced by the presence of hopanes (hop-17(21)-ene, hop-13(18)-ene and 17\(\beta\)(H)-hop-22(29)-ene, Fig. 5), are also of minor importance.

Regarding PAHs, the presence of retene (7-Isopropyl-1-methylphenanthrene) also reflects inputs from terrestrial plants, mainly conifers (Wakeham et al., 1980) or inputs related to pinewood combustion (Ramdahl, 1983). However, retene represented less that 4 % of TPAH\textsubscript{25} in all stations, except station H05 in which it accounted for ∼18 % of total PAHs (see also Sect. 5.3).

5.2.2 Anthropogenic sources

Amongst aliphatic hydrocarbons, a series of C\textsubscript{27}–C\textsubscript{35} hopanes, a commonly used persistent geochemical indicator of oil pollution even in highly weathered oils (Wang et al., 1999), was identified in all samples (Fig. 5) exhibiting a dominant thermodynamically stable 17\(\alpha\)(H), 21\(\beta\)(H)-configuration, with 17\(\beta\)(H), 21\(\alpha\)(H)- compounds being less prominent, while extended C\textsubscript{31}–C\textsubscript{35} homologues were present as
pairs of the C22 diastereoisomers (22S and 22R) with a 22S/22S+22R ratio value close to 0.6. These patterns typify oil-derived hydrocarbons (Mackenzie, 1984) indicating pollutant inputs from fossil fuel products.

The UCM recorded in all stations indicates chronic oil pollution of deep EMS sediments (Brassell and Eglinton, 1980; Farrington and Quinn, 1973). Supportive to the above, its relative abundance compared to the total resolved aliphatic hydrocarbons (TRes) (UCM/TRes = 3.7 on average, Table 2) is a positive indication of contribution from degraded petroleum products (Simoneit, 1984). 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, which can persist in sediments for decades (Scarlett et al., 2007, and references therein).

The elevated abundance of NA with Cn > 35 at some stations points to enhanced contribution of heavy fuel oil residuals (Brooks et al., 1954; Hsieh et al., 2000), while Cn ≤ 23 NA without odd/even carbon preference (CPI_{14–23} ~ 1) likely derive from fossil inputs (light diesel, Wang et al., 1999) and/or reworked algal material (Saliot, 1981). However, the presence of the isoprenoid alkanes pristane (Pr) and phytane (Ph) along with the Cn ≤ 23 NA in corresponding stations with a ratio Pr/Ph < 1 (Table 2) argues for a fossil origin of the Cn ≤ 23 n-alkanes.

Regarding PAHs, the dominance of alkylated homologues relative to the unsubstituted compound mainly within the phenanthrene series but also within the dibenzothiophene, pyrene and chrysene series, together with the high abundance of parent PAH with ≥ 4 rings (Fig. 2b), reflects an admixture of PAHs deriving from both unburned fossil fuels (petroleum) and pyrolytic/combustion sources (Laflamme and Hites, 1978; Sporstøl et al., 1983; Wakeham et al., 1980).

We further applied a number of diagnostic PAH ratios proposed by Yunker et al. (2002) in order to further assess PAH sources in the study area (Table 3). However, these ratios should be considered with caution as their values may change to different extents during the environmental fate of PAHs (Tobiszewski and Namieśnik, 2012, and references therein).

The Flth/(Flth + Pyr) and IndP/(IndP + BgP) ratios exhibit values > 0.50, averaging 0.60 ± 0.04 and 0.56 ± 0.02, respectively, indicative of pyrolytic/combustion sources for these compounds (grass, wood and coal combustion). The BaA/(BaA + Chry) ratio ranged between 0.15 and 0.35 (average 0.26 ± 0.04), indicating rather an admixture of both pyrolytic and fossil contributions. In the lower MW range the C0/(C0 + C1) Phe ratio ranged between 0.33 and 0.70 (average 0.51 ± 0.10), indicating varying elevated contributions of pyrolytic/combustion (ratio > 0.5) or petroleum related (ratio < 0.5) phenanthrene sources in the study area. However, within the phenanthrene series the sum of C1-, C2- and C3-alkylated homologues accounted for 58–85 % of ∑Phe (average 72 %), indicating that even at stations where C0/(C0 + C1) Phe ratio values are > 0.5, the large
proportion of determined total phenanthrenes is related to petroleum-derived alkylated homologues contribution.

The ratio of total phenanthrenes ($\sum$ Phe) mostly derived from petrogenic inputs and $\sum$ COMB representing pyrolytic / combustion PAHs ($\sum$ Phe / $\sum$ COMB) ranged between 0.22 and 0.87 (Table 3), averaging 0.45 ± 0.19, implying that overall PAH mixtures in the study area derive from dominant pyrolytic sources. However, PAHs deriving from pyrolytic / combustion sources are strongly associated with fine combustion particles (soot and/or char black carbon) that protect them from degradation during transport from initial sources, through the water column and in sediments (Gogou et al., 1996; Simo et al., 1997; Tolosa et al., 1996; Dachs and Eisenreich, 2000; Yunker et al., 2002). In contrast, several studies have highlighted the selective degradation of low-MW labile compounds such as phenanthrene and its methyl derivatives in the marine environment (e.g., Bouloubassi et al., 2012; Simo et al., 1997; Tsapakis et al., 2003). Unlike PAHs of pyrolytic origin, these compounds enter the water column mainly through air–water diffusive exchange (Castro-Jiménez et al., 2012) or are directly introduced into surface waters following the release of petroleum products (Wang et al., 1999). Direct and indirect evidence of biodegradation has been suggested as an important factor affecting low-MW PAHs’ abundance during transport in the water column (Berrojalbiz et al., 2009, 2011). Indeed, atmospheric inputs of phenanthrenes in the Mediterranean Sea are reported to be two orders of magnitude higher than settling fluxes (Castro-Jiménez et al., 2012; Dachs et al., 1997; Deyme et al., 2011; Tsapakis et al., 2006). As a consequence, an apparent predominance of pyrolytic / combustion PAHs is commonly observed in marine sediments unless outstanding petroleum-related inputs have occurred.

Long-range atmospheric transport has been recognized as an important pathway for the introduction of both low- and high-MW PAHs and anthropogenic aliphatic hydrocarbons (e.g., UCM) across the EMS (Castro-Jiménez et al., 2012; Gogou et al., 1996; Tsapakis et al., 2003; Tsapakis and Stefanou, 2005). Concentrations of PAHs in background aerosols of the study area have been reported to be rather uniform in remote areas away from major urban centers or point sources (Castro-Jiménez et al., 2012; Tsapakis et al., 2003; Tsapakis and Stefanou, 2005). However, PAH composition of background EMS aerosols and subsequent air–water interactions are subjected to strong variability due to the interplay of several factors such as air-mass trajectory variations, deposition mode (dry/wet) and several chemical and physical processes such as gas–particle phase distributions and transformation reactions, which are often difficult to evaluate on the long-term (Tsapakis and Stefanou, 2005, 2007; see also Sect. 2). Petroleum inputs related to direct discharges from merchant shipping and / or oil transportation in the EMS have been reported to be elevated along shipping routes. Fig. 6 presents oil spills’ normalized density reported for the study area regarding the year span 1999–2004 (Ferraro et al., 2007) and main EMS tanker/crude oil shipping pathways (REMPEC, 2008).
5.3 Regional characteristics of sedimentary aliphatic and polycyclic aromatic hydrocarbons

Cluster analysis (joining clustering method) was applied to group stations with similar \(n\)-alkane or PAH profiles (see Sect. 3.2). Thus, stations are clustered into three main groups according to their \(n\)-alkane composition (Fig. 7). Cluster I stations (RED2.1, RED4, RED5, H04 and H07) are characterized by high abundances of Ter.NA along with low-MW homologues (\(C_n \leq 23\)). Cluster II stations (RED8, RED1.1, IER01, H12, RED15.1, RED9, H01, RED13 and Rho02) are characterized by high abundances of Ter.NA and low concentrations of both low and higher-chain NA. Stations in cluster III (RED3, RED3.1, RED7, H02, Her01, Her03, H05 and H03) are characterized by high abundances of Ter.NA along with the presence of long-chain NA homologues (\(C_n > 35\)).

With regard to their TPAH\(_{25}\) composition characteristics, stations are also clustered into three main groups (Fig. 8). Cluster I stations (RED2.1, RED3.1, RED3, RED4, RED5, RED7, H03, H07, H04, H01, IER01 and H12) are characterized by elevated abundance of alkylated homologues within the phenanthrene, dibenzothiophene, pyrene and chrysene series, indicating enhanced relative contribution of petrogenic PAHs. Cluster II stations (RED8, RED1.1, RED13, RED9, RED15.1, H02, Her03, Her01 and Rho02) display maximum values for high-MW parent compounds along with dominance of parent phenanthrene, pyrene and chrysene, indicating predominance of pyrolytic PAHs. Finally, cluster III (station H05) is characterized by the highest concentration of retene (\(\sim 18\%\) of TPAH\(_{25}\)), a naturally derived PAH (see Sect. 5.2.1), while the low relative abundance of alkylated compounds and high contribution of \(\sum\)COMB (\(> 50\%\) of TPAH\(_{25}\)) indicate pyrolytic PAH predominance.

Taking into consideration the facts deriving from cluster analysis and spatial distribution of aliphatic and polycyclic aromatic hydrocarbons concentrations discussed above, the regional characteristics of hydrocarbon mixtures in the study area can be assessed. For this purpose, the ratio of total phenanthrenes to pyrolytic / combustion PAHs (\(\sum\)Phe / \(\sum\)COMB) is also depicted (Fig. 9a). The latter, varying between 0.22 and 0.87 (Table 3), allows for the assessment of fossil vs. pyrolytic / combustion PAH mixtures spatial trends (e.g., Bouloubassi et al., 2001, 2012).

5.3.1 Ionian Sea

Deep basins of the central Ionian Sea (stations H02, H03, H04 and H05) display the highest levels, on average, of both anthropogenic inputs and terrestrial natural inputs, reflected in both absolute and OC-normalized TAHC, UCM, Ter.NA and TPAH\(_{25}\) concentrations, in comparison to both northwestern Levantine deep basins and the Cretan Sea...
High UCM and UCM/OC-normalized concentrations (maximum values at station H03) indicate chronic oil pollution of surface sediments, while the elevated contribution from heavy oil residuals as inferred by \(n\)-alkanes with \(C_n > 35\) (Fig. 7, stations H02, H03 and H05) and light diesel inputs (Fig. 7, station H04) is indicative of strong fossil inputs. \(\sum\text{Phe}/\sum\text{COMB}\) and \(C_0/(C_0+C_1)\) Phe ratio values (Fig. 9a,b) along with PAHs profile (Fig. 8) further indicate an increase in the relative abundance of petrogenic contributions from east to west. Indeed, stations H02, H03 and H04 are located along the main tanker/crude oil shipping pathway from Greece to Italy, displaying a high density of oil spills, with maximum in the area around station H04 (Fig. 6).

In the northern Ionian Sea, station H07 located off the Gulf of Taranto in southern Italy lies in an area subjected to anthropogenic pressure (Cardellicchio et al., 2007). Our hydrocarbon data indicate enhanced fossil inputs, reflected in the PAHs profile, the elevated \(\sum\text{Phe}/\sum\text{COMB}\) ratio values and the abundance of short-chain \(n\)-alkanes (Figs. 7b,c; 8b,c; 9a; Table 3). However, TAHC, TPAH\(_{25}\) and TAHC/OC-, TPAH\(_{25}\)/OC-normalized concentrations (Tables 2,3) point to a rather moderate pollutant load, while Ter.NA and Ter.NA/OC-normalized concentrations also reflect low terrestrial biogenic inputs, in comparison to the neighboring deep basins of the central Ionian Sea. Station H12 in the northeastern Ionian Sea, although located along a main shipping route from the Aegean Sea to the Adriatic Sea characterized by a high density of oil spills (Fig. 6), displays minimum values of TAHC, UCM, TPAH\(_{25}\) and Ter.NA concentrations (Tables 2,3; Figs. 3,4), indicating minimum pollutant load and terrestrial contributions amongst studied sites.

### 5.3.2 Cretan Sea (southern Aegean Sea) and western Cretan–Antikythera Straits

Cretan Sea stations (RED4, RED5, RED8, RED9) display, on average, lower pollutant load and terrestrial inputs compared to the central Ionian Sea deep basins and the northwestern Levantine deep basins, as inferred from TAHC, Ter.NA, UCM, TPAH\(_{25}\) absolute and OC-normalized concentrations (Tables 2,3; see also Sect. 4.3). \(\sum\text{Phe}/\sum\text{COMB}\) ratio values (Fig. 9a, Table 3), abundance of short-chain \(n\)-alkanes (Fig. 7b,c) and PAHs profile (Fig. 8b,c) indicate an enhanced contribution of fossil inputs at stations RED4 and RED5. At stations located in the western Cretan–Antikythera Straits and southern Crete (H01, RED3, RED3.1 and RED7, respectively), the abundance of long-chain \(n\)-alkanes (Fig. 7b,c) and PAHs profile characteristics (Fig. 8b,c), along with \(\sum\text{Phe}/\sum\text{COMB}\) and \(C_0/(C_0+C_1)\) Phe ratio values (Fig. 9a, b; Table 3), are indicative of strong fossil inputs in this area. Moreover, station RED3.1 located in the western Cretan Straits' canyons displays high TAHC, UCM, Ter.NA, TPAH\(_{25}\) absolute and OC-normalized concentrations (Tables 2,3), comparable to those found, those found in central Ionian Sea deep basins, and a twofold increase of concentrations in comparison to the neighboring RED3 located in the upper slope of the adjacent margin. Station RED7 located in
In order to assess the main processes driving hydrocarbons' distribution in deep-sea sediments of the study area, correlation analysis was performed for sedimentary aliphatic and polycyclic aromatic hydrocarbons concentrations (per dry weight and OC-normalized), OC content, water column depth and sedimentological parameters of collected sediments. Statistically significant correlations are presented in Table 4.

TAHC, UCM, NA, Ter.NA, TPAH$_{25}$, ∑COMB and ∑Phe concentrations show significant correlation with OC, indicating that OC exerts an important control on the distribution of both natural and anthropogenic hydrocarbons in the study area. This is in agreement with earlier observations in coastal and open-sea marine sediments (Bouloubassi et al., 2012; De Luca et al., 2004; Gogou et al., 2000; Mayer, 1993; Oros and Ross, 2004; Readman et al., 2002; Tsapakis et al., 2003; Witt, 1995; Yang, 2000) and is attributed to the high affinity of hydrophobic aliphatic and polycyclic aromatic hydrocarbons to organic matter.

TAHC show higher correlation to OC than TPAH$_{25}$ in terms of absolute (per dry weight) concentrations, reflected in both correlation coefficient values and level of significance, while although TAHC and TPAH$_{25}$ absolute concentrations correlate significantly at the 0.01 level, TAHC/OC- and TPAH$_{25}$/OC-normalized concentrations exhibit less significant correlation. The above imply that although OC exerts the main control on the distribution of both TAHC and TPAH$_{25}$ in the study area, the dispersal of PAHs is probably affected by additional factors, such as the partitioning between natural OC and combustion-derived elemental (black) carbon that has been reported to exert major control on PAHs’ distribution in sediments (Accardi-Dey and Gschwend, 2002, 2003). Consistently, TAHC/OC- and ∑COMB/OC-normalized concentrations do not exhibit any significant correlation, probably due to the fact that high-MW pyrolytic/combustion PAHs (∑COMB) show a higher affinity to elemental carbon rather than OC as a carrier phase (Boehm and Farrington, 1984; Gustafsson et al., 1997), while, in contrast, TAHC/OC- and ∑Phe/OC-normalized concentrations are significantly correlated at the 0.01 level. This trend probably reflects the fact that low-MW phenanthrenes (mostly of fossil origin), related to the dissolved and colloidal phases in the water column, are more efficiently absorbed by organic-rich particles, e.g., phytoplankton and fecal pellets, which constitute the major vehicles for
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Table 4. Summary of correlation coefficients (r) for aliphatics and PAHs, and OC-normalized concentrations.
particulate OC sinking in the deep sea (Berrojalbiz et al., 2009; Bouloubassi et al., 2006; Castro-Jiménez et al., 2012; Dachs et al., 1996, 1997).

The partitioning of aliphatic and polycyclic aromatic hydrocarbons in sediments has also been related to specific grain-size properties (i.e., clays, silts and/or sands; Boehm and Farrington, 1984; Bouloubassi et al., 2012; Prah and Carpenter, 1984). However, in our data set there is no significant correlation between aliphatic and polycyclic aromatic hydrocarbons’ concentrations and grain-size characteristics of collected sediments (Table 4). This implies that hydrocarbon phase associations may not be similar amongst various source materials and/or different regions in the study area, while an overprint resulting from point sources (mainly fossil due to intense maritime traffic) could also blur potential associations, and thus should be considered. Although extreme caution should be exercised when considering interpolations in wide geographical areas, since the overall low density of available stations may not allow appreciation of occurring variations, no significant correlation between aliphatic and polycyclic aromatic hydrocarbons’ concentrations and grain size was found even when limiting the data set to specific sub-regions (Ionian Sea, Cretan Sea, northwestern Levantine Sea; data not shown).

Overall, concentrations of total aliphatic hydrocarbons (TAHC) correlate with water column depth (Table 4), indicating that deep EMS basins act as their repository. However distinct trends are observed for various aliphatic components. Anthropogenic UCM concentrations (both absolute and OC-normalized) are better correlated with water column depth than terrestrial plant n-alkanes (Table 4), implying enhanced accumulation of fossil aliphatic hydrocarbons in deep-basin sediments relative to biogenic terrestrial ones. This is further supported by the significant correlation of CPI24-35 ($r = -0.559; p = 0.006$) and UCM/TrEs ($r = 0.656; p = 0.007$) with water column depth. Several factors could explain these trends. UCM is known to be more refractory than biogenic hydrocarbons (Simoneit, 1982), while different transport pathways and/or phase associations for natural and fossil aliphatic hydrocarbons may also have impacted on their distribution and fate. Moreover, although long-range atmospheric transport constitutes a major transport pathway for both terrestrial plant and fossil n-alkanes in the open EMS, the latter are also directly introduced into surface waters following the release of petroleum products (see Sect. 5.2).

Regarding PAHs, the lack of correlation between TPAH25, $\Sigma$COMB, $\Sigma$Phe concentrations and water column depth (Table 4) could probably be attributed to the partitioning of PAHs between natural OC and combustion-derived black carbon as discussed above. However, the selective degradation of low-MW phenanthrenes and differences in transport mechanisms/phase associations of individual PAH compounds discussed in Sect. 5.2 should also be considered. Amongst PAHs, retene does not correlate with terrestrial n-alkanes (Ter.NA) despite their common origin, while retene does not exhibit significant correlation either with OC. However, retene correlated significantly with high-MW pyrolytic/combustion PAHs ($\Sigma$COMB), indicating an overall probable relative significant contribution from sources related to pinewood combustion rather than terrestrial plant resins.

Lack of correlation between Ter.NA and $\Sigma$COMB concentrations also indicate different sources and/or transport pathways for naturally derived terrestrial n-alkanes and pyrolysis-combustion-derived PAHs. The above is in agreement with the fact that terrestrial n-alkanes are transported in aerosols, which constitute the likely major transport pathway of both Ter.NA and $\Sigma$COMB in the open EMS (see Sects. 2 and 5.2), both as plant waxes and smoke from biomass burning (Bendle et al., 2007; Yunker et al., 2011), while instead pyrolysis/combustion-derived $\Sigma$COMB compounds’ transport and dispersal is associated with fine soot and/or char black carbon combustion particles (Yunker et al., 2002, and references therein). Finally, NA concentrations significant correlation to $\Sigma$Phe could be attributed to the constituent characteristics of total n-alkanes, which except for Ter.NA, that account for an average of 50% of their total sum (see Sect. 5.2 and Table 2), comprise also of a large percentage of labile aliphatic compounds whose high relative abundance, as in the case of $\Sigma$Phe, is likely attributed to enhanced petroleum-related inputs in specific areas.

Water masses’ circulation characteristics also seem to influence regional features and distribution patterns of hydrocarbons in the study area. The low hydrocarbon content of station H12 located in the northeastern Ionian Sea, evidenced by the minimum values of TAHC, UCM, TPAH25, Ter.NA and corresponding OC-normalized concentrations (Tables 2,3; Sect. 5.3.1), is probably related to its low OC content (0.15%, Table 1) as a result of strong near-bottom currents that could lead to the resuspension and dispersal of sedimentary material (Poulos et al., 1999). Indeed, station H12 is predominantly composed (~80%) of poorly sorted silt with sand-sized fraction representing ~5% of the total mass (Pedrosa-Pàmies, unpublished data).

Deep Ionian Sea basins display high accumulation of both terrestrial-related natural inputs and petroleum-related anthropogenic inputs in comparison to both northwestern Levantine deep basins and Cretan Sea (Tables 2,3; Sects. 4.3 and 5.3.1). The renewal time of the Ionian deep and bottom waters is approximately 58 yr (Schlitzer et al., 1991), and thus deep Ionian Sea basins may act as a long-term repository of hydrocarbons exported from the Adriatic Sea, since the latter is their main deep-water source (see Sect. 2). Supportive to the above, stations H05 and H03 located along the outflow of deep Adriatic waters in the Ionian Sea present elevated Ter.NA and TAHC absolute and OC-normalized concentrations (Table 2) with an increasing trend from the shallower H05 to the deeper station H03, while station H05 also
This trend could be attributed to water masses’ circulation patterns of the Aegean Sea and mesoscale activity at the Cretan Straits exit, along with chemical characteristics of low-MW petrogenic PAHs. The latter, entering the water column through air–water diffusive exchange or directly into surface waters following the release of petroleum products, occur mainly in the dissolved phase, and thus display longer residence time in the water column prior to their settling, leading to a potential subjection to long-distance transport. The general cyclonic circulation of the Aegean Sea results in an almost constant net outflow, in the upper 400 m of depth, towards the EMS observed in the western Cretan Straits (Kontoyiannis et al., 1999, 2005). Surface water masses are also transformed during winter in the central Aegean Sea (and the Cyclades Plateau) into denser intermediate water which then fills the Cretan Basin, finally outflowing to the EMS through the Cretan Straits (Gertman et al., 2006). This transfer may be also be enhanced during periods of deep-water formation in the Aegean Sea, when dense water outflows through the eastern and western Cretan Straits’ canyons (Lykousis et al., 2011). Moreover, water masses exiting the Cretan Straits are subject to the influence of permanent/transient mesoscale gyres presented in Fig. 10. The above likely contribute to the southward transfer of petrogenic PAHs introduced into surface waters of the central Aegean Sea, comprising an important advective source of fossil-related PAHs for waters of the southern Aegean Sea and western Cretan–Antikythera Straits, with elevated inputs also reflected, following their subsequent settling, in their increased relative abundance in surface sediments.

In this procedure, the western Cretan Straits’ canyons and southern Crete deep basins (stations RED3.1 and RED7) seem to represent a significant sink for hydrocarbons, reflected in the almost twofold elevated values of TAHC, UCM, NA and TPAH₂₅ concentrations (Tables 2,3; Sect. 5.3.2), in agreement with earlier observations regarding the transfer and distribution of organic pollutants in deep-canyon settings (Bouloubassi et al., 2012; Dachs et al., 1997; Fang et al., 2009; Salvadó et al., 2012). The fact that the station located within the canyons (RED3.1) shows an approximately twofold increase in OC content compared to the neighboring station (RED3) located in the upper slope of the adjacent margin (Table 1) is in agreement with earlier observations of fine-grained and OC-rich sediment transfer in the western Cretan Straits’ canyons (Kerhervé et al., 1999; Pusceddu et al., 2010). Indeed, station RED3.1, and also RED7 in southern Crete, are mainly composed of silt and clay fractions (Pedrosa-Pàmies, unpublished data) that likely exert an important control on the enhanced accumulation of TAHC, UCM, NA and TPAH₂₅, but also Ter.NA, reflected in their elevated OC-normalized concentrations in these stations (Tables 2,3; Sect. 4.3), in agreement with earlier reports on the preferential partitioning/accumulation of aliphatic and polycyclic aromatic hydrocarbons in fine-grained sediment.

Fig. 10. Spatial contour map of % \(\Sigma\text{Phe}\) contribution in the central Aegean Sea, Cretan Sea (southern Aegean Sea), western Cretan–Antikythera Straits and northwestern Levantine surface sediments. Data regarding central Aegean Sea sediments are reported by Hatzianestis and Sklivagou (2001), data regarding Cretan Sea sediments are a combination of data reported in this study and data reported by Hatzianestis and Sklivagou (2001), while data regarding northwestern Levantine sediments are reported in this study. % \(\Sigma\text{Phe}\) are attributed to outstanding petroleum-related inputs, followed by an elevated contribution of % \(\Sigma\text{Phe}\) in the southern Aegean Sea (Cretan Sea) surface sediments. These data combined with results reported in this study (Fig. 10) evidence a decreasing southward trend for sedimentary % \(\Sigma\text{Phe}\) contribution from the central Aegean Sea to the Cretan Sea and western Cretan–Antikythera Straits.

This trend could be attributed to water masses’ circulation patterns of the Aegean Sea and mesoscale activity at the Cretan Straits exit, along with chemical characteristics of low-MW petrogenic PAHs. The latter, entering the water column through air–water diffusive exchange or directly into surface waters following the release of petroleum products, occur mainly in the dissolved phase, and thus display longer residence time in the water column prior to their settling, leading to a potential subjection to long-distance transport. The general cyclonic circulation of the Aegean Sea results in an almost constant net outflow, in the upper 400 m of depth, towards the EMS observed in the western Cretan Straits (Kontoyiannis et al., 1999, 2005). Surface water masses are also transformed during winter in the central Aegean Sea (and the Cyclades Plateau) into denser intermediate water which then fills the Cretan Basin, finally outflowing to the EMS through the Cretan Straits (Gertman et al., 2006). This transfer may be also be enhanced during periods of deep-water formation in the Aegean Sea, when dense water outflows through the eastern and western Cretan Straits’ canyons (Lykousis et al., 2011). Moreover, water masses exiting the Cretan Straits are subject to the influence of permanent/transient mesoscale gyres presented in Fig. 10. The above likely contribute to the southward transfer of petrogenic PAHs introduced into surface waters of the central Aegean Sea, comprising an important advective source of fossil-related PAHs for waters of the southern Aegean Sea and western Cretan–Antikythera Straits, with elevated inputs also reflected, following their subsequent settling, in their increased relative abundance in surface sediments.

In this procedure, the western Cretan Straits’ canyons and southern Crete deep basins (stations RED3.1 and RED7) seem to represent a significant sink for hydrocarbons, reflected in the almost twofold elevated values of TAHC, UCM, NA and TPAH₂₅ concentrations (Tables 2,3; Sect. 5.3.2), in agreement with earlier observations regarding the transfer and distribution of organic pollutants in deep-canyon settings (Bouloubassi et al., 2012; Dachs et al., 1997; Fang et al., 2009; Salvadó et al., 2012). The fact that the station located within the canyons (RED3.1) shows an approximately twofold increase in OC content compared to the neighboring station (RED3) located in the upper slope of the adjacent margin (Table 1) is in agreement with earlier observations of fine-grained and OC-rich sediment transfer in the western Cretan Straits’ canyons (Kerhervé et al., 1999; Pusceddu et al., 2010). Indeed, station RED3.1, and also RED7 in southern Crete, are mainly composed of silt and clay fractions (Pedrosa-Pàmies, unpublished data) that likely exert an important control on the enhanced accumulation of TAHC, UCM, NA and TPAH₂₅, but also Ter.NA, reflected in their elevated OC-normalized concentrations in these stations (Tables 2,3; Sect. 4.3), in agreement with earlier reports on the preferential partitioning/accumulation of aliphatic and polycyclic aromatic hydrocarbons in fine-grained sediment.

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fractions (Boehm and Farrington, 1984; Bouloubassi et al., 2012; Prahl and Carpenter, 1984).

6 Conclusions

Aliphatic and polycyclic aromatic hydrocarbons’ profile characteristics, source-specific molecular markers and their diagnostic indices reveal mixed contributions from both natural and anthropogenic compounds accumulating in deep-sea surface sediments of the eastern Mediterranean Sea (EMS). Natural hydrocarbons derive from both autochthonous marine (planktonic and bacterial inputs) and allochthonous (terrestrial vegetation, mainly higher plant waxes) sources, with the terrestrial fingerprint being the predominant one, probably due to the ultra-oligotrophic character of the eastern Mediterranean and the labile character of the marine-derived short-chain hydrocarbons. Anthropogenic inputs are reflected by PAHs of pyrolytic origin, related mainly to atmospheric inputs, and by fossil compounds both atmospherically derived and from intense maritime activities in the EMS, with the latter resulting in chronic oil pollution of surface sediments, as evidenced by the persistence of unresolved hydrocarbon mixture in all sampling sites.

Determined aliphatic and polycyclic aromatic hydrocarbons in the study area occur at levels comparable to those reported for open marine sites of the western Mediterranean Sea and worldwide, receiving low anthropogenic inputs. Amongst the deep EMS basins, the central Ionian Sea displays elevated levels of both anthropogenic and natural inputs, followed by deep basins of the northwestern Levantine and Cretan seas. Concentrations of both aliphatic and polycyclic aromatic hydrocarbons exhibit significant correlation with OC contents, indicating that the latter exerts a main control on their transport, fate and ultimate accumulation in deep EMS basins. However, the composition of hydrocarbon mixtures display significant regional variability, reflecting the relative importance of sources and differences in transport pathways and/or phase associations of biogenic terrestrial hydrocarbons and anthropogenic fossil and pyrolysis/combustion-derived hydrocarbons, which impact on their overall distribution and fate. Circulation patterns also seem to influence hydrocarbons’ regional features and distribution patterns, likely comprising an important advective source for fossil-related PAHs from the central Aegean Sea to the southern Aegean Sea and, subsequently, to the western Cretan–Antikythera Straits.

Major findings of this study highlight the role of deep EMS basins as repositories of both natural and anthropogenic hydrocarbons, while fine-grained and OC-rich sediment transfer likely exerts an important control on the enhanced accumulation of aliphatic and polycyclic aromatic hydrocarbons in the western Cretan Straits’ canyons and the southern Crete deep basins.

References


