Biogeosciences Discuss., 9, 19165–19197, 2012
www.biogeosciences-discuss.net/9/19165/2012/
doi:10.5194/bgd-9-19165-2012

Biogeosciences Discussions

Downward fluxes of elemental carbon, metals and polycyclic aromatic hydrocarbons in settling particles from the deep Ionian Sea (NESTOR site), Eastern Mediterranean

C. Theodosi[1], C. Parinos[2], A. Gogou[2], A. Kokotos[1], S. Stavrakakis[2], V. Lykousis[2], J. Hatzianestis[2], and N. Mihalopoulos[1]

[1]Environmental Chemistry Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece
[2]Institute of Oceanography, Hellenic Centre for Marine Research (HCMR), 46.7 km Athens-Sounion Av., 19013 Anavyssos, Attiki, Greece

Received: 30 November 2012 – Accepted: 11 December 2012
– Published: 21 December 2012

Correspondence to: N. Mihalopoulos (mihalo@chemistry.uoc.gr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

To assess sources and major processes controlling vertical transport of both anthropogenic and natural chemical species in deep basins of the Eastern Mediterranean Sea (SE Ionian Sea, Nestor site), we performed chemical characterization (elemental carbon, major and trace metals and polycyclic aromatic hydrocarbons) of marine sinking particles. Sediment traps were deployed at five successive depths, 700 m, 1200 m, 2000 m, 3200 m and 4300 m from the sea surface, during the period of May 2007 to October 2008. Fluxes of all measured species exhibited minimum values from January to March 2008 and maximum from April to September 2008, with an evident covariance revealing a common and rapid vertical transport mechanism from 700 m down to 4300 m depth. Crustal matter flux from atmospheric deposition plays an important role in the temporal variability of particulate matter with significant contribution from biogenic constituents namely the seasonal succession in the export of planktonic biomass, expressed by particulate organic carbon (POC), carbonates and biogenic Si fluxes (Stavrakakis et al., 2012). Tracers (elemental carbon, retene) of the devastating forest fires occurred in August 2007 in southern Greece, were detected at sediment trap material in all depths with a delay of 15 days at 4300 m, indicating a rapid and well-coupled transport of sinking particulate material between the sea-surface and deep layers of the Eastern Mediterranean Sea. Lateral inputs of pollutants at the deepest trap (4300 m) are probably of importance, due to the influence of deep Adriatic water at the study site.

1 Introduction

The Eastern Mediterranean Sea (EMS), due to its semi enclosed nature, is an area subjected to intense anthropogenic pressure (EEA, 2006), more specifically intense particulate and dissolved atmospheric inputs from the northern and central Europe transferring primary pollutants (Castro-Jiménez et al., 2012; Gogou et al., 1996; Koçak

BGD
9, 19165–19197, 2012

et al., 2012; Mara et al., 2009; Tsapakis and Stefanou, 2005) and the well known influence of Sahara dust events from northern Africa, containing natural crustal material (Guerzoni et al., 1999; Herut et al., 2005; Jickells, 1995; Ridame and Guieu, 2002; Saydam and Senyuva, 2002). The EMS continental runoffs and rivers contribution should also be considered since mesoscale variability enhances exchange between the continental shelf and slope waters. Additionally, the EMS receives substantial amounts of petroleum discharges, mainly along shipping routes (UNEP, 2010). The on-going industrialization of Europe (in particular Eastern Europe) and southern Mediterranean countries will probably lead to increasing trends for pollutant inputs to the area.

Once particulate matter and associated pollutants are deposited to the sea-surface, non soluble airborne particles can be repackaged and adsorbed within biomineral aggregates and be transferred directly through the water column with them (Buat-Ménard et al., 1989). Whilst, dissolved matter can also be incorporated into the pool of marine particulate matter either actively by biological uptake (Bruland et al., 1991) or passively by scavenging (Fisher et al., 1991). In general, dissolved matter is exported to the deep-sea with the downward flux of aggregates in the form of marine snow (Lampitt et al., 2001; Passow, 2004), which is accelerated by vertical migrations of zooplankton and production of fast sinking faecal pellets (Dachs et al., 2002; Fowler, 1977). Large size particles such as faecal pellets and large aggregates (marine snow) exhibit high settling velocities (50–200 $m\,d^{-1}$) and presumably collect and scavenge amounts of mineral particles too small to sediment individually (Passow, 2004).

Elemental Carbon (EC) which is considered to be a good tracer of combustion processes (fossil fuel combustion, namely urban emissions from road transport as well as biomass burning) is emitted directly in the particulate phase and is therefore always primary material (Pio et al., 2011). Metals such as Al, Fe, Cu and Cr usually originate from soil dust or mechanical abrasion processes. Cd, V and Ni are generally considered to have anthropogenic emission sources, such as vehicular, industrial emissions and resuspension (Lough et al., 2005; Salma and Maenhaut, 2006; Sternbeck et al., 2002). Specifically V and Ni have been used as fuel-oil combustion tracers (Lough

BGD
9, 19165–19197, 2012

et al., 2005). Furthermore it has been reported (Weckwerth, 2001) that Cu derives from brake linings, while Fe, Cu and Ba are the three predominant elements identified in the debris, regardless of the material used in the brake lining (Adachi and Tainosho, 2004; Lough et al., 2005).

Polycyclic aromatic hydrocarbons (PAHs) constitute a unique class of persistent organic pollutants with carcinogenic and mutagenic properties (Samanta et al., 2002 and references therein). They originate from various anthropogenic activities including combustion/pyrolysis of fossil fuels, biomass burning, industrial processes, petroleum processing and transportation (Laflamme and Hites, 1978; Neff, 1979; Wakeham et al., 1980). Atmospheric deposition is considered an important pathway for the introduction of PAHs across the EMS (Castro-Jiménez et al., 2012; Gogou et al., 1996) while since PAHs are main constitutes of petroleum enhanced petroleum discharges in the area are also of major importance.

Despite the important information obtained by analyzing sediment trap material, only few studies have quantified the flux of major and trace metals in the Mediterranean Sea, mainly in the western basin (Heimburger et al., 2010, 2012; Martin et al., 2009; Migon et al., 2002), while in turn the Mediterranean is rich in sediment trap studies reporting PAH settling fluxes (Bouloubassi et al., 2006; Dachs et al., 1996; Deyme et al., 2011; Gogou, 1998; Lipiatou et al., 1993; Raoux et al., 1999; Tsapakis et al., 2006). According to our knowledge, no work has been performed to quantify the flux of trace metals in the Eastern Mediterranean Sea.

The present study quantifies for the first time simultaneous determination of elemental carbon (EC), metals and PAH fluxes in the SE Ionian Sea at a sediment trap line deployed in NESTOR basin (Eastern Mediterranean) from May 2007 to October 2008 at five successive water column depths (700 m, 1200 m, 2000 m, 3200 m and 4300 m) and examines the role of seasonal changes in the biochemical composition of settling particles (presented by Stavrakakis et al., 2012) as a driving force for their export to the deep Ionian Sea basins. Delineation of the strong variability of vertical fluxes by time-series studies is essential for understanding pollutant's fate and building

BGD
9, 19165–19197, 2012

pollutant budgets in the Mediterranean Sea (Marine Strategy Framework Directive – 2008/56/EC).

2 Materials and methods

2.1 Sampling

Sediment trap deployment is described in detail by Stavrakakis and Lykousis (2011) and Stavrakakis et al. (2012). Briefly, one mooring line, NESTOR 4.5, was deployed in SE Ionian Sea, Greece (21°28.93′ E, 36°32.96′ N; Fig. 1) within the framework of KM3NeT project. The mooring line was deployed at 4500 m depth instrumented with five automated time-series sediment traps (Technicap PPS3/3; Heussner et al., 1990) set at 700 m, 1200 m, 2000 m, 3200 m and 4300 m depth. Samples were collected on a two-week basis from 20 May 2007 to 15 October 2008. However, due to technical difficulties samples were not obtained for the periods of 16–31 October 2007 and 16–21 April 2008 at all depths.

2.2 Analysis

After recovery all samples were divided into aliquots for determination of elemental carbon (EC), major (Al, Mn and Fe) and trace metal (V, Cr, Ni, Cu, Cd and Pb) and polycyclic aromatic hydrocarbons (PAHs). All subsamples were filtered through pre-weighted and pre-combusted (450 °C, 6h) Whatman GF/F and were freeze-dried prior to analysis. A short description of the analytical techniques used for the analysis of major compound groups is presented below.

Elemental carbon: Analysis of sediment trap material for EC was performed using the Thermal-Optical Transmission (TOT) technique (Birch and Cary, 1996) on a Sunset Laboratory OC/EC Analyzer, as described in detail by Theodosi et al. (2010a).

Major and trace elements: Filters processed for major and trace metals were subjected to digestion with concentrated nitric acid (puriss. p.a., Fluka Prod. No.84380)

BGD
9, 19165–19197, 2012

under controlled conditions (Berghof Microwave System-2, Teflon vessels (DAP – 60 K, 60ml/40bar). After cooling to room temperature, the digested solution was transferred to an acid-cleaned polyethylene container and stored in the freezer. The solutions thus obtained were finally analyzed by Inductively Coupled Plasma Mass Spectrometry (*ICP-MS,Thermo Electron X Series)*, following the technique described in detail by Theodosi et al. (2010b). Indium was added as an internal standard to the samples prior to ICP-MS analysis and calibration curves were performed for each analytical batch using standard certified solutions by CPI International (r^2 = 0.9999).

Polycyclic aromatic hydrocarbons: Filters processed for polycyclic aromatic hydrocarbons were initially spiked with a mixture of perdeuterated internal standards ([$^2H_{10}$]phenanthrene, [$^2H_{10}$]pyrene, [$^2H_{12}$]chrysene, [$^2H_{12}$]perylene and [$^2H_{12}$]benzo[ghi]perylene) and were analyzed applying a modified protocol after Gogou et al. (1998). Details regarding the analytical procedure and instrumental analysis are described in detail by Parinos et al. (2012). Twenty-one PAHs, parent (unsubstitued) compounds with 2–6 aromatic rings and alkyl-substituted homologues were determined. A list of the studied compounds along with their corresponding abbreviations in the text is presented in Fig. 2. $TPAH_{21}$ refers hereafter to the total sum of PAHs monitored.

3 Results and discussion

Average fluxes of individual compounds reported in this study are time-mass flux weighted means, since the sampling interval is not constant and the temporal variability of mass flux must be taken into account (Heussner et al., 2006). Mass flux and particulate organic carbon (POC) flux data as well as processes controlling their temporal and depth variability are addressed in detail by Stavrakakis et al., (2012). In order to better assess the variability of the individual compounds reported in this manuscript, POC temporal distribution will also be depicted (Fig. 3c, d).

BGD
9, 19165–19197, 2012

3.1 Composition of settling particles

3.1.1 Elemental carbon

EC fluxes during the studied period ranged from 0.03 to 6.77 mg m^{-2} d^{-1} accounting for 2.4 to 2.9 % of the particulate matter flux at all depths (Table 1).

The EC seasonal and depth related flux distributions are depicted in Figs. 3 c, d and 4b. An almost identical variation of EC was evident between the two upper traps (700 m and 1200 m), the two traps deployed at 2000 m and 3200 m, while the deepest trap (4300 m) was characterized by a slightly different trend. EC flux follows a decreasing trend with depth from nearly 1.88 mg m^{-2} d^{-1} at 700 m to 0.41 mg m^{-2} d^{-1} at 3200 m. Since EC is not participating in the food chain, the decrease with depth most probably indicates coating of EC with soluble material. It should be noted that the decrease in the EC flux with depth was not evident at the deepest trap (4300 m), suggesting the occurrence of lateral transport of particulate matter at deep basins of the Ionian Sea. For more details on transport patterns see Stavrakakis et al. (2012).

EC flux reached its highest values during late spring/summer periods (April to August; Figs. 3c, d and 4b), coinciding with POC and Total mass flux distribution (Figs. 3a–d, 4a). In particular, the highest EC fluxes were recorded during summer 2008 at the three upper traps (average of all three traps being 3.50 ± 2.23 mg m^{-2} d^{-1}, with average for the whole sampling period 1.73 ± 1.65 mg m^{-2} d^{-1}).

3.1.2 Major and trace metals

The average values of major and trace metal fluxes are depicted in Table 1. Crustal derived element (Al, Fe and Mn) fluxes ranged from 4.20×10^{-4} to 9.46 mg m^{-2} d^{-1}, gradually decreasing from the shallower to the deeper traps. Highest values were generally found at 700 m depth with values ranging from 3.28×10^{-3} to 7.88 mg m^{-2} d^{-1} and lowest values at 3200 m depth ranging from 4.20×10^{-4} to 1.51 mg m^{-2} d^{-1}. A concomitant increase in crustal element fluxes is evident at 4300 m suggesting lateral transport.

BGD
9, 19165–19197, 2012

The fluxes of anthropogenic metals (V, Ni, Cd and Pb) at the shallower traps were characterized by very high values, ranging from 2.57×10^{-3} to 1.22 $\mu g\,m^{-2}\,d^{-1}$ at 700 m, which trended to decrease slightly, as in the case of crustal elements, with increment of collecting depth, from 7.56×10^{-4} at 700 m to 1.90 $\mu g\,m^{-2}\,d^{-1}$ at 3200 m. An increase was also apparent at 4300 m, attributed to lateral transport (see Sect. 3.4).

Crustal matter flux was determined using Fe or Al as tracers of crustal elements, assuming a relative ratio of 4.5 % and 7.1 % for each sample, respectively (Guieu et. al., 2002; Wedepohl, 1995). The average crustal content of the sediment trap material in the study area, using Fe as reference, ranged from 45 % to 54 % indicating that crustal material is the most important constituent of sinking material, as demonstrated also by Stavrakakis et al. (2012).

3.1.3 Polycyclic aromatic hydrocarbons

A typical molecular profile of PAHs in sinking particles at 700 m and 4300 m depth in the study area is presented in Fig. 2. Phenanthrene and its methyl- and dimethyl-homologues dominated the molecular profile of low molecular weight PAHs (≤ 3 aromatic rings) at both depths. Their sum, referred to hereafter as $\sum$Phe, averaged 42 ± 6 % of $TPAH_{21}$. As for higher MW PAHs (≥ 4 aromatic rings) of pyrolytic origin (Neff, 1979), their sum, referred to hereafter as $\sum$COMB, accounted on average for 39 ± 8 % of $TPAH_{21}$. Their profile was dominated by benzo[*ghi*]perylene primarily and benzofluoranthenes secondarily. Perylene (MW 252) is not comprised in $\sum$COMB sum since it may have natural sources (Venkatesan, 1988). Retene was the major naturally-derived PAH determined in this study (Ramdahl, 1983).

Average fluxes of $TPAH_{21}$, $\sum$Phe and $\sum$COMB at 700 m and 4300 m depth are presented in Table 1. PAH fluxes varied significantly with $TPAH_{21}$ flux ranging from 8.87 to 211 $ng\,m^{-2}\,d^{-1}$. $\sum$Phe fluxes ranged from 3.85 to 115 $ng\,m^{-2}\,d^{-1}$, while $\sum$COMB fluxes from 2.77 to 56.4 $ng\,m^{-2}\,d^{-1}$. PAH fluxes were higher at 700 m, ranging from 12.6 to 211 $ng\,m^{-2}\,d^{-1}$, than at 4300 m were values between 8.87 and 133 $ng\,m^{-2}\,d^{-1}$ were

BGD
9, 19165–19197, 2012

recorded. In contrary, average PAH concentrations were slightly higher at 4300 m (Table 1). $TPAH_{21}$ flux temporal variability is presented in Fig. 5. $TPAH_{21}$ flux at 700 m presented maxima during summer of 2008 with peaks at late June, late July and high fluxes throughout August, while in turn, at 4300 m $TPAH_{21}$ flux presented maxima at late spring, late April and throughout May 2008, in agreement with mass flux fluctuations in corresponding depths for the same periods (Fig. 4a).

3.2 Comparison with literature data

Table 2 presents fluxes of PAHs, major and trace metals reported in previous sediment trap studies in the Mediterranean Sea. Fluxes of major and trace metals reported in this study can be only compared to previous studies in the Western Mediterranean Sea. Furthermore, despite the different sampling periods and the possibility of interannual variation, fluxes presented for major and trace elements are comparable and in fact lower to those reported for Ligurian Sea (DYFAMED, Martin et al., 2009; Migon et al., 2002).

As for PAHs, fluxes reported in this study are comparable to those reported for the open Western Mediterranean Sea (Bouloubassi et al., 2006) and Alboran Sea (Dachs et al., 1996), higher than those previously reported for the Eastern Mediterranean Sea (Gogou, 1998; Tsapakis et al., 2006) and considerably lower than those reported in settings such as coastal and near continent Ligurian Sea (DYFAMED, Deyme et al., 2011; Lipiatou et al., 1993) and French coast (Raoux et al., 1999).

3.3 Origin of natural and anthropogenic compounds in the deep Ionian Sea

The composition of the settling particulate matter described above reflects contributions from both natural and anthropogenic sources in the study site.

Correlations between the various metals and EC at all depths, both in terms of fluxes and mass ratios were studied. The fact that all elements, regardless of their origin, are strongly and significantly ($p < 0.01$) intercorrelated when fluxes are considered,

BGD
9, 19165–19197, 2012

suggests a common transport mechanism in the deep layers of the Ionian Sea (Nestor site).

Furthermore in terms of mass ratios, statistically significant correlations ($p < 0.01$) are observed between elements of same origin but also between elements of different origin. More specifically in terms of concentrations for two indicative water depths, 700 m and 4300 m, statistically significant correlations are observed between crustal species (e.g. Al, Fe) and anthropogenic species (e.g. V, Ni). For the latter, which have been used as fuel-oil combustion tracers (Lough et al., 2005), a comparatively good correlation was observed for the trap deployed at 700 m ($r = 0.48$), with no significant correlation at the deepest trap providing evidence that the atmosphere is an important pathway, demonstrating residual oil combustion as a contributing source. Regarding Al and Fe, of crustal origin, a strong correlation was observed, as expected in the deepest trap ($r = 0.74$).

Elements of "mixed", crustal and anthropogenic origin reveal considerable correlation amongst them (e.g. Fe vs. V, Ni; $r > 0.45$ at 700 m and Fe vs. V, Cu, Pb; $r > 0.54$ at 4300 m). Particularly interesting are the intercorrelations of crustal originated elements Al and Fe with V and Mn in the shallower (Fe vs. V, Mn $r > 0.71$) and the deepest trap (Al, Fe vs. V, Mn; $r > 0.78$).

Furthermore, in order to determine the prevailing source of elements in the area, the Enrichment Factor (EF) of all elements relative to the Saharan end-member was calculated, using Fe as crustal marker (Chester et al., 1990). By convention, an arbitrary average EF value lower than 10 is taken as an indication that an element has a predominant reference material source. In contrast, EF higher than 10 is considered to indicate that a significant proportion of an element has a non-reference material source. For our data the low EF (< 10) for all studied elements and depths indicates significant contribution from a crustal source.

In the PAHs family, the predominance of 3-ring alkylated homologues (phenanthrene series) and the presence of parent compounds with ≥ 4 aromatic rings (Fig. 2), indicate a contribution of both petrogenic and pyrolytic PAHs in shallow and deep waters of the

BGD
9, 19165–19197, 2012

study area (Neff, 1979; Wakeham et al., 1980). Moreover, diagnostic ratios have been used to infer conclusions regarding the origin and different sources of PAHs at both depths (Yunker et al., 2002). The Flth/(Flth+Pyr), IndP/(IndP+BgP), BaA/(BaA+Chry) and 1.7/(1.7 + 2.6) C_2-Phe ratios (Fig. 6a, b) evidence the presence of PAHs deriving from multiple sources such as wood, coal and petroleum combustion, along with petroleum residues during summer of 2008.

Concentrations of pyrolytic PAHs (∑COMB) correlate significantly with EC concentrations at 700 m depth ($r = 0.679$, $p < 0.01$). This result is consistent with the strong association of PAH derived from pyrolytic combustion sources to fine combustion soot particles as reported elsewhere (Dachs and Eisenreich, 2000; Dachs et al., 2002; Gustafsson et al., 1997) and emphasizes the importance of soot particle association as a driving force for pyrolytic PAH export out of the photic zone. The lack of correlation between ∑COMB-EC concentrations at 4300 m indicates a decoupling between surface and deep waters in the study area. However lateral inputs of particulate matter at this depth (e.g. Adriatic deep water, see Stavrakakis et al., 2012) should be considered as a possible masking factor for ∑COMB-EC concentrations association.

3.4 Seasonal, depth related distribution of natural and anthropogenic compounds and their driving parameters in deep Ionian Sea

Figure 4a clearly shows that total mass flux of particulate matter at the 4 upper traps (700 m, 1200 m, 2000 m and 3200 m) is characterized by a slight decrease with increasing depth (Stavrakakis et al., 2012). Comparison of the seasonal patterns reveals that similar periods of high and low fluxes are observed for all measured natural and anthropogenic compounds in our study (Figs. 2–5) and major biochemical species (Stavrakakis et al., 2012). However, the aforementioned observation was stronger and more evident at the 4 upper traps (Fig. 4). In contrast the seasonal decrease in the flux of all constituents recorded at 4300 m did not follow the patterns described for total mass flux, thus providing supporting evidence that lateral transport of particulate matter is of importance in the area at least at this depth.

BGD
9, 19165–19197, 2012

Mass flux temporal variability in the study area is subjected to strong seasonality which is driven by the succession of plankton communities in the overlying surface layer. According to this, export patterns associated to biologically driven processes, are expressed by particulate organic carbon (POC), carbonates and biogenic Si fluxes (Stavrakakis et al., 2012). These authors also suggested that atmospheric dust inputs, witnessed by the enhanced fluxes of the lithogenic fraction during certain periods of the time-series flux experiment, are also crucial.

As it is clearly seen in Fig. 3a, b for the time series of total mass fluxes and total atmospheric deposition mass fluxes (Mihalopoulos and Theodosi, unpublished data) a similar pattern in their variability is evident with a time lag of 15–30 days in the deepest trap. Crustal material could be an important driver as it comprises more than a half of the sinking mass. Theodosi et al. (2012) have shown that atmospheric deposition of dust can entirely account for the measured levels of crustal material in sediment traps. Deposition measurements of dust on Crete island showed that during 2008 dust deposition was 38 % higher compared to 2007 (Mihalopoulos and Theodosi, unpublished data). As measurements on Crete have more a regional than local significance this result concerns the majority of the Eastern Mediterranean basin. The increase in dust deposition (8.8 to 14.1 $g\,m^{-2}\,yr^{-1}$, in 2007 and 2008 respectively) could explain the increase in mass flux between 2007 and 2008 by almost the same amount, associated with an increase in fluxes of all analysed elements. The recorded maxima in mass flux from May 2008 to September 2008, not coinciding with atmospheric deposition is attributed to mixed biogenic fluxes (e.g. increase in the carbonate and opal contents during the second phase of this period; Stavrakakis et al., 2012).

Note also that there is a covariance between crustal mass ratio variability and the variability of mass flux indicating the important role of crustal material (Fig. 7), deriving mainly from the atmosphere (at least at the upper traps; Fig. 3a). The importance of atmosphere-seawater coupling is further highlighted in the following section.

BGD
9, 19165–19197, 2012

3.5 Transport of organic pollutants to deep basins of the Eastern Mediterranean Sea during massive forest fires of summer 2007 in Greece

Strong winds, heat waves and extended droughts in several areas across Greece during the summer of 2007, resulted in the brake out of severe forest fires which devastated a total of 670 000 acres (2700 km^2) of forest, olive groves and farmlands. 370 000 (1500 km^2) of the total 670 000 acres of forests were burnt in western and southern Peloponnese, Southern Greece, from 23 till 30 August 2007.

Turquety et al. (2009) reported that the CO burden emitted during those 7 days of the Peloponnese fires (estimated at about 0.321 Tg CO) accounted for approximately 40 % of the expected annual anthropogenic emissions for this region. Satellite images (Fig. 8) clearly show the existence of fire plumes to the south-west, directly over the sampling site, across the Mediterranean towards Libya and Tunisia in North Africa, as the last week of August 2007 was characterized by strong North-Easterly winds above Greece (Turquety et al., 2009).

Stavrakakis and Lykousis (2011) reported that during the Peloponnese fires period, a peak in total mass flux was recorded at 700 m which was also recorded after 15-days at all depths. The authors concluded that this peak was due to the atmospheric transport and deposition of elemental carbon emitted from the fire, as indicated by the presence of microscope visible charcoal fragments. As verified by our results, such peak for the EC flux was recorded for the trap at 700 m (Table 3). More specifically, EC flux presented a clear maxima for the period from 16 to 31 August 2007 (Fig. 4b), 2 $mg\,m^{-2}\,d^{-1}$, value which is a factor of 8–9 times higher compared to the value measured before and after this sampling period (1–15 August and 1–15 September; 0.2 $mg\,m^{-2}\,d^{-1}$ and 0.3 $mg\,m^{-2}\,d^{-1}$, respectively). This increase in EC flux was also clearly observed at 1200 m and 2000 m with a 15-days delay. At the same time, the average EC mass ratio at 700 m was equal to 33.4 $mg\,g^{-1}$ during the period of forest fires (16 to 31 August 2007), increased by a factor of 1.1–1.4 compared to the periods of 1–15 August

BGD
9, 19165–19197, 2012

and 1–15 September of the same year. Similar tendency with a 15-days delay can be observed at 1200 and 2000 m.

A number of facts inferring from the analysis of PAHs further support the above statement (Table 3). Retene's concentration showed similar trends not only as an absolute concentration but also as a percentage of the total sum of PAHs ($TPAH_{21}$). At 4300 m depth, concentration of retene increased from 39.5 ng g^{-1} for the period from 16 to 31 August 2007 to 128 ng g^{-1} in the following days (1 to 15 September 2007). The percent of retene for $TPAH_{21}$ increased from 4 % to 12 % for the same period. Retene is a common diterpenoid constituent of conifer resins in temperate climates (Laflamme and Hites, 1978) and is rapidly formatted during pinewood combustion (Ramdahl, 1983). Thus forest soils and forest fires constitute the principal sources of retene in the marine environment through riverine inputs and atmospheric deposition (Lipiatou and Saliot, 1991).

Pimanthrene (1.7 C_2-Phe) another common diterpenoid constituent of plant resins, especially from coniferous trees showed similar trends with retene (Table 3). At 4300 m of depth, concentration of pimanthrene increased from 15.1 ng g^{-1} for the period from 16 to 31 August 2007 to 25.3 ng g^{-1} in the following days (1 to 15 September 2007). Its percent for $TPAH_{21}$ also increased from 1.4 % to 2.4 %. $TPAH_{21}$ flux (Fig. 5) following the total mass flux trend increased from 16.6 to 112 ng m^{-2} d^{-1} at 4300 m during the aforementioned periods.

An important outcome of the massive 2007 summer forest fires that must be also taken into consideration is that the high values of the Flth/(Flth+Pyr) (> 0.50) recorded at both 700 m and 4300 m of depth during the following winter 2008 period indicating wood and coal combustion sources, could be attributed to increased continental run-offs and/or river discharges of PAHs accumulated in soils of burned forest areas, as a result of soil leaching and extended erosion during winter period rainfalls.

To conclude, the above indicate that forest fire emissions undergo a very rapid and significant transport and deposition even to the deepest basins of the Eastern Mediterranean Sea, through atmospheric deposition of wood and grass charcoal black carbon

BGD
9, 19165–19197, 2012

emitted from burning plants tissue which provide matrices stable enough to trap and stabilize PAHs, allowing their efficient transport to deep basins (Yunker et al., 2011 and references therein). Indeed transport time ranged from a few days at the upper trap (700 m) to less than 15 days down to 4300 m depth.

4 Conclusions

The most evident characteristic of the oligotrophic environment studied was the fact that elemental carbon, metals and polycyclic aromatic hydrocarbons fluxes decreased from the surface towards the deeper water layers of the Ionian Sea. The covariance which is evident between all measured species reveals a common transport mechanism, driven by the seasonal succession of planktonic species, crustal matter and anthropogenic inputs. This concomitant temporal variability occurring in the upper marine layer is not apparent at near bottom trap suggesting that lateral transport of particulate matter, most probably related to the influence of Adriatic deep water mass, is of importance in the study area.

The chemical species described in this study, related to sinking matter reflect contribution from both natural and anthropogenic sources in deep Ionian Sea basins. Crustal originated elements (Al, Fe and Mn) and elements characteristic of anthropogenic sources (V, Ni, Cd and Pb) presented the same seasonal variability, suggesting that the common transport mechanism to the sampling site is atmospheric deposition. Molecular profile and diagnostic ratios of PAHs indicate a contribution of both petrogenic and pyrolytic PAHs in shallow and deep waters of the study area, deriving from multiple sources such as wood, coal and petroleum combustion along with petroleum residues during summer of 2008, with soot particle association being a major driving force for pyrolytic PAH export out of the photic zone.

Forest fire emissions found to undergo a rapid, less than 15 days, and significant transport and deposition to the deep basins of the Eastern Mediterranean Sea during summer fires of 2007 in western and southern Peloponnese, Greece, through

BGD
9, 19165–19197, 2012

atmospheric atmospheric transport and deposition of charcoal black carbon and associated organic compounds, emitted during the forest fire.

Acknowledgements. This work has been supported by KM3NET IP (EU/FP6) and HERMIONE IP (EU/FP7) projects. Many thanks to the officers and crew of R/V AEGAEO (Hellenic Centre for Marine Research, Greece) for their precious help during deployments and recoveries of the sediment traps. We would also like to thank G. Kambouri and I. Stavrakaki for the preliminary treatment of sediment trap samples. CT and NM acknowledge financial support from EU IP project Perseus (Grant agreement 287600).

References

Adachi, K. and Tainosho, Y.: Characterization of heavy metal particles embedded in tire dust, Environ. Int., 30, 1009–1017, doi:10.1016/j.envint.2004.04.004, 2004.

Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, Aerosol Sci. Tech., 25, 221–241, 1996.

Bouloubassi, I., Méjanelle, L., Pete, R., Fillaux, J., Lorre, A., and Point, V.: PAH transport by sinking particles in the open Mediterranean Sea: a 1 year sediment trap study, Mar. Pollut. Bull., 52, 560–571, doi:10.1016/j.marpolbul.2005.10.003, 2006.

Bruland, K. W., Donat, J. R., and Hutchins, D. A.: Interactive influences of bioactive trace metals on biological production in oceanic waters, Limnol. Oceanogr., 36, 1555–1577, 1991.

Buat-Menard, P.: Non-steady-state biological removal of atmospheric particles from Mediterranean surface waters, Nature, 340, 131–134, 1989.

Castro-Jiménez, J., Berrojalbiz, N., Wollgast, J., and Dachs, J.: Polycyclic aromatic hydrocarbons (PAHs) in the Mediterranean Sea: atmospheric occurrence, deposition and decoupling with settling fluxes in the water column, Environ. Pollut., 166, 40–47, doi:10.1016/j.envpol.2012.03.003, 2012.

Chester, R., Nimmo, M., Murphy, K. J. T., and Nicolas, E.: Atmospheric trace metals transported to the western Mediterranean: data from a station on Cap Ferrat, in: Water Pollution Research Reports, vol. 20, edited by: Martin J. M. and Barth H., Commission of the European Communities, 597–612, 1990.

BGD

9, 19165–19197, 2012

Dachs, J., Bayona, J. M., Fowler, S. W., Miquel, J. C., and Albaigés, J.: Vertical fluxes of polycyclic aromatic hydrocarbons and organochlorine compounds in the western Alboran Sea (southwestern Mediterranean), Mar. Chem., 52, 75–86, 1996.

Dachs, J., and Eisenreich, S. J.: Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons, Environ. Sci. Tech., 34, 3690–3697, doi:10.1021/es991201+, 2000.

Dachs, J., Lohmann, R., Ockenden, W. A., Méjanelle, L., Eisenreich, S. J., and Jones, K. C.: Oceanic biogeochemical controls on global dynamics of persistent organic pollutants, Environ. Sci. Tech., 36, 4229–4237, doi:10.1021/es025724k, 2002.

Deyme, R., Bouloubassi, I., Taphanel-Valt, M. H., Miquel, J. C., Lorre, A., Marty, J. C., and Méjanelle, L.: Vertical fluxes of aromatic and aliphatic hydrocarbons in the Northwestern Mediterranean Sea, Environ. Pollut., 159, 3681–3691, doi:10.1016/j.envpol.2011.07.017, 2011.

European Environment Agency: Priority issues in the Mediterranean environment, EEA Report no. 4, EEA, Copenhagen, 2006.

Fisher, N. S., Nolan, C. V., and Fowler, S. W.: Scavenging and retention of metals by zooplankton fecal pellets and marine snow, Deep Sea Res. Pt. I, 38, 1261–1275, 1991.

Fowler, S. W.: Trace elements in zooplankton particulate products, Nature, 269, 51–53, doi:10.1038/269051a0, 1977.

Gogou, A.: Study of the biogeochemical cycle of natural and anthropogenic organic compounds in northeastern Mediterranean region, PhD thesis, University of Crete, Greece, 160–163 pp., 1998.

Gogou, A., Stratigakis, N., Kanakidou, M., and Stephanou, E. G.: Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories, Org. Geochem., 25, 79–96, doi:10.1016/s0146-6380(96)00105-2, 1996.

Gogou, A. I., Apostolaki, M., and Stephanou, E. G.: Determination of organic molecular markers in marine aerosols and sediments: one-step flash chromatography compound class fractionation and capillary gas chromatographic analysis, J. Chromatogr. A, 799, 215–231, doi:10.1016/s0021-9673(97)01106-0, 1998.

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loÿe-Pilot, M. D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., and Ziveri, P.: The role of

BGD
9, 19165–19197, 2012

atmospheric deposition in the biogeochemistry of the Mediterranean Sea, Prog. Oceanogr., 44, 147–190, doi:10.1016/s0079-6611(99)00024-5, 1999.
Guieu, C., Loÿe-Pilot, M. D., Ridame, C., and Thomas, C.: Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the western Mediterranean Sea, J. Geoph. Res., 107, 4258, doi:10.1029/2001JD000582, 2002.
Gustafsson, Ö., Haghseta, F., Chan, C., Macfarlane, J., and Gschwend, P. M.: Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability, Environ. Sci. Tech., 31, 203–209, doi:10.1021/es960317s, 1997.
Heimbürger, L.-E., Migon, C., Losno, R., Miquel, J.-C., Leblond, N., and Cossa, D.: Factors controlling the temporal variability of mass and trace metal downward flux at 1000 m depth at the DYFAMED site (Northwestern Mediterranean Sea), Biogeosciences Discuss., 7, 2549–2567, doi:10.5194/bgd-7-2549-2010, 2010.
Heimbürger, L. E., Cossa, D., Thibodeau, B., Khripounoff, A., Mas, V., Chiffoleau, J. F., Schmidt, S., and Migon, C.: Natural and anthropogenic trace metals in sediments of the Ligurian Sea (Northwestern Mediterranean), Chem. Geol., 291, 141–151, doi:10.1016/j.chemgeo.2011.10.011, 2012.
Herut, B., Zohary, T., Krom, M. D., Mantoura, R. F. C., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., and Frede Thingstad, T.: Response of East Mediterranean surface water to Saharan dust: on-board microcosm experiment and field observations, Deep-Sea Res. Pt. II, 52, 3024–3040, doi:10.1016/j.dsr2.2005.09.003, 2005.
Heussner, S., Ratti, C., and Carbonne, J.: The PPS 3 time-series sediment trap and the trap sample processing techniques used during the ECOMARGE experiment, Cont. Shelf Res., 10, 943–958, 1990.
Heussner, S., Durrieu de Madron, X., Calafat, A., Canals, M., Carbonne, J., Delsaut, N., and Saragoni, G.: Spatial and temporal variability of downward particle fluxes on a continental slope: lessons from an 8-yr experiment in the Gulf of Lions (NW Mediterranean), Mar. Geol., 234, 63–92, doi:10.1016/j.margeo.2006.09.003, 2006.
Jickells, T.: Atmospheric inputs of metals and nutrients to the oceans: their magnitude and effects, Mar. Chem., 48, 199–214, doi:10.1016/0304-4203(95)92784-p, 1995.
Koçak, M., Theodosi, C., Zarmpas, P., Séguret, M. J. M., Herut, B., Kallos, G., Mihalopoulos, N., Kubilay, N., and Nimmo, M.: Influence of mineral dust transport on the chemical composition and physical properties of the Eastern Mediterranean aerosol, Atmos. Environ., 57, 266–277, doi:10.1016/j.atmosenv.2012.04.006, 2012.

BGD
9, 19165–19197, 2012

Laflamme, R. E. and Hites, R. A.: The global distribution of polycyclic aromatic hydrocarbons in recent sediments, Geochim. Cosmochim. Ac., 42, 289–303, 1978.
Lampitt, R. S., Bett, B. J., Kiriakoulakis, K., Popova, E. E., Ragueneau, O., Vangriesheim, A., and Wolff, G. A.: Material supply to the abyssal seafloor in the northeast Atlantic, Prog. Oceanogr., 50, 27–63, doi:10.1016/s0079-6611(01)00047-7, 2001.
Lipiatou, E. and Saliot, A.: Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western Mediterranean Sea, Mar. Chem., 32, 51–71, 1991.
Lipiatou, E., Marty, J. C., and Saliot, A.: Sediment trap fluxes of polycyclic aromatic hydrocarbons in the Mediterranean Sea, Mar. Chem., 44, 43–54, 1993.
Lough, G. C., Schauer, J. J., Park, J. S., Shafer, M. M., Deminter, J. T., and Weinstein, J. P.: Emissions of metals associated with motor vehicle roadways, Environ. Sci. Tech., 39, 826–836, doi:10.1021/es048715f, 2005.
Mara, P., Mihalopoulos, N., Gogou, A., Daehnke, K., Schlarbaum, T., Emeis, K. C., and Krom, M.: Isotopic composition of nitrate in wet and dry atmospheric deposition on Crete in the eastern Mediterranean Sea, Global Biogeochem. Cy., 23, GB4002, doi:10.1029/2008GB003395, 2009.
Martín, J., Sanchez-Cabeza, J. A., Eriksson, M., Levy, I., and Miquel, J. C.: Recent accumulation of trace metals in sediments at the DYFAMED site (Northwestern Mediterranean Sea), Marine Pollution Bulletin, 59, 146–153, doi:10.1016/j.marpolbul.2009.03.013, 2009.
Migon, C., Sandroni, V., Marty, J. C., Gasser, B., and Miquel, J. C.: Transfer of atmospheric matter through the euphotic layer in the northwestern Mediterranean: seasonal pattern and driving forces, Deep-Sea Res. Pt. II, 49, 2125–2141, doi:10.1016/s0967-0645(02)00031-0, 2002.
Neff, J.: Polycyclic Aromatic Hydrocarbons. Sources, Fates And Biological Effects, Applied Science Publ., London, 262 pp., 1979.
Parinos, C., Gogou, A., Bouloubassi, I., Pedrosa-Pàmies, R., Hatzianestis, I., Sànchez-Vidal, A., Rousakis, G., Velaoras, D., Krokos, G., and Lykousis, V.: Occurrence, sources and transport pathways of natural and anthropogenic hydrocarbons in deep-sea sediments of the Eastern Mediterranean Sea, Biogeosciences Discuss., 9, 17999–18038, doi:10.5194/bgd-9-17999-2012, 2012.
Passow, U.: Switching perspectives: Do mineral fluxes determine particulate organic carbon fluxes or vice versa?, Geochem. Geophy. Geosyst., 5, Q04002, doi:10.1029/2003GC000670, 2004.

BGD
9, 19165–19197, 2012

Pio, C., Cerqueira, M., Harrison, R. M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artíñano, B., and Matos, M.: OC/EC ratio observations in Europe: re-thinking the approach for apportionment between primary and secondary organic carbon, Atmos. Environ., 45, 6121–6132, doi:10.1016/j.atmosenv.2011.08.045, 2011.

Ramdahl, T.: Retene – a molecular marker of wood combustion in ambient air, Nature, 306, 580–582, 1983.

Raoux, C., Boyona, J. M., Miquel, J. C., Teyssie, J. L., Fowler, S. W., and Albaigés, J.: Particulate fluxes of aliphatic and aromatic hydrocarbons in near-shore waters to the northwestern Mediterranean Sea, and the effect of continental runoff, Estuar. Coast. Shelf Sci., 48, 605–616, doi:10.1006/ecss.1998.0458, 1999.

Ridame, C. and Guieu, C.: Saharan input of phosphate to the oligotrophic water of the open western Mediterranean sea, Limnol. Oceanogr., 47, 856–869, 2002.

Salma, I. and Maenhaut, W.: Changes in elemental composition and mass of atmospheric aerosol pollution between 1996 and 2002 in a Central European city, Environ. Pollut., 143, 479–488, doi:10.1016/j.envpol.2005.11.042, 2006.

Samanta, S. K., Singh, O. V., and Jain, R. K.: Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation, Trends in Biotechnol., 20, 243–248, doi:10.1016/s0167-7799(02)01943-1, 2002.

Saydam, A. C. and Senyuva, H. Z.: Deserts: can they be the potential suppliers of bioavailable iron?, Geophys. Res. Lett., 29, 1911–1913, 2002.

Schlitzer, R.: Ocean Data View, http://odv.awi.de, 2011.

Stavrakakis, S. and Lykousis, V.: Interannual mass flux variations of settling particles in the NESTOR basins, S E. Ionian Sea (E. Mediterranean), Greece, Nucl. Instrum. Methods A, 626–627, S99-S101, doi:10.1016/j.nima.2010.04.076, 2011.

Stavrakakis, S., Lykousis, V., Gogou, A., Krasakopoulou, E., Kontoyiannis, H., Rousakis, G., Karageorgis, A. P., Velaoras, D., Perivoliotis, L., Kambouri, G., and Stavrakaki, I.: Downward fluxes of sinking particulate matter in the deep Ionian Sea (Nestor site), Eastern Mediterranean: seasonal and interannual variability, Biogeosciences Discuss., in press, 2012.

Sternbeck, J., Sjödin, A., and Andréasson, K.: Metal emissions from road traffic and the influence of resuspension – results from two tunnel studies, Atmos. Environ., 36, 4735–4744, doi:10.1016/s1352-2310(02)00561-7, 2002.

BGD
9, 19165–19197, 2012

Theodosi, C., Im, U., Bougiatioti, A., Zarmpas, P., Yenigun, O., and Mihalopoulos, N.: Aerosol chemical composition over Istanbul, Sci. Total Environ., 408, 2482–2491, doi:10.1016/j.scitotenv.2010.02.039, 2010a.

Theodosi, C., Markaki, Z., Tselepides, A., and Mihalopoulos, N.: The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern Mediterranean seawater, Mar. Chem., 120, 154–163, doi:10.1016/j.marchem.2010.02.003, 2010b.

Theodosi, C., Stavrakakis, S., Koulaki, F., Stavrakaki, I., Moncheva, S., Papathanasiou, E., Sanchez-Vidal, A., Koçak, M., and Mihalopoulos, N.: The significance of atmospheric inputs of major and trace metals to the Black Sea, J. Mar. Syst., 109–110, 94–102, doi:10.1016/j.jmarsys.2012.02.016, January 2013.

Tsapakis, M., and Stephanou, E. G.: Polycyclic aromatic hydrocarbons in the atmosphere of the Eastern Mediterranean, Environ. Sci. Tech., 39, 6584–6590, doi:10.1021/es050532l, 2005.

Tsapakis, M., Apostolaki, M., Eisenreich, S., and Stephanou, E. G.: Atmospheric deposition and marine sedimentation fluxes of polycyclic aromatic hydrocarbons in the eastern Mediterranean basin, Environ. Sci. Tech., 40, 4922–4927, doi:10.1021/es060487x, 2006.

Turquety, S., Hurtmans, D., Hadji-Lazaro, J., Coheur, P.-F., Clerbaux, C., Josset, D., and Tsamalis, C.: Tracking the emission and transport of pollution from wildfires using the IASI CO retrievals: analysis of the summer 2007 Greek fires, Atmos. Chem. Phys., 9, 4897–4913, doi:10.5194/acp-9-4897-2009, 2009.

UNEP/MAP/MEDPOL: Sub-Regional Assessment of the Status of Marine and Coastal Ecosystems and of Pressures to the Marine and Coastal Environment Eastern Mediterranean Sea, UNEP(DEPI)/MED WG.350/Inf.4, Barcelona, Spain, 37–38, 2010.

Venkatesan, M. I.: Occurrence and possible sources of perylene in marine sediments-a review, Mar. Chem., 25, 1–27, 1988.

Wakeham, S. G., Schaffner, C., and Giger, W.: Polycyclic aromatic hydrocarbons in recent lake sediments. I. Compounds having anthropogenic origins, Geochim. Cosmochim. Ac., 44, 403–413, 1980.

Weckwerth, G.: Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany), Atmos. Environ., 35, 5525–5536, doi:10.1016/s1352-2310(01)00234-5, 2001.

Wedepohl, H.: The composition of the continental crust, Geochim. Cosmochim. Ac, 59, 1217–1232, 1995.

BGD

9, 19165–19197, 2012

Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., and Sylvestre, S.: PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, Org. Geochem., 33, 489–515, doi:10.1016/s0146-6380(02)00002-5, 2002.
Yunker, M. B., Macdonald, R. W., Snowdon, L. R., and Fowler, B. R.: Alkane and PAH biomarkers as tracers of terrigenous organic carbon in Arctic Ocean sediments, Org. Geochem., 42, 1109–1146, 2011.

BGD
9, 19165–19197, 2012

Table 1. Average fluxes and concentrations of elemental carbon, metals and PAHs measured at sediment traps deployed at 700 m, 1200 m, 2000 m, 3200 m and 4300 m depth.

	Depth									
	700 m		1200 m		2000 m		3200 m		4300 m	
	$mg\,m^{-2}\,d^{-1}$	$mg\,g^{-1}$	$mg\,m^{-2}\,d^{-1}$	$mg\,g^{-1}$	$mg\,m^{-2}\,d^{-1}$	$mg\,g^{-1}$	$mg\,m^{-2}\,d^{-1}$	$mg\,g^{-1}$	$mg\,m^{-2}\,d^{-1}$	$mg\,g^{-1}$
EC	1.88E+00	2.83E+01	1.72E+00	2.74E+01	1.58E+00	2.86E+01	4.10E−01	2.37E+01	1.17E+00	2.45E+01
Al	2.56E+00	4.33E−02	2.24E+00	4.15E−02	2.04E+00	4.23E−02	6.34E−01	4.50E−02	1.69E+00	4.39E−02
V	3.71E−03	5.60E−05	3.40E−03	5.56E−05	2.86E−03	5.21E−05	8.65E−04	5.62E−05	2.56E−03	6.22E−05
Cr	5.41E−03	1.01E−04	5.58E−03	1.17E−04	3.09E−03	6.41E−05	9.45E−04	6.83E−05	2.77E−03	8.09E−05
Mn	3.56E−02	5.53E−04	3.24E−02	5.17E−04	2.66E−02	4.96E−04	6.49E−03	4.26E−04	2.11E−02	5.15E−04
Fe	1.55E+00	2.26E−02	1.40E+00	2.19E−02	1.15E+00	2.01E−02	3.47E−01	2.18E−02	1.03E+00	2.41E−02
Ni	1.70E−03	2.15E−05	1.44E−03	1.75E−05	1.18E−03	1.52E−05	2.06E−04	9.19E−06	1.09E−03	1.84E−05
Cu	1.95E−03	2.65E−05	2.10E−03	3.27E−05	2.13E−03	3.99E−05	6.41E−04	3.64E−05	2.06E−03	5.05E−05
Cd	4.36E−05	9.98E−07	4.42E−05	1.47E−06	2.99E−05	1.31E−06	1.71E−05	1.84E−06	3.27E−05	1.06E−06
Pb	2.16E−03	3.81E−05	2.06E−03	4.01E−05	1.88E−03	4.30E−05	6.03E−04	4.59E−05	1.56E−03	4.15E−05
$TPAH_{21}$	49.5[a]	612[b]							42.3[a]	780[b]
∑Phe	22.7[a]	280[b]							18.0[a]	332[b]
∑COMB	17.7[a]	219[b]							13.9[a]	255[b]

[a] $ng\,m^{-2}\,d^{-1}$
[b] $ng\,g^{-1}$

BGD
9, 19165–19197, 2012

Table 2. Fluxes of PAHs and metals in the study area in comparison to those reported in other sediment trap studies in the Mediterranean Sea.

Location	Compounds	Study period	Trap depth (m)	Flux ($ng\,m^{-2}\,d^{-1}$)	Reference
Ionian Sea, Eastern Mediterranean	PAH_{21}	May 2007–Oct 2008	700, 4300	8.87–211	This study
Alboran Sea, Western Mediterranean	PAH_{15}	Mar 1992–May 1992	250, 500, 750	220–240	Dachs et al. (1996)
French coast, Western Mediterranean	PAH_{25}	Jan 1988–Aug 1990	80	120–10500	Raoux et al. (1999)
Ligurian Sea, Western Mediterranean	PAH_{12}	Mar 1987–Jun 1987	200, 2000	300–910	Lipiatou et al. (1993)
Ligurian Sea, Western Mediterranean	PAH_{35}	Dec 2000–Jul 2002	200, 1000	40–4740	Deyme et al. (2011)
Open Western Mediterranean Sea	PAH_{25}	Apr 2001–May 2002	250, 2850	6–239	Bouloubassi et al. (2006)
Ionian Sea, Eastern Mediterranean	PAH_{35}	May 2001–Oct 2001	186,1426, 2837	22–28	Tsapakis et al. (2006)
Cretan Sea, Eastern Mediterranean	PAH_{15}	Jan 1995–Aug 1995	200, 1500	3–31	Gogou (1998)
Ionian Sea, Eastern Mediterranean	Al	May 2007–Oct 2008	700, 1200, 2000, 3200, 4300	0.05–9.46*	This study
	Cd			0.76–209	This study
	Pb			75.2–8260	This study
Ligurian Sea, Western Mediterranean	Al	Oct 1997–Apr 1998	200	3.9 ± 4.2*	Migon et al. (2002)
	Cd			80 ± 60	Migon et al. (2002)
	Pb			4900 ± 4900	Migon et al. (2002)

* $mg\,m^{-2}\,d^{-1}$

BGD
9, 19165–19197, 2012

Table 3. Retene, pimanthrene ($ng\,g^{-1}$ and $\%\,TPAH_{21}$) and $TPAH_{21}$ flux for 4300 m depth and EC fluxes ($mg\,m^{-2}\,d^{-1}$) and mass ratios ($mg\,g^{-1}$) for the trap deployed at 700 m during and after the Peloponnese fires in August 2007.

	Depth	01–15 Aug 2007	16–31 Aug 2007 (fires period)	01–15 Sep 2007	16–30 Sep 2007
Retene ($ng\,g^{-1}$)	4300 m	21.8	39.5	128	58.4
Retene ($\%\,TPAH_{21}$)	4300 m	3.9	3.6	11.9	9.2
1.7 C_2-Phe ($ng\,g^{-1}$)	4300 m	9.06	15.1	24.3	10.9
1.7 C_2-Phe ($\%TPAH_{21}$)	4300 m	1.11	1.36	2.35	1.73
$TPAH_{21}$ flux ($ng\,m^{-2}\,d^{-1}$)	4300 m	30.4	16.6	112	8.87
EC ($mg\,m^{-2}\,d^{-1}$)	2000 m	0.6	0.8	2.1	0.7
EC ($mg\,g^{-1}$)	2000 m	35.8	37.2	34.1	31.5
EC ($mg\,m^{-2}\,d^{-1}$)	1200 m	1.1	0.5	1.9	0.2
EC ($mg\,g^{-1}$)	1200 m	39.8	29.7	34.7	27.1
EC ($mg\,m^{-2}\,d^{-1}$)	700 m	0.2	2.0	0.3	0.2
EC ($mg\,g^{-1}$)	700 m	24.6	33.4	30.3	24.2

Results are not available for PAHs in the upper trap, while for EC in the deepest trap.

BGD
9, 19165–19197, 2012

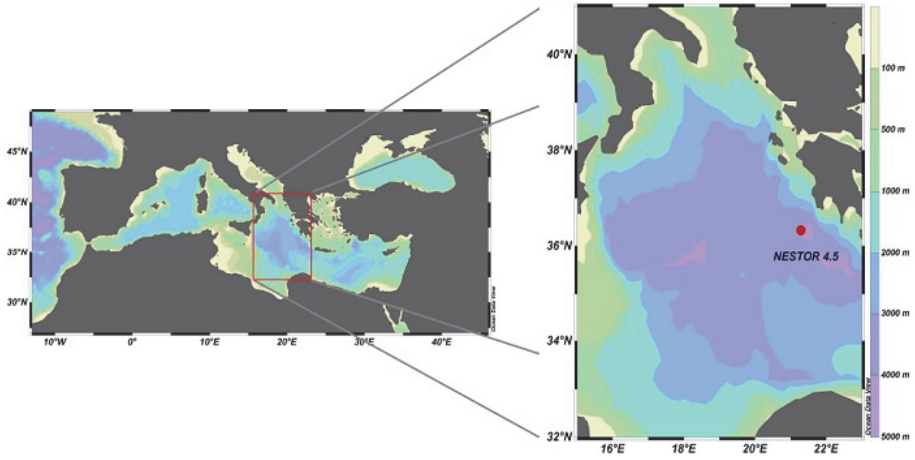

Fig. 1. Location of the sediment trap line deployed in NESTOR basin (SE. Ionian Sea, Eastern Mediterranean). The map was produced using Ocean Data View (Schlitzer, 2011).

BGD
9, 19165–19197, 2012

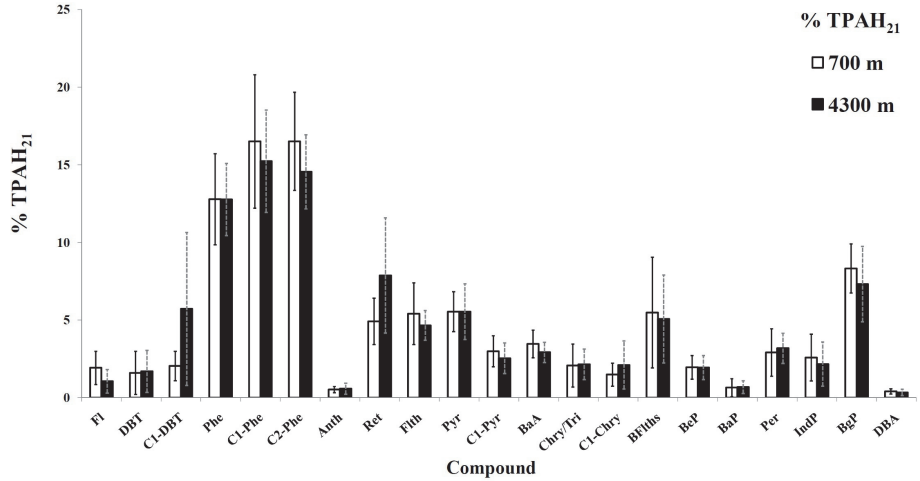

Fig. 2. Molecular profile of PAHs in sinking particles at 700 m and 4300 m depth with mean abundances normalized as percentage of the total sum of PAHs monitored ($TPAH_{21}$) and standard errors. PAH abbreviations: Fluorene (Fl); dibenzothiophene (DBT); methyl-dibenzothiophenes (C_1-DBT); phenanthrene (Phe); methyl-phenanthrenes (C_1-Phe); dimethyl-phenanthrenes (C_2-Phe); anthracene (Anth); retene (Ret); fluoranthene (Flth); pyrene (Pyr); methyl-pyrenes (C_1-Pyr); benzo[*a*]anthracene (BaA); chrysene/triphenylene (Chry/Tri); methyl-chrysenes (C_1-Chry); benzo[*b*/*j*/*k*]fluoranthene (BFlths); benzo[*e*]pyrene (BeP); benzo[*a*]pyrene (BaP); perylene (Per); indeno[1,2,3-*cd*]pyrene (IndP); benzo[*ghi*]perylene (BgP) and dibenzo[*a*,*h*]anthracene (DBA).

BGD
9, 19165–19197, 2012

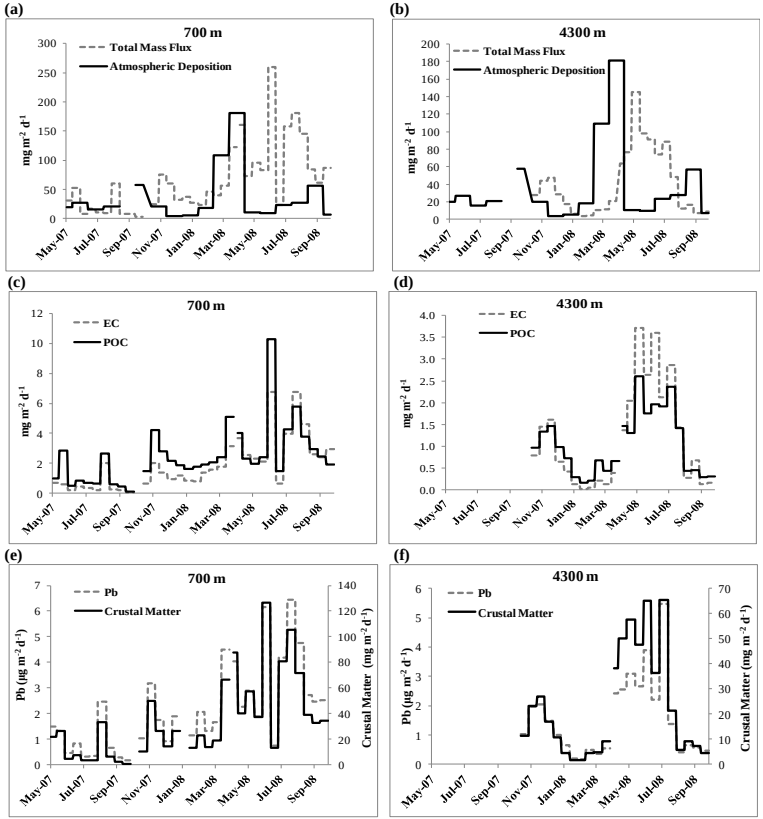

Fig. 3. Time series of atmospheric deposition flux and total mass flux (Stavrakakis et al., 2012) (**a**, **b**), particulate organic carbon (POC) and elemental carbon (**c**, **d**), crustal matter and lead at 700 m and 4300 m depth. Atmospheric Deposition Flux, Total Mass Flux, particulate organic carbon, elemental carbon and crustal matter are expressed in $mg\,m^{-2}\,d^{-1}$, whilst lead in $\mu g\,m^{-2}\,d^{-1}$.

BGD
9, 19165–19197, 2012

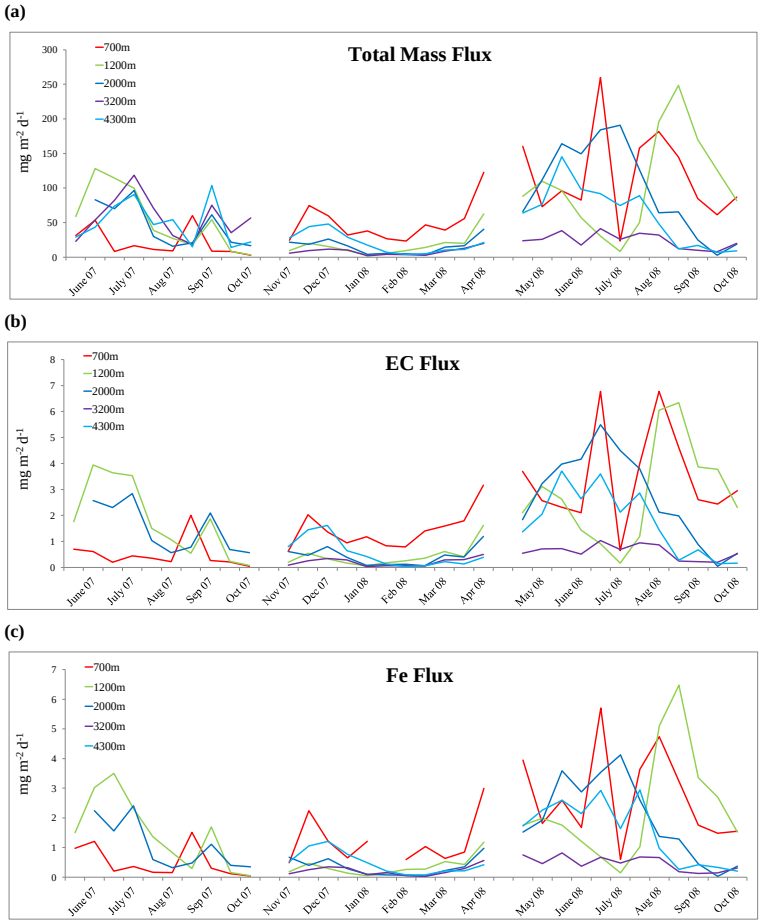

Fig. 4. Time series of Total Mass Flux **(a)**, elemental carbon **(b)** and iron **(c)**, expressed in mg m^{-2} d^{-1} at all five collective depths

BGD
9, 19165–19197, 2012

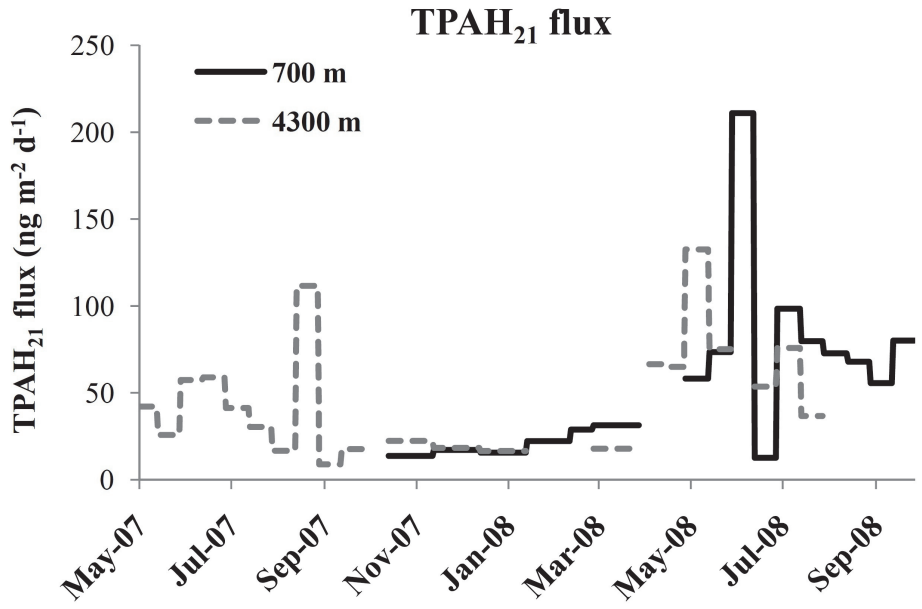

Fig. 5. Temporal variability of $TPAH_{21}$ flux at 700 m and 4300 m depth in the study area.

BGD
9, 19165–19197, 2012

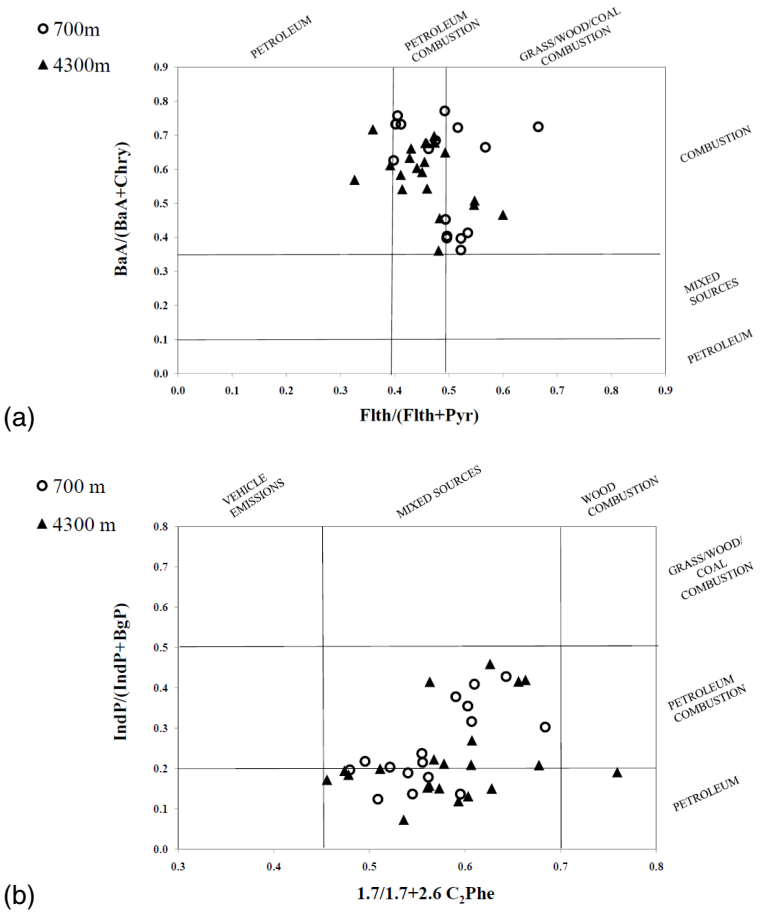

Fig. 6. PAH co-plots of BaA/(BaA + Chry) vs. Flth/(Flth + Pyr) ratio **(a)** and IndP/(IndP + BgP) vs. 1.7/1.7 + 2.6 C_2-Phe ratio **(b)** at 700 m and 4300 m depth, along with areas specific to given sources.

BGD
9, 19165–19197, 2012

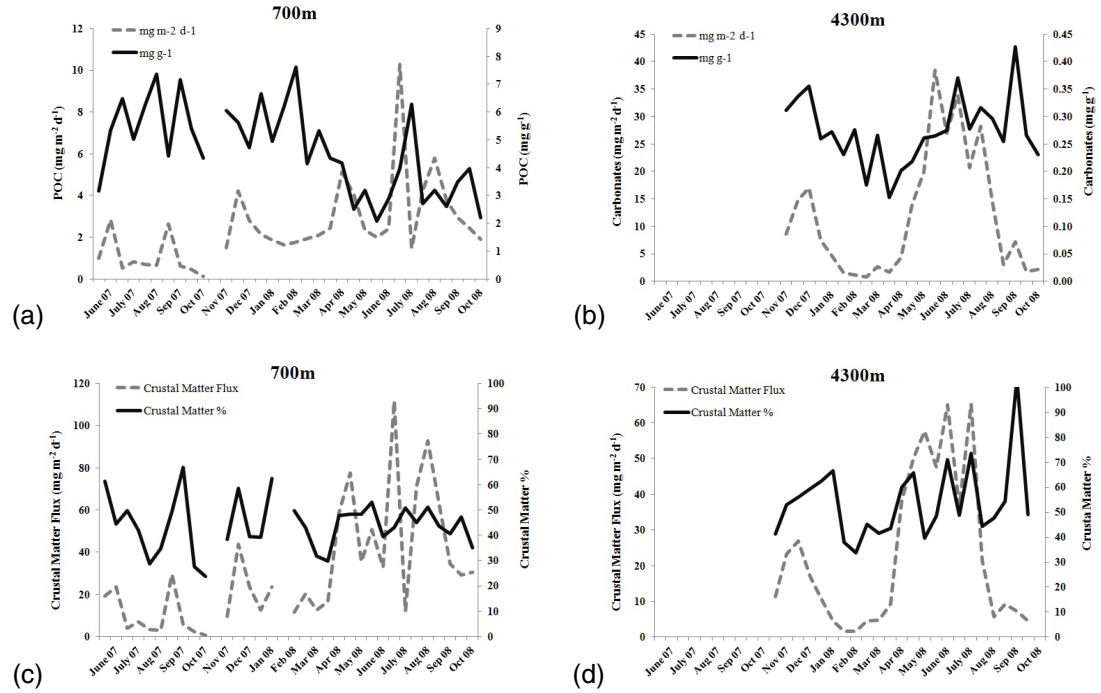

Fig. 7. Time series of particulate organic carbon **(a, b)** and crustal matter **(c, d)** at 700 m and 4300 m for both fluxes (mg m^{-2} d^{-1}) and mass ratios (mg g^{-1}) in elemental carbon, while in terms of fluxes (mg m^{-2} d^{-1}) and percentages (%) in the crustal matter

BGD
9, 19165–19197, 2012

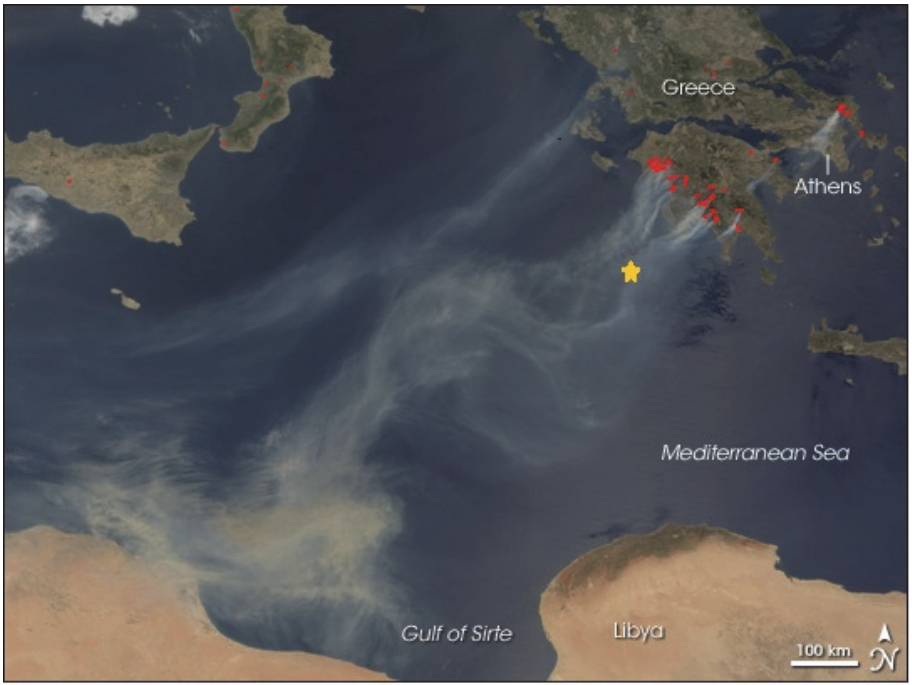

Fig. 8. Aqua-MODIS sensor satellite image above southern Greece for the 26th of August 2007 showing aerosol transport from the burning Peloponnese over the sampling site and across the Mediterranean Sea. Adapted from NASA's earth observatory (http://earthobservatory.nasa.gov/IOTD/view.php?id=7996). The orange dot indicates the location of the mooring line, NESTOR 4.5

BGD
9, 19165–19197, 2012