



Polycyclic aromatic hydrocarbons in atmospheric aerosols

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Polycyclic aromatic hydrocarbons in atmospheric aerosols and air–sea exchange in the Mediterranean

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Abstract

Polycyclic aromatic hydrocarbons (PAH) concentration in air of the central and eastern Mediterranean in summer 2010 was $1.45 (0.30\text{--}3.25) \text{ ng m}^{-3}$, with $\approx 8\%$ in the particulate phase, associated with particles $< 0.25 \mu\text{m}$. The diffusive air–sea exchange fluxes of fluoranthene and pyrene were mostly found net-depositional or close to phase equilibrium, while retene was net-volatilisation in a large sea region. Regional fire activity records in combination with box model simulations suggest that seasonal depositional input of retene from biomass burning into the surface waters during summer is followed by an annual reversal of air–sea exchange, while inter-annual variability is dominated by the variability of the fire season. It is concluded that future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air–sea exchange.

1 Introduction

The marine atmospheric environment is a receptor for polycyclic aromatic hydrocarbons (PAHs) which are advected from combustion sources on land (power plants, biomass burning, road transport). Marine sources may be significant near transport routes (ship exhaust). Long-range transport from urban and industrial sources on land are the predominant sources of PAHs in the Mediterranean (Masclat et al., 1988; Tzapakis et al., 2003 and 2006; Tzapakis and Stephanou, 2005a). A number of PAHs are semivolatile (vapour pressures at 298 K in the range $10^{-6}\text{--}10^{-2} \text{ Pa}$) and, hence partition between the gas and particulate phases of the atmospheric aerosol, influenced by temperature, particulate phase chemical composition and particle size (Keyte et al., 2013). Upon deposition to surface water PAHs partition between the aqueous and particulate (colloidal and sinking) phases and may bioaccumulate in marine food chains (Lipiatou and Salot, 1991; Dachs et al., 1997; Tzapakis et al., 2003; Berrojalbiz et al., 2011). They were also found enriched in the sea-surface microlayer relative to

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subsurface water (Lim et al., 2007; Guitart et al., 2010). Semivolatile PAHs may be subject to re-volatilisation from the sea surface (reversal of air–sea exchange), similar to chlorinated semivolatile organics (Bidleman and McConnell, 1995), in case high concentrations in surface water would build up. This had been predicted by multicompartamental modelling for 2–4 ring PAHs for polluted coastal waters and also the open ocean (Greenfield and Davis, 2005; Lammel et al., 2009a) and was indeed observed in coastal waters off the northeastern United States (Lohmann et al., 2011). Field studies in the open sea found net-deposition to prevail whenever determined (e.g. Tsapakis et al., 2006; Balasubramanian and He, 2010; Guitart et al., 2010; Castro-Jiménez et al., 2012; Mai, 2012). However, some 3–4 ring parent PAHs, among them fluorene (FLU), fluoranthene (FLT) and pyrene (PYR), were reported to be close to phase equilibrium in the Mediterranean, Black and North seas (Castro-Jiménez et al., 2012; Mai, 2012), and net volatilisation of FLT and PYR was observed in the open southeastern Mediterranean Sea in spring 2007 (Castro-Jiménez et al., 2012).

The aim of the measurements on board RV Urania was to investigate levels of organic pollutants in summer in Mediterranean air and gain insights about sources and phase partitioning in the aerosol of these substances. This study is on the cycling of PAHs in the marine atmosphere.

2 Methods

2.1 Sampling

Samples were taken during the RV Urania cruise, 27 August–12 September 2010 (see Supplement (SM), Fig. S1). PAHs were collected in the gaseous and particulate phases using high volume samplers (Digitel) equipped with one glass fibre filter (Whatman) and one polyurethane foam (PUF) plug (Gumotex Břeclav, density 0.030 g cm^{-3} , 50 mm diameter, cleaned by extraction in acetone and dichloromethane, 8 h each, placed in a glass cartridge) in series. Particle size was classified in the particulate phase us-

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The first portion of the extract was fractionated on a silica column (5 g of silica 0.063–0.200 mm, activated 12 h at 150 °C). The first fraction (10 mL n-hexane) containing aliphatic hydrocarbons was discarded. The second fraction (20 mL DCM) containing PAHs was collected and then reduced by stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into an insert in a vial. Terphenyl was used as syringe standard, final volume was 200 μ L. GC-MS analysis was performed on a 6890N GC equipped with a 60 m \times 0.25 mm \times 0.25 μ m DB5-MS column (Agilent J&W, USA) coupled to 5973N MS (Agilent, USA). The MS was operated in EI+ mode with selected ion recording (SIR). The targeted compounds are the 16 EPA priority PAHs (i.e., naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), indeno(123cd)pyrene (IPY), dibenzo(ah)anthracene (DBA), benzo(ghi)perylene (BPE)), 10 more parent PAHs (i.e., benzo(ghi)fluoranthene (BGF), cyclopenta(cd)pyrene (CPP), triphenylene (TPH), benzo(j)fluoranthene (BJF), benzo(k)fluoranthene (BKF), benzo(e)pyrene (BEP), perylene (PER), dibenz(ac)anthracene (DCA), anthranthrene (ATT), and coronene (COR)), and one alkylated PAH, retene (RET). The injection volume was 1 μ L. Terphenyl was used as internal standard.

Each one GFF and PUF field blank, *b*, were taken for high-volume sampling under as far as possible identical manipulations on site. No QFF field blank was taken for impactor sampling, but instead the mean of values of the QFF substrates of the 2 uppermost impactor stages (in total 5) was taken. The respective *b* value was subtracted from sample values. The limit of quantification needs to take the accuracy of the blank level into account. In lack of a measure for the variation of the field blank, the relative standard deviation (SD) of field blanks from earlier field campaigns, (σ_c/b_c), on a high-mountain site (high-volume sampling summer 2007, $n = 5$; Lammel et al., 2009b) and in the Mediterranean (impactor sampling summer 2008, $n = 6$; Lammel et al., 2010a) was used ($\sigma = (\sigma_c/b_c) \times b$). The identical samplers, sampling and analysis protocols for

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all analytes had been applied. Values below the sum of the field blank value (from this campaign) and 3 relative SDs of the field blank values (from the previous campaigns) were considered $< \text{LOQ}$ ($\text{LOQ} = b + 3\sigma$). NAP and ACY were excluded from the data set, because of the lack of blank values. The field blank values of most other analytes were below instrument LOQ in high-volume PUF and GFF samples. However, higher field LOQs, up to (6–25) pgm^{-3} (according to sampled volume of air) resulted for ANT, PYR and RET, and up to (45–180) pgm^{-3} for ACE, FLN, PHE and FLT in PUF. Field LOQs of PAHs in impactor QFF samples were below instrumental LOQ for most substances, but in the range (8–15) pgm^{-3} for ACE, ANT, and FLT, $\approx 55 \text{pgm}^{-3}$ for FLN, and 120–140 pgm^{-3} for NAP and PHE.

The instrument limit of quantification (LOQ), which is based on the lowest concentration of calibration standards used, was 0.5 ng, corresponding to 0.5–2.5 pgm^{-3} for high-volume samples, $\approx 8 \text{pgm}^{-3}$ for impactor samples, 6–10 pgm^{-3} for semivolatile PAHs determined in passive air samples and up to 200 pgm^{-3} for non volatile PAHs in passive air samples.

Water samples (2–2.5 L) were extracted immediately after their collection using solid phase extraction on C_{18} Empore discs using a vacuum manifold device. Disks were stored closed in glass vials in a freezer and transported to the processing laboratory, PAHs were eluted from disks using 40 mL of dichloromethane. The above listed PAHs were analysed the same way as the the air samples. LOQ was 0.1ngL^{-1} .

Other trace constituents and meteorological parameters

Ozone was measured with an absorption method (Teledyne-API model 400A UV) on the top deck (10 m above sea surface). Meteorological parameters (air temperature, humidity, wind direction and velocity) and oceanographic parameters were determined aboard.

2.3 Models of gas-particle partitioning

The data set is used to test gas-particle partitioning models for semivolatile organics in terms of the organics' mass size distribution and size dependent particulate matter (PM) composition. The models assume different processes to determine gas-particle partitioning, i.e. an adsorption model (Junge–Pankow; Pankow, 1987), and two absorption models (i.e. K_{OA} models; Finizio et al., 1997; Harner and Bidleman, 1998). Absorption is into particulate OM. We refrain from testing dual adsorption and absorption models (e.g. Lohmann and Lammel, 2004) as no soot data or PM chemical composition data are available. Particulate mass fraction, θ , and partitioning coefficient, K_p , are defined by the concentrations in the 2 phases:

$$\theta = c_p / (c_p + c_g)$$

$$K_p = c_p / (c_g \times c_{TSP}) = \theta / [(1 - \theta) \times c_{TSP}]$$

with c_p and c_g in units of ng m^{-3} , c_p representing the whole particle size spectrum.

Different models describe different processes to quantify differences in ad- and absorption between compounds. The Junge–Pankow model uses the vapour pressure of the subcooled liquid p_L^0 , $\theta = c_J S / (p_L^0 + c_J S)$, (data taken from Lei et al., 2002), c_J should be approximately 171 Pa cm for PAHs (Pankow, 1987). The aerosol particle surface, S , was not measured and a typical value for maritime aerosols is adopted instead ($4.32 \times 10^{-7} \text{ cm}^{-1}$; Jaenicke, 1988). Harner and Bidleman, 1998, use the log K_{OA} and f_{OM} : $\log K_p = \log K_{OA} + \log f_{OM} - 11.91$; and Finizio et al., 1997, uses only the K_{OA} as predictor (data taken from Ma et al., 2010): $\log K_p = 0.79 \times \log K_{OA} - 10.01$. The range of the fraction of OM used here is based on Putaud et al., 2004 (16% lower limit) and Spindler et al., 2012 (45% upper limit).

2.4 Air-sea diffusive mass exchange calculations

State of phase equilibrium is addressed by fugacity calculation, based on the Whitman two-film model (Liss and Slater, 1974; Bidleman and McConnell, 1995). The fugacity

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ratio (FR) is calculated as:

$$FR = f_a/f_w = C_a RT_a / (C_w H_{Tw, salt})$$

with gas-phase concentration C_a (ng m^{-3}), dissolved aqueous concentration C_w (ng m^{-3}), universal gas constant R ($\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$), water temperature and salinity corrected Henry's law constant $H_{Tw, salt}$ ($\text{Pa m}^3 \text{mol}^{-1}$), and air temperature T_a (K). Values $0.3 < FR < 3.0$ are conservatively considered to not safely differ from phase equilibrium, as propagating from the uncertainty of the Henry's law constant, $H_{Tw, salt}$, and measured concentrations (e.g., Bruhn et al., 2003; Castro-Jiménez et al., 2012; Zhong et al., 2012). This conservative uncertainty margin is also adopted here, while $FR > 3.0$ indicates net deposition and $FR < 0.3$ net volatilisation. The diffusive air–seawater gas exchange flux (F_{aw} , $\text{ng m}^{-2} \text{day}^{-1}$) is calculated according to the Whitman two-film model (Bidleman and McConnell, 1995; Schwarzenbach et al., 2003):

$$F_{aw} = k_{ol}(C_w - C_a RT_a / H_{Tw, salt})$$

with air–water gas exchange mass transfer coefficient k_{ol} (m h^{-1}), accounting for resistances to mass transfer in both water (k_w , m h^{-1}) and air (k_a , m h^{-1}) (see Bidleman and McConnell, 1995; Zhong et al., 2012; and references therein).

2.5 Non-steady state 2-box model

The air–sea mass exchange flux of RET is simulated by a non-steady state zero-dimensional model of intercompartmental mass exchange (Lammel, 2004). This 2-box model predicts concentrations by integration of two coupled ordinary differential equations that solve the mass balances for the two compartments, namely the atmospheric marine boundary layer (MBL) and seawater surface mixed layer. Processes considered in air are dry (particle) deposition, removal from air by reaction with the hydroxyl radical, and air–sea mass exchange flux (dry gaseous deposition), while in seawater

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export (settling) velocity, deposition flux from air, air–sea mass exchange flux (volatilisation), and degradation (as 1st order process) are considered. All input parameters are listed in the SM, Table S2.

Atmospheric depositions related to emissions from open fires are assumed to provide the only source for seawater RET. These are available as daily time series for the East Mediterranean domain (28–45° N, 8–30° E) through the fire-related PM_{2.5} emissions as provided by the Global Fire Assimilation System (GFASv1.0; Kaiser et al., 2012) in combination with an emission factor (207 mg RET in PM_{2.5} (kg fuel burnt)⁻¹; Schmidl et al., 2008). The fire emissions are averaged over the domain and assumed to disperse within the MBL only. This is justified due to the assumed underestimation of the fire related emissions and ignorance of other (emission) sources. The 2-box model is run for the years 2005–2010, for the east Mediterranean domain (28–45° N, 8–30° E) with a 1 h time resolution. Fluxes in the range $F_{em} = (0.30 \pm 1.46) \text{ ng m}^{-2} \text{ h}^{-1}$ (positive defined upward) are simulated (using the initially estimated parameter set, Table S2). GFAS uses global satellite observations of fire radiative power to estimate daily dry matter combustion rates and fire emission fluxes. The GFAS system partly corrects for observational gaps (e.g. due to cloud cover) and detects fires in all biomes, except for very small fires (lower detection limit of around 100–1000 m² effective fire area).

2.6 Analysis of long-range advection of air

So-called retroplumes are generated using operational weather prediction model data and a Lagrangian particle dispersion model, FLEXPART (Stohl et al., 1998, 2005). Hereby, 50 000 particles per hour were released and followed backwards in time for 5 days. The model output is a 3-D distribution of residence time.

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3 Results and discussion

3.1 PAH concentrations in air and seawater

The mean total (i.e., sum of gaseous and particulate) $\Sigma 25$ PAHs concentration is 1.45 ng m^{-3} (time-weighted), and ranged from $0.30\text{--}3.25 \text{ ng m}^{-3}$ (high-volume samples). The spatial variability of PAH levels in the Mediterranean is large, determined by long-range advection (Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006). The levels found in this study in the southeastern Mediterranean are for most substances lower than found earlier (Table 2). The variability of advection or advection in combination with different routes taken by a vessel being influenced differently by coastal or ship emission plumes may explain this difference. Diagnostic ratios (BAA/(BAA + CHR), FLT/(FLT + PYR); Dvorská et al., 2011) in some of the samples (No. 2, 4, 7, 8, and 15) reflect the influence of traffic and industrial sources. We investigated the potential source distribution of individual samples collected along the cruise (Sect. 2.6) and found that indeed maxima of PAH concentrations corresponded with air masses having resided over large urban areas, and, vice versa, low concentrations corresponded with no or benign hit of such areas (illustrated in Fig. S5). This perception is supported by the ozone data i.e., 53 (47–65) ppbv during influence from urban areas but 37 (33–62) ppbv otherwise.

It had been pointed out that the source distribution around the Mediterranean may cause a west-east gradient, leading to higher concentrations found in the Ionian Sea and Sicily region (ISS) than in the southeastern Mediterranean (SEM; Berrojalbiz et al., 2011). This gradient is somewhat reflected in our results, as levels in the ISS exceeded levels in the SEM (Table 2a).

The PAH concentrations in seawater near Crete (samples No. 7 and 8a) are very similar to those found in fall 2001 and winter-spring 2002 (Tsapakis et al., 2006; FLT = $0.15(0.11 - 0.21) \text{ ng L}^{-1}$, PYR = $0.12(0.07 - 0.17) \text{ ng L}^{-1}$).

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3.2 Gas-particle partitioning

Only a small mass fraction of the total, $\theta = 0.08$, is found in the particulate phase, confirming earlier findings from remote sites in the region (Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006; Table 3c). The particulate mass fraction, θ , of four semivolatile PAHs varied considerably along track (see SM Fig. S2). θ is thought to be strongly influenced by temperature and doubling per 13 K cooling was found in a Mediterranean environment (Lammel et al., 2010b) apart from PM composition. An exploration of the temperature dependence is not possible, because of only little temperature variation during the cruise ($T_{\text{mean_sample}} = 21 - 27^\circ\text{C}$, Fig. S2). For similar temperatures higher θ values had been observed at sites on the region influenced by urban and industrial sources (Mandalakis et al., 2002; Tsapakis and Stephanou, 2005b; Akyüz and Cabuk, 2010), which is probably related to the influence of higher organic and soot PM mass fractions. Gas-particle partitioning models (Table 3) underpredict θ , except the Finizio et al., 1997, model for one substance, TPH. θ predicted by the Junge–Pankow (JP) model comes closest. Due to the lack of OC/EC data an extended examination is not possible.

In size-segregated samples PAH was almost exclusively quantified in particle size fractions $< 0.25 \mu\text{m a.e.d.}$ ($< \text{LOQ}$ in the other stages; Table 1a). No similar measurements from the open sea or even clean coastal sites exist to compare with. However, the observation here is in line with observations at continental sites in central and southern Europe: there, mass median diameters of PAHs were found to be in the accumulation range, mostly $0.5\text{--}1.4 \mu\text{m}$ (Schnelle et al., 1995; Kiss et al., 1998; Lammel et al., 2010b and 2010c), but also a second, coarse mode was found (up to $2.4 \mu\text{m}$; Chrysikou et al., 2009).

3.3 Fugacity ratio and air–sea exchange flux

Fugacity ratios (Fig. 1a) and vertical fluxes (Fig. 1b) could be quantified for FLT, PYR and RET. The uncertainty window of $\text{FR} = f_{\text{a}}/f_{\text{w}} = 0.3 - 3.0$ is based on the uncertainty

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of $H_{\text{Tw, salt}}$. Values $\text{FR} > 3.0$ indicate net deposition, $\text{FR} < 0.3$ indicate net volatilisation. For RET both water and air concentrations of sample No. 2 were $< \text{LOQ}$.

FLT and PYR are indicated to be close to phase equilibrium, with most of the FR values within the uncertainty range, one sample (No. 1) indicating deposition of FLT and one or two (No. 9 and 13) indicating volatilisation of FLT and PYR, respectively. In comparison with earlier observations of FLT and PYR air–sea exchange in the SEM in 2001/02 and 2007 (Tsapakis et al., 2006; Castro-Jiménez et al., 2012) and considering spatial and temporal variabilities no trend, in particular no reversal of air–sea exchange is indicated. This comparison is detailed in the SM, S2.2.1.

RET, however, is found net-volatilisation throughout most of the cruise (Fig. 1). Among the highest fluxes ($> 50 \text{ ng m}^{-3} \text{ d}^{-1}$) are some samples with very low FR, < 0.03 . Fugacity of RET from water is supported by its Henry's law coefficient ($11 \text{ Pa m}^3 \text{ mol}^{-1}$ at 298 K) which is higher than for CHR ($0.53 \text{ Pa m}^3 \text{ mol}^{-1}$) and FLT ($2.0 \text{ Pa m}^3 \text{ mol}^{-1}$). RET is commonly considered as biomarker for coniferous wood combustion (Ramdahl, 1983). A decrease in wildfires could explain the suspected RET volatilisation. Integrated over the domain and the year 2010, fires released 7.2 PJ fire radiative energy, which translates into around 22.2 Gg of $\text{PM}_{2.5}$ emitted (Fig. 2). Compared to the $\text{PM}_{2.5}$ emissions of the years 2003 to 2012, the year 2010 had the lowest emissions, equivalent to 46 % of the 2003–2012 mean, and only 18 % of the peak emissions of the year 2007 (Fig. 2d). As typical for the East Mediterranean region, the fire season in 2010 started by the end of June and ended by early October. The Urania cruise measurements took place between 27.8. and 12.9., i.e. towards the end of the main burning season (Fig. 2c). During the first half of the Urania cruise, widespread fire activity was observable in the entire domain, with most intense fires occurring in Southern Italy, Sicilia and along the East coast of the Adriatic and the Ionian Sea (notably in Albania and Greece) (Fig. 2a).

The hypothesis that seasonal depositional input of RET into the surface waters during the fire season (summer) triggers reversal of diffusive air–sea exchange, at least in the year 2010, are tested by box model (Sects. 2.5 and S1.3) runs. Two scenar-

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ios are considered, an “Initially Estimated Parameter Set” (IEPS) representing mean values for environmental parameters, and an “Upper Estimate Parameter Set” (UEPS) which represents realistic environmental conditions favouring seawater pollution (SM, Table S3). Simulated diffusive air–sea exchange flux, F_{aw} , during 2005–2010 initialised by the UEPS is shown in Fig. 3a and by the IEPS in the SM, Fig. S3, and during the observations (cruise of RV Urania, 27 August–9 September 2010) initialised by the UEPS in Fig. 3b.

The model confirms the hypothesis that seasonal depositional input of RET into the surface waters during the fire season (July–September, typically in the range $F_{aw} = 10^{-2} - 10^1 \text{ ng m}^{-2} \text{ d}^{-1}$ under IEPS) is followed by a period of prevailing flux reversal, typically $F_{aw} = 10^{-2} - 10^0 \text{ ng m}^{-2} \text{ d}^{-1}$, which in the years 2008–2010 started in October and lasted until the onset of the fire season, but eventually started later in the years 2005–2007 (at least under IEPS). The volatilisation flux is predicted smaller in magnitude than the net-deposition flux during the fire season, but correspondingly, i.e. higher after intense fire seasons. The high RET volatilisation flux, indicated by measured C_a and C_w , seems to be dominated by biomass burning in the region in the previous fire season. F_{aw} is predicted highly fluctuating, also during the observational period (Fig. 3b). Even under UEPS the model is underpredicting F_{aw} (Fig. 3b). The sensitivity to input uncertainties (SM S1.2) may explain part of the underestimate, but not up to one order of magnitude.

4 Conclusions

PAH pollution of the atmospheric Mediterranean environment was below previous observations at the beginning of the decade (2001/02; Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006), also considering possible losses during sampling. This might reflect emission reductions.

Three gas-particle partitioning models were tested and found to underpredict the particulate mass fraction in most of the samples (four PAHs i.e., BAA, TPH, CHR and

BBF). Although input parameters were incomplete these results confirm the earlier insight that additional processes on the molecular level need to be included, beyond adsorption (Junge–Pankow model) and absorption in OM (K_{oa} models), namely both adsorption and absorption (Lohmann and Lammel, 2004) or even a complete description of molecular interactions between sorbate and PM matrix (Goss and Schwarzenbach, 2001).

Simulations with a non-steady state 2-box model confirm the hypothesis that seasonal depositional input of RET from biomass burning into the surface waters during summer is followed by a period of flux reversal. The volatilisation flux is smaller in magnitude than the net-deposition flux during the previous months, but correspondingly, i.e. higher after intense fire seasons. Future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air–sea exchange. Because of non-diffusive emission from the sea surface, such as aerosol suspension from sea spray and bubble bursting (Woolf, 1997; Qureshi et al., 2009; Albert et al., 2012), the true volatilisation may have exceeded the diffusive flux significantly.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys-discuss.net/14/5963/2014/acpd-14-5963-2014-supplement.pdf>.

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**Table 1b.** Continued.

	n_{LOQ}	mean (min–max)
PHE	1	1.1
RET	12	0.1 (< 0.1–0.5)
FLT	10	0.1 (< 0.1–0.3)
PYR	7	0.2 (< 0.2–0.9)

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Table 2a. Gaseous **(a)** and particulate **(b)** concentrations in air (mean (min–max), ng m^{-3}) of selected PAH compared to other studies in the Ionian Sea and Sicily region (ISS) and in the southeastern Mediterranean (SEM). RV = research vessel cruise.

	ISS		SEM			
	RV 2010 this study	RV 2006, 2007 Castro-Jiménez et al. (2012)	RV 2010 this study	RV 2006, 2007 Castro-Jiménez et al. (2012)	Finokalia 2001/02 ⁽¹⁾ Tsapakis et al. (2006)	Finokalia 2000–2002 ⁽²⁾ Tsapakis and Stephanou (2005a)
FLN	0.16 (0.03–0.40)	2.25 (1.27–5.65)	0.07 (0.02–0.34)	0.69 (0.36–1.23)	1.05 (0.15–1.67)	1.8 (0.2–5.7)
PHE	0.52 (0.15–1.11)	7.00 (3.52–15.45)	0.35 (0.14–1.41)	3.94 (2.50–6.35)	4.78 (1.75–7.78)	7.3 (1.5–27.7)
ANT	0.04 (0.01–0.10)	0.37 (0.18–0.55)	0.04 (0.01–0.22)	0.20 (0.16–0.30)	0.61 (0.12–1.31)	0.9 (0.1–4.5)
FLT	0.138 (0.053–0.311)	0.05 (0.02–0.07)	0.10 (0.06–0.36)	0.007 (0.003–0.011)	0.82 (0.12–1.69)	1.8 (0.07–6.0)
PYR	0.139 (0.044–0.287)	0.04 (0.02–0.06)	0.12 (0.05–0.56)	0.006 (0.003–0.009)	0.65 (0.14–0.97)	0.9 (0.1–2.8)
CHR	0.012 (0.007–0.02)	0.09 (0.03–0.23)	0.014 (0.011–0.037)	0.03 (0.02–0.05)	0.18 (0.06–0.33)	0.2 (< 0.001–0.6)

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Table 2b. Continued.

	ISS		RV 2010 this study	SEM		Finokalia 2000–2002 ⁽²⁾ Tsapakis and Stephanou (2005a)
	RV 2010 this study	RV 2006, 2007 Castro-Jiménez et al. (2012)		RV 2006, 2007 Castro-Jiménez et al. (2012)		
FLN	0.43 (< 0.60–< 1.13)	0.001 (0.0009–0.002)	0.25 (< 0.33–< 1.36)	0.0013 (0.0011–0.0016)	0.02 (< 0.001–0.01)	
PHE	0.88 (< 1.22–< 2.28)	0.06 (0.01–0.12)	0.51 (< 0.67–< 2.76)	0.04 (0.01–0.13)	0.05 (0.004–0.2)	
ANT	0.10 (< 0.14–< 0.26)	0.007 (0.0009–0.012)	0.06 (< 0.08–< 0.32)	0.009 (0.0007–0.023)	0.004 (< 0.001–0.02)	
FLT	0.40 (< 0.56–< 1.04)	0.099 (0.01–0.19)	0.23 (< 0.31–< 1.26)	0.049 (0.01–0.12)	0.1 (0.04–0.2)	
PYR	0.05 (< 0.07–< 0.13)	0.109 (0.016–0.216)	0.03 (< 0.04–< 0.16)	0.057 (0.012–0.142)	0.04 (0.01–0.01)	
BAA	0.01 (0.0004–0.03)	0.013 (0.006–0.023)	0.003 (0.0004–0.01)	0.018 (0.004–0.046)	0.03 (0.003–0.1)	
CHR	0.02 (0.003–0.08)	0.04 (0.01–0.08)	0.01 (0.003–0.02)	0.043 (0.012–0.101)	0.1 (0.02–0.3)	
BBF	0.03 (0.01–0.10)	0.029 (0.012–0.045)	0.01 (0.004–0.03)	0.033 (0.010–0.060)	0.04 (< 0.001–0.2)	
BKF	0.02 (0.003–0.06)	0.015 (0.005–0.027)	0.005 (0.002–0.02)	0.089 (0.005–0.333)	0.04 (< 0.001–0.2)	
BAP	0.03 (0.002–0.07)	0.009 (0.04–0.016)	0.01 (< 0.025–0.01)	0.034 (0.005–0.081)	0.02 (0.01–0.05)	
BJF	0.02 (0.01–0.08)	0.015 (0.014–0.016)	0.01 (0.002–0.03)	0.010 (0.008–0.011)	–	
BEP	0.03 (0.01–0.09)	0.03 (0.02–0.05)	0.01 (0.004–0.03)	0.046 (0.017–0.093)	0.04 (0.01–0.1)	
PER	0.03 (< 0.022–0.01)	0.002 (0.0005–0.004)	0.02 (< 0.012–0.002)	0.026 (0.0001–0.068)	0.004 (< 0.001–0.01)	
IPY	0.04 (< 0.02–0.09)	18.32 (5.57–31.55)	0.02 (< 0.012–0.019)	0.009 (0.002–0.013)	0.03 (0.009–0.2)	
BPE	0.03 (< 0.02–< 0.04)	0.026 (0.017–0.042)	0.02 (< 0.012–0.02)	0.081 (0.012–0.210)	0.03 (0.010–0.09)	

⁽¹⁾ Months September and October 2001, February, April and May 2002. No particulate data reported.

⁽²⁾ 24 h per month between February 2000 and February 2002.

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Table 3a. Gas-particle partitioning of selected PAHs (mean \pm sd (median), ng m^{-3}), observed and predicted by the models Junge–Pankow, 1987 (JP), Harner and Bidleman (1998) (HB), and Finizio et al. (1997) (F), expressed as **(a)** particulate mass fraction, θ , and **(b)** $\log K_p$ of this study.

	Observed	JP	HB	F
BAA	0.51 ± 0.28 (0.47)	0.18 ± 0.07 (0.18)	0.08–0.20	0.18
TPH	0.27 ± 0.13 (0.26)	0.24 ± 0.10 (0.24)	0.23–0.46	0.37
CHR	0.35 ± 0.15 (0.35)	0.31 ± 0.13 (0.32)	0.09–0.21	0.19
BBF	0.88 ± 0.40 (0.94)	0.91 ± 0.40 (0.97)	0.49–0.73	0.59

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Table 3b. Continued.

	Observed	JP	HB	F
BAA	-1.28 ± 1.00 (−0.96)	-1.97 ± 1.14 (−1.84)	−2.43 to −1.98	−1.89
TPH	-1.77 ± 1.27 (1.45)	-1.80 ± 1.07 (−1.63)	−1.91 to −1.46	−1.48
CHR	-1.59 ± 1.18 (1.34)	-1.65 ± 1.01 (−1.46)	−2.41 to −1.96	−1.87
BBF	-0.94 ± 0.19 (−0.24)	-0.52 ± 0.66 (−0.74)	−1.41 to −0.96	−1.08

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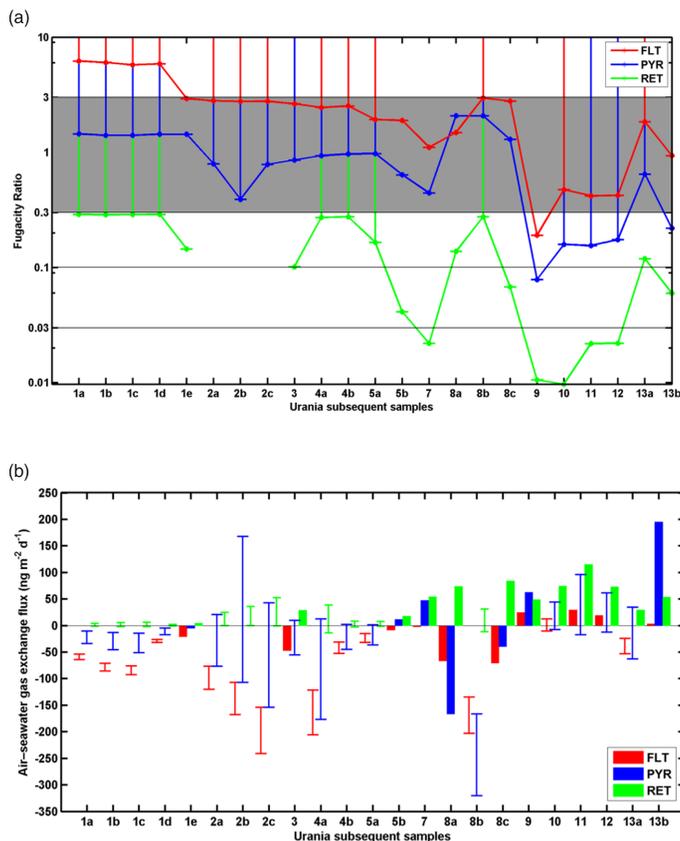


Fig. 1. Air-sea exchange, **(a)** fugacity ratios $FR = f_a/f_w$ (volatilisation > 3 , deposition < 0.3 , grey area insignificant deviation from phase equilibrium) and **(b)** flux F_{aw} ($\text{ng m}^{-2} \text{d}^{-2}$; volatilisation > 0 , deposition < 0) of FLT, PYR and RET along the cruise of R/V Urania. Error bars indicate sea water concentration $C_w < \text{LOQ}$. The x-axis depicts the correspondence of sequential pairs of air samples (1–13) and water samples **(a–e)**.

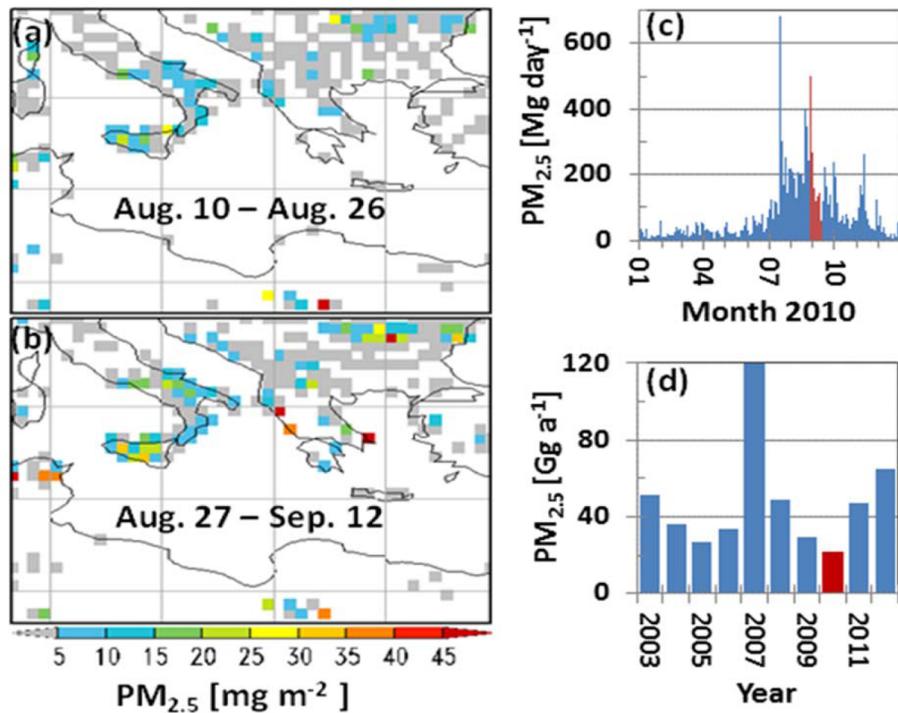


Fig. 2. Spatial pattern of fire-related $\text{PM}_{2.5}$ emissions (Global Fire Assimilation System GFASv1.0; Kaiser et al., 2012) for the East Mediterranean ($28\text{--}45^\circ\text{N}/8\text{--}30^\circ\text{E}$), **(a)** time integral of 10–26 August, **(b)** time integral of 27 August–12 September 2010, given as sum over each period in mg m^{-2} . Areas with no observed fire activity are displayed in white. Temporal pattern of domain-integrated **(c)** daily total $\text{PM}_{2.5}$ emissions over 2010 **(c)** and yearly total $\text{PM}_{2.5}$ emissions over 2003 to 2012. Labeled in red is **(c)** the the period of the Urania cruise (27 August–11 September 2010) **(d)** and the year 2010.

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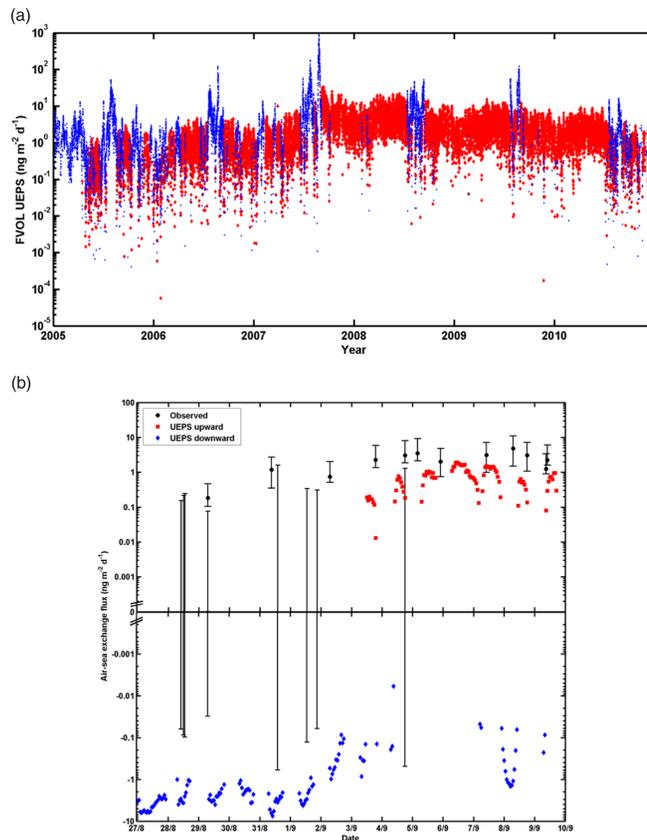


Fig. 3. Diffusive air–sea exchange flux, F_{aw} , of RET ($\text{ng m}^{-2} \text{d}^{-1}$; downward in blue and upward in red) using the upper estimate parameter set (UEPS) for the Eastern Mediterranean (28–45° N/8–30° E) **(a)** model predicted for 1.1.2005–31.12.2010 and **(b)** model predicted and observed (black) for 27.8.–9.9.2010. Hourly mean data filtered against off-shore winds (see text). Error bars including both signs of F_{aw} reflect $C_w < \text{LOQ}$.

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