Air-sea exchange and gas-particle partitioning of polycyclic aromatic hydrocarbons in the Mediterranean

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Abstract

Polycyclic aromatic hydrocarbons concentration in air of the central and eastern Mediterranean in summer 2010 was 1.45 (0.30-3.25) ng m^{-3} (sum of 25 PAHs), with 8 (1-17) % in the particulate phase, almost exclusively associated with particles <0.25 µm. The total deposition flux of particulate PAHs was 0.35-0.80 µg m^{-2} $year^{-1}$. The diffusive air-sea exchange fluxes of fluoranthene and pyrene were mostly found net-depositional or close to phase equilibrium, while retene was net-volatilisational 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. One third of primary retene sources to the sea

region in the period 2005-2010 returned to the atmosphere as secondary emissions from surface seawaters. 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.

Capsule: Polycyclic aromatic hydrocarbons phase distributions in marine aerosols, direction of air-sea exchange and open fires as a possible source characterised in the Mediterranean

Keywords: polycyclic aromatic hydrocarbons, long-range transport, air-sea exchange, open fires

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, domestic heating). 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 (Masclet et al., 1988; Tsapakis et. al, 2003 and 2006; Tsapakis and Stephanou, 2005a). A number of PAHs are semivolatile (vapour pressures at 298 K in the range 10^{-6}-10^{-2} 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 Saliot, 1991; Dachs et al., 1997; Tsapakis

et. al, 2003; Berrojalbiz et al., 2011). They were also found enriched in the sea-surface microlayer relative to 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 multicompartmental 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 Supplementary Material (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 using high-volume filter sampling (F = 68 m^3 h^{-1}, model HVS110, Baghirra, Prague) and low-volume impactor sampling (F = 0.54 m^3 h^{-1}, Sioutas 5-stage cascade, PM_{10} inlet, cutoffs 2.5, 1.0. 0.5, 0.25 µm of aerodynamic particle size and back-up filter, impaction on quartz fibre filters (QFF), SKC Inc., Eighty Four, USA, sampler Baghirra PM_{10-35}). In total 15 high-volume filter samples, exposed 8-36 h (230-1060 m^3 of air), and 3 low-volume impactor samples, exposed 5 d, were collected. Water sampling was performed using the stainless steel ROSETTE active sampling device equipped with 24 Niskin bottles (volume of 10 l) deployed in water at 1.5 m depth for surface water sampling.

PAH sampling on GFF and in PUF can be subject to losses related to oxidation of sorbed PAH by ozone (Tsapakis and Stephanou, 2003). This artifact is species-specific and the more pronounced the higher the ozone concentration and the longer the sampling time. Among the PAHs addressed benzo(a)pyrene and pyrene have been identified as particularly vulnerable to oxidation. Based on such sampling artefact quantification studies (Tsapakis and Stephanou, 2003; Galarneau et al., 2006) and ozone levels (Table 1a) and sampling times (Table S1) we expect that total PAHs are underestimated by up to 50% in the gas-phase and by up to 25% in the particulate phase.

With the aim to characterize the potential influences of ship-bourne emissions on the samples, passive air samplers with PUF disks were exposed at 5 different locations on board during 16 days. The PAH levels of these samples indicated that ship-based contamination was negligible.

2.2 PAHs analyses and quality assurance

For PAH analysis all samples were extracted with dichloromethane in an automatic extractor (Büchi B-811). Surrogate recovery standards (D8-naphthalene, D10-phenanthrene, D12-perylene) were spiked on each PUF and GFF prior to extraction. The volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on a silica gel column.

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 µL. GC-MS analysis was performed on a 6890N GC equipped with a 60m x 0.25mm x 0.25µm 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 µL. Terphenyl was used as internal standard.

Field blank values, b, were gained from GFFs and PUFs manipulated in the field, as far as possible identical to the samples, except without switching the high-volume sampler on. No QFF field blank was taken for impactor sampling. As no PAHs were detectedin the stages corresponding to 2.5-10 µm (all PAHs < limit of detection in all such samples), instead the mean of values of the QFF substrates of the 2 uppermost impactor stages (in total 6) 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 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 <LOQ (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) pg m^{-3} (according to sampled volume of air) resulted for ANT, PYR and

RET, and up to (45-180) pg m^{-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) pg m^{-3} for ACE, ANT, and FLT, ≈55 pg m^{-3} for FLN, and 120-140 pg m^{-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 pg m^{-3} for high-volume samples, ≈8 pg m^{-3} for impactor samples, 6-10 pg m^{-3} for semivolatile PAHs determined in passive air samples and up to 200 pg m^{-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 on GC/MS (Agilent GC 6890N coupled to an Agilent single quadrupole MS 5973N operating in electron impact ionisation mode). LOQ was 0.1 ng L^{-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 (15 high-volume samples of separate gas and particulate phase concentrations) 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. Adsorption to soot is a significant gas---particle partitioning processes for PAHs, but no soot data or PM chemical composition data are available. We, therefore, refrain from testing dual adsorption and absorption models (e.g. Lohmann and Lammel, 2004). 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 (4.32×10^{-7} 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).

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185 **2.4 Air-sea diffusive mass exchange calculations**

186 State of phase equilibrium is addressed by fugacity calculation, based on the Whitman two-
187 film model (Liss and Slater, 1974; Bidleman and McConnell, 1995**)**. The fugacity ratio (FR)
188 is calculated as:

189

190 $FR = f_a/f_w = C_a R T_a / (C_w H_{Tw,salt})$

191

192 with gas-phase concentration C_a (ng m^3), dissolved aqueous concentration C_w (ng m^3),
193 universal gas constant R (Pa m^3 mol^{-1} K^{-1}), water temperature and salinity corrected Henry's
194 law constant $H_{Tw,salt}$ (Pa m^3 mol^{-1}), and air temperature T_a (K). C_w is derived from the bulk
195 seawater concentration:

196

197 $C_w = C_{bulk} /(1 + K_{POC} C_{POC} + K_{DOC} C_{DOC})$

198

199 with C_{POC} and C_{DOC} from Pujo-Pay et al., 2011, K_{POC} and K_{DOC} from Karickhoff et al, 1981,
200 Lüers and ten Hulscher 1996, Rowe et al, 2009, and Ma et al, 2010. Values 0.3< FR <3.0 are
201 conservatively considered to not safely differ from phase equilibrium, as propagating from
202 the uncertainty of the Henry's law constant, $H_{Tw,salt}$, and measured concentrations (e.g., Bruhn
203 et al., 2003; Castro-Jiménez et al., 2012; Zhong et al., 2012). This conservative uncertainty
204 margin is also adopted here, while FR >3.0 indicates net deposition and FR <0.3 net
205 volatilisation. The diffusive air–seawater gas exchange flux (F_{aw}, ng m^{-2} 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}), defined as

$$1/k_{ol} = 1/k_w + RT_a/(k_a H_{Tw,salt})$$

with $k_a = (0.2U_{10} + 0.3)*(D_{i,air}/D_{H2O,air})^{0.61} \times 36$, $k_w = (0.45U_{10}^{1.64}) \times (Sc_i/Sc_{CO2})^{-0.5} \times 0.01$. U_{10} is the wind speed at 10 meter height above sea level (m s^{-1}), $D_{i,air}$ and $D_{H2O,air}$ are the temperature dependent diffusivities of substance *i* and H_2O in air, and Sc_i and Sc_{CO2} are the Schmidt numbers for substance *i* and CO_2 (see Bidleman and McConnell, 1995; Zhong et al. 2012; and references therein). U_{10}, T_a, T_w and air pressure are taken from the ship based measurements.

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). RET is selected, because of the prevalence of one dominating source. 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 export (settling) velocity, deposition flux from air, air-sea mass exchange flux (volatilisation), and degradation (as 1^{st} 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 ± 1.46) ng m^{-2} 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 m^2 effective fire area).

2.6 Analysis of long-range advection of air

Distributions of potential sources can be identified by inverse modelling using meteorological input data (Stohl et al., 2003; Eckhardt et al., 2007). So-called retroplumes are generated

using operational weather prediction model data and a Lagrangian particle dispersion model, FLEXPART (Stohl et al., 1998, 2005). Hereby, 50000 virtual particles per hour were 'released' and followed backwards in time for 5 days. The model output is a 3-D distribution of residence time.

3. Results and discussion

3.1 PAH concentrations in air and seawater

The mean total (i.e., sum of gaseous and particulate) Σ25 PAHs concentration is 1.45 ng m^{-3} (time-weighted; 1.54 with values <LOQ replaced by LOQ/2, see Table 1a), and ranged from 0.30-3.25 ng m^{-3}. 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). In the ISS some PAHs are found somewhat higher than previously measured i.e., FLT and PYR (in the gas-phase) and BAP and PER (in the particulate phase). Due to a sampling artefact BAP and other particulate phase PAHs could be underestimated by up to 25% (aforementioned, section 2.1). The seasonality of emissions and the variability of advection or advection in combination with different cruise routes being influenced differently by coastal or ship emission plumes can have a large influence and may explain these differences. On the other hand, the duration of temporal averaging atmospheric concentrations was similar across the various studies. 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 (section 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 air masses without apparent passage of such areas (illustrated in Fig. S5). This finding 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).

Most PAH concentrations in surface seawater were <LOQ, while FLT, PYR and RET were quantified in at least part of the samples (Table 1b). These observed seawater contamination levels are comparable to levels found in the region 2 and 1 decades ago (Lipiatou et al., 1997; Tsapakis et al., 2003). The concentrations 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) ng L^{-1} , PYR = 0.12 (0.07-0.17) ng L^{-1}.

Table 1. Concentrations of PAHs found in (a.) air (total, i.e. sum of gas and particulate phases, ng m^{-3}) and (b.) seawater (total, i.e. sum of dissolved and particulate, ng L^{-1}) as time-weighted mean (min-max). n_{LOQ} = number of samples > LOQ (out of 15 air and 23 seawater samples). PAHs with concentrations <LOQ in all samples not listed. For calculation of mean values <LOQ were replaced by LOQ/2. Ozone levels are given, too (ppbv).

a)

	n_{LOQ}	mean (min-max)

ACE	4	0.025 (<0.020–0.089)
FLN	10	0.137 (<0.030–0.396)
PHE	15	0.581 (0.144–1.41)
ANT	13	0.043 (0.008–0.22)
RET	14	0.016 (0.006–0.030)
FLT	15	0.262 (0.053–0.795)
PYR	15	0.203 (0.044–0.564)
BAA	15	0.01 (0.0014–0.031)
CHR	15	0.04 (0.012–0.092)
TPH	15	0.018 (0.007–0.032)
BBN	11	0.018 (0.001–<0.085)
BBF	15	0.021 (0.004–0.102)
BKF	14	0.012 (0.002–<0.085)
BAP	12	0.015 (0.001–<0.085)
BGF	15	0.021 (0.005–0.067)
CPP	7	0.012 (0.001–<0.085)
BJF	15	0.016 (0.002–0.079)
BEP	14	0.019 (0.004–0.088)
PER	7	0.012 (0.001–0.1)
IPY	7	0.022 (0.008–0.094)
BPE	6	0.02 (0.009–0.085)
COR	5	0.016 (0.002–0.1)

Σ25 PAHs		1.539 (0.44–4.694)
Ozone		42 (33 – 65)

b)

	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)

Table 2 Gaseous (a) and particulate (b) concentrations in air (time-weighted 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). For calculation of means values <LOQ were replaced by LOQ/2. RV = research vessel cruise.

a)

	ISS		SEM			
	RV August-September 2010	RV June 2006, May 2007	RV August-September 2010	RV June 2006, May 2007	Finokalia September-October 2001, February, March and July 2002 (1)	Finokalia November 2000-February 2002(2)
	this study	Castro-Jiménez 2012	this study	Castro-Jiménez 2012	Tsapakis et al. 2006	Tsapakis & Stephanou 2005

FLN	0.18 (0.050–0.40)	2.25 (1.27–5.65)	0.11 (<0.027–0.34)	0.69 (0.36–1.23)	1.05 (0.15–1.67)	1.8 (0.2–5.7)
PHE	0.59 (0.14–1.10)	7.00 (3.52–15.45)	0.51 (0.14–1.41)	3.94 (2.50–6.35)	4.78 (1.75–7.78)	7.3 (1.5–27.7)
ANT	0.064 (<0.021–0.10)	0.37 (0.18–0.55)	0.067 (<0.013–0.22)	0.20 (0.16–0.30)	0.61 (0.12–1.31)	0.9 (0.1–4.5)
FLT	0.15 (0.053–0.31)	0.05 (0.02–0.07)	0.15 (0.061–0.37)	0.007 (0.003–0.011)	0.82 (0.12–1.69)	1.8 (0.07–6.0)
PYR	0.15 (0.044–0.29)	0.04 (0.02–0.06)	0.19 (0.058–0.56)	0.006 (0.003–0.009)	0.65 (0.14–0.97)	0.9 (0.1–2.8)
CHR	0.013 (0.0071–0.021)	0.09 (0.03–0.23)	0.018 (0.012–0.037)	0.03 (0.02–0.05)	0.18 (0.06–0.33)	0.2 (<0.001–0.6)
Sum of 6 PAHs	1.1	9.8	1.0	4.9	8.1	12.9

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305 b)

	ISS		SEM		
	RV August-September 2010	RV June 2006, May 2007	RV August-September 2010	RV June 2006, May 2007	Finokalia November 2000-February 2002
	this study	Castro-Jiménez 2012	this study	Castro-Jiménez 2012	Tsapakis & Stephanou 2005

FLN	<0.92 (<0.60–<1.1)	0.001 (0.0009–0.002)	<0.66 (<0.33–<1.4)	0.0013 (0.0011–0.0016)	0.02 (<0.001–0.01)
PHE	<1.9 (<1.2–<2.3)	0.06 (0.01–0.12)	<1.6 (<0.66–<2.7)	0.04 (0.01–0.13)	0.05 (0.004–0.2)
ANT	<0.21 (<0.14–<0.26)	0.007 (0.0009–0.012)	<0.16 (<0.07–<0.32)	0.009 (0.0007–0.023)	0.004 (<0.001–0.02)
FLT	<0.85 (<0.56–<1.0)	0.099 (0.01–0.19)	<0.62 (<0.30–<1.3)	0.049 (0.01–0.12)	0.1 (0.04–0.2)
PYR	<0.11 (<0.070–<0.13)	0.109 (0.016–0.216)	<0.08 (<0.044–<0.16)	0.057 (0.012–0.142)	0.04 (0.01–0.01)
BAA	0.0065 (<0.0018–0.025)	0.013 (0.006–0.023)	0.0030 (<0.0006–0.0080)	0.018 (0.004–0.046)	0.03 (0.003–0.1)
CHR	0.021 (0.0030–0.076)	0.04 (0.01–0.08)	0.010 (0.0033–0.020)	0.043 (0.012–0.101)	0.1 (0.02–0.3)
BBF	0.028 (<0.0018–0.010)	0.029 (0.012–0.045)	0.014 (0.0042–0.033)	0.033 (0.010–0.060)	0.04 (<0.001–0.2)
BKF	0.015 (<0.0018–0.057)	0.015 (0.005–0.027)	0.0065 (0.0018–0.015)	0.089 (0.005–0.333)	0.04 (<0.001–0.2)

BAP	0.016 (<0.0009–0.072)	0.009 (0.04–0.016)	0.0052 (<0.0011–0.0098)	0.034 (0.005–0.081)	0.02 (0.01–0.05)
BJF	0.021 (<0.0018–0.079)	0.015 (0.014–0.016)	0.011 (0.0023–0.031)	0.010 (0.008–0.011)	-
BEP	0.023 (<0.0018–0.088)	0.03 (0.02–0.05)	0.011 (0.0035–0.025)	0.046 (0.017–0.093)	0.04 (0.01–0.1)
PER	0.0028 (<0.00096–0.011)	0.002 (0.0005–0.004)	0.00085 (<0.0006–0.0021)	0.026 (0.0001–0.068)	0.004 (<0.001–0.01)
IPY	0.020 (<0.00096–0.094)	0.018 (0.006–0.032)	0.0043 (<0.00052–0.019)	0.009 (0.002–0.013)	0.03 (0.009–0.2)
BPE	<0.0014 (<0.00096–0.0018)	0.026 (0.017–0.042)	0.0067 (<0.00052–0.020)	0.081 (0.012–0.210)	0.03 (0.010–0.09)
Sum of 15 PAHs	0.15	1.06	0.06	0.54	0.54

[(1)] months Sep and Oct 2001, Feb, Apr and May 2002. No particulate data reported.

[(2)] 24h per month between Feb 2000 and Feb 2002

3.2 Gas-particle partitioning

310 Only a small mass fraction of the total, $\theta = 0.08$, is found in the particulate phase, confirming
311 earlier findings from remote sites in the region (Tsapakis and Stephanou, 2005a; Tsapakis et
312 al., 2006; Table 3c). The particulate mass fraction, θ, of four semivolatile PAHs varied
313 considerably along track (see SM Fig. S2). θ is thought to be strongly influenced by
314 temperature and doubling per 13 K cooling was found in a Mediterranean environment
315 (Lammel et al., 2010b) apart from PM composition. We refrain from an exploration of the
316 vapour pressure (p_{L0}) dependence of θ (or K_p): a low time resolution implies lack of
317 representativeness of the temperature measurement for the phase change (Pankow and
318 Bidleman, 1992), non-equilibrium conditions cannot be excluded (but are likely as a
319 consequence of time resolution; Hoff et al., 1998) and supporting physical and chemical
320 aerosol parameters, necessary to relate are lacking.
321 of only little temperature variation during the cruise (T_{mean_sample} = 21-27°C, Fig. S2). For
322 similar temperatures higher θ values had been observed at sites on the region influenced by
323 urban and industrial sources (Mandalakis et al., 2002; Tsapakis and Stephanou, 2005b; Akyüz
324 and Cabuk, 2010), which is probably related to the influence of higher organic and soot PM
325 mass fractions. Gas-particle partitioning models (Table 3) underpredict θ, except the Finizio
326 et al., 1997, model for one substance, TPH. θ predicted by the Junge-Pankow (JP) model
327 comes closest. A number of semivolatile PAHs could not be included in this test of gas-
328 particle partitioning models as concentrations in either the gas-phase (CPP, BBF, BJF), or the
329 particulate phase (FLT, PYR, BBN) did not exceed LOQ or no insufficient input data were
330 available (BBF). The neglect of adsorption to soot, not covered by the gas-particle
331 partitioning models tested, may explain at least part of the underprediction (Lohmann and
332 Lammel, 2004). Due to the lack of OC/EC data an extended examination is not possible.

In size-segregated samples particulate PAH mass was almost exclusively found in the size fraction <0.25 µm a.e.d. (<LOQ in the other stages, except 0.002 ng m^{-3} CPP in the size fraction corresponding to 0.5-1.0 µm; S2.1, Table S4). Most particulate phase PAHs, 40%, have been found associated with particles <0.5µm out of 5 size ranges in the marine background aerosol of the sea region (coast of Crete, November 1996 – June 1997; Kavouras and Stephanou, 2002). At continental sites in central and southern Europe mass median diameters of PAHs were found to be in the accumulation range, mostly 0.5-1.4 µm (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 µm; Chrysikou et al., 2009).

Table 3. Gas-particle partitioning of selected PAHs (mean ± sd (median)), 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.

a)

	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

b)

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

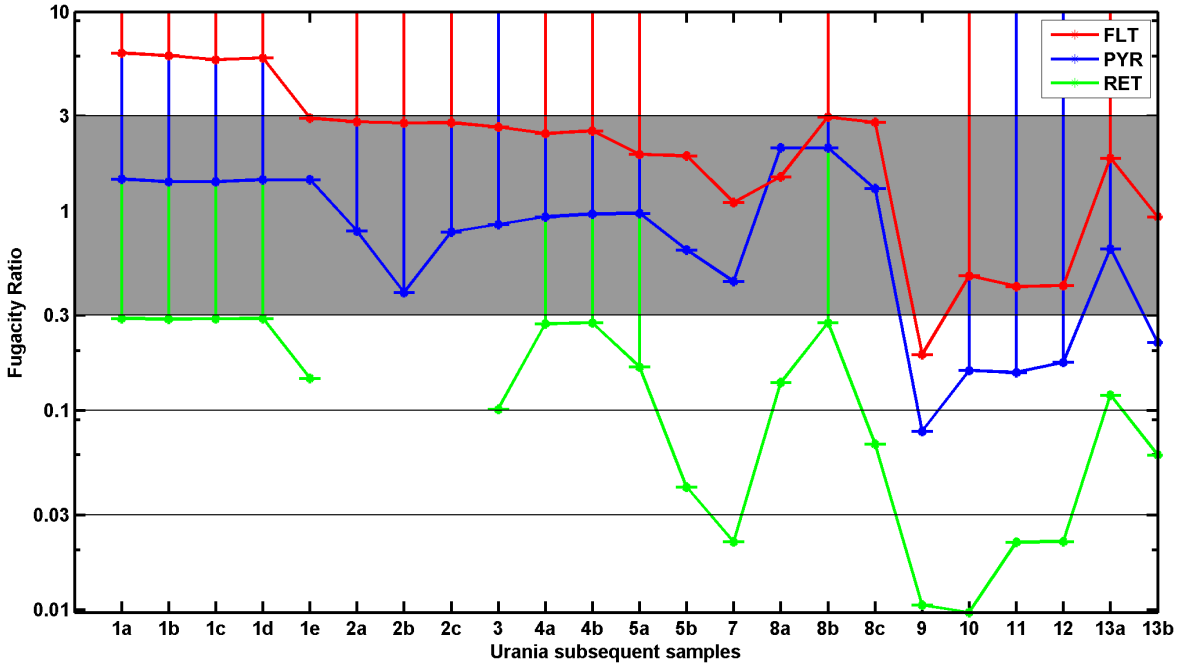
350

351 **3.3 Fugacity ratio and air-sea exchange flux**

352 Fugacity ratios (Fig. 1a) and vertical fluxes (Fig. 1b) could be quantified for FLT, PYR and
353 RET. The uncertainty window of FR = f_a/f_w = 0.3 - 3.0 is based on the uncertainty of $H_{Tw,salt}$.
354 Values FR >3.0 indicate net deposition, FR <0.3 indicate net volatilisation. For RET both
355 water and air concentrations of sample No. 2 were <LOQ. Transfer coefficients were k_w <<
356 k_a.

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

362 a.



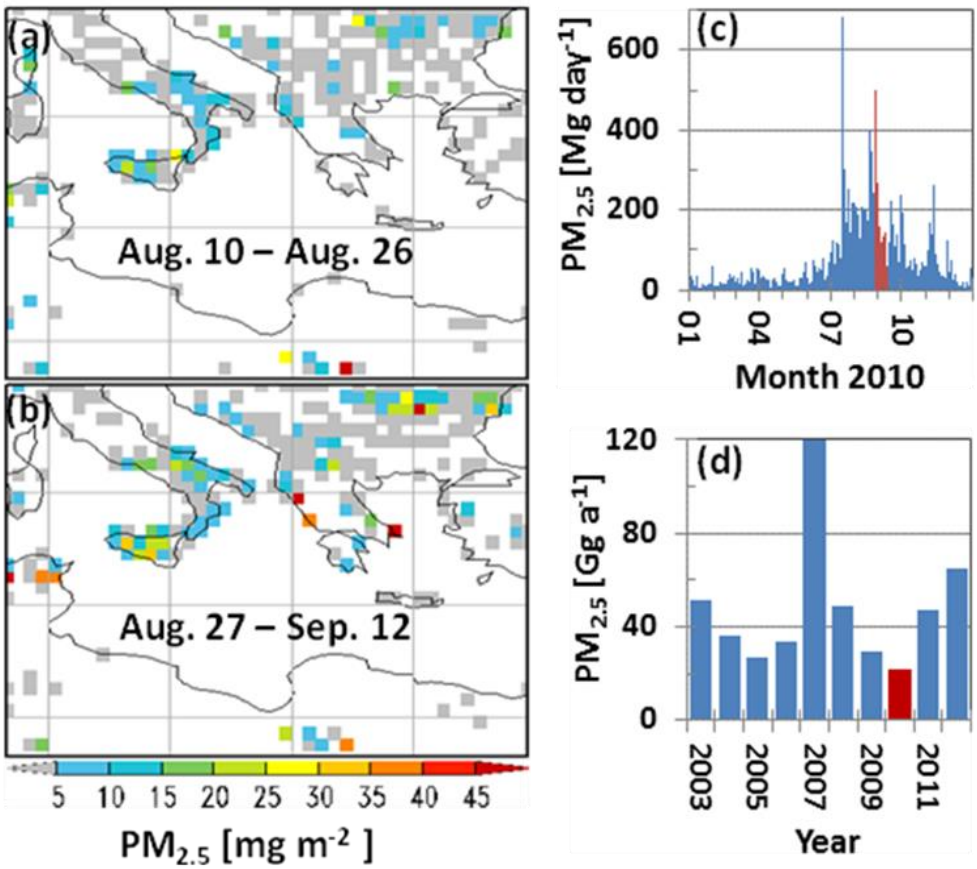
b.

FLT and PYR were found 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-volatilisational throughout most of the cruise (Fig. 1). Among the highest fluxes (> 50 ng m^2 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 Pa m^3 mol^{-1} at 298 K) which is higher than for CHR (0.53 Pa m^3 mol^{-1}) and FLT (2.0 Pa m^3 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 $PM_{2.5}$ emitted (Fig. 2). Compared to the $PM_{2.5}$ 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 observed 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).

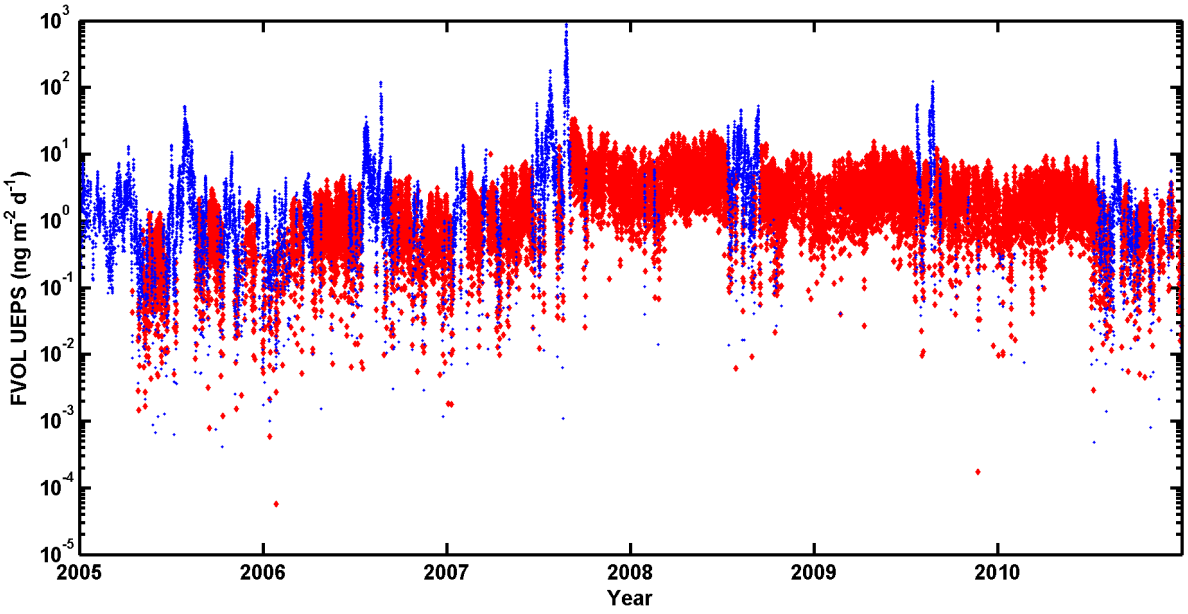
Fig. 2. Spatial pattern of fire-related $PM_{2.5}$ emissions (Global Fire Assimilation System GFASv1.0; Kaiser et al., 2012) for the East Mediterranean (28-45°N/8-30°E), (a) time integral of August 10-26, (b) time integral of August 27 - September 12, 2010, given as sum

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 $PM_{2.5}$ emissions over 2010 (c) and yearly total $PM_{2.5}$ emissions over 2003 to 2012. Labelled in red is (c) the the period of the Urania cruise (27 August – 11 September 2010) (d) and the year 2010.



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 (sections 2.5 and S1.3) runs. Two scenarios 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

405 flux, F_{aw}, during 2005-2010 initialised by the UEPS is shown in Fig. 3a and by the IEPS in
406 the SM, Fig. S3, and during the observations (cruise of RV Urania, 27.8.-9.9.2010) initialised
407 by the UEPS in Fig. 3b.
408 The model confirms the hypothesis that seasonal depositional input of RET into the surface
409 waters during the fire season (July-September, typically in the range $F_{aw} = 10^{-2}$-10^{1} ng m^{-2} d^{-1}
410 under IEPS) is followed by a period of prevailing flux reversal, typically $F_{aw} = 10^{-2}$-10^{0} ng m^{-2} d^{-1}
411 , which in the years 2008-10 started in October and lasted until the onset of the fire
412 season, but eventually started later in the years 2005-07 (at least under IEPS). The
413 volatilisation flux is predicted smaller in magnitude than the net-deposition flux during the
414 fire season, but correspondingly, i.e. higher after intense fire seasons. The high RET
415 volatilisation flux, indicated by measured C_a and C_w, seems to be dominated by biomass
416 burning in the region in the previous fire season. F_{aw} is predicted highly fluctuating, also
417 during the observational period (Fig. 3b). Even under UEPS the model is underpredicting F_{aw}
418 (Fig. 3b). The sensitivity to input uncertainties (SM S1.2) may explain part of the
419 underestimate, but not up to one order of magnitude. Neglected RET sources to seawater,
420 such as riverine input may explain part of the discrepancy.
421
422 Fig. 3. Diffusive air-sea exchange flux, F_{aw}, of RET (ng m^{-2} d^{-1}; downward in blue and
423 upward in red) using the upper estimate parameter set (UEPS) for the Eastern Mediterranean
424 (28-45°N/8-30°E) (a.) model predicted for 1.1.2005-31.12.2010 and (b.) model predicted and
425 observed (black) for 27.8.-9.9.2010. Hourly mean data filtered against off-shore winds (see
426 text). Error bars including both signs of F_{aw} reflect C_w <LOQ.a.



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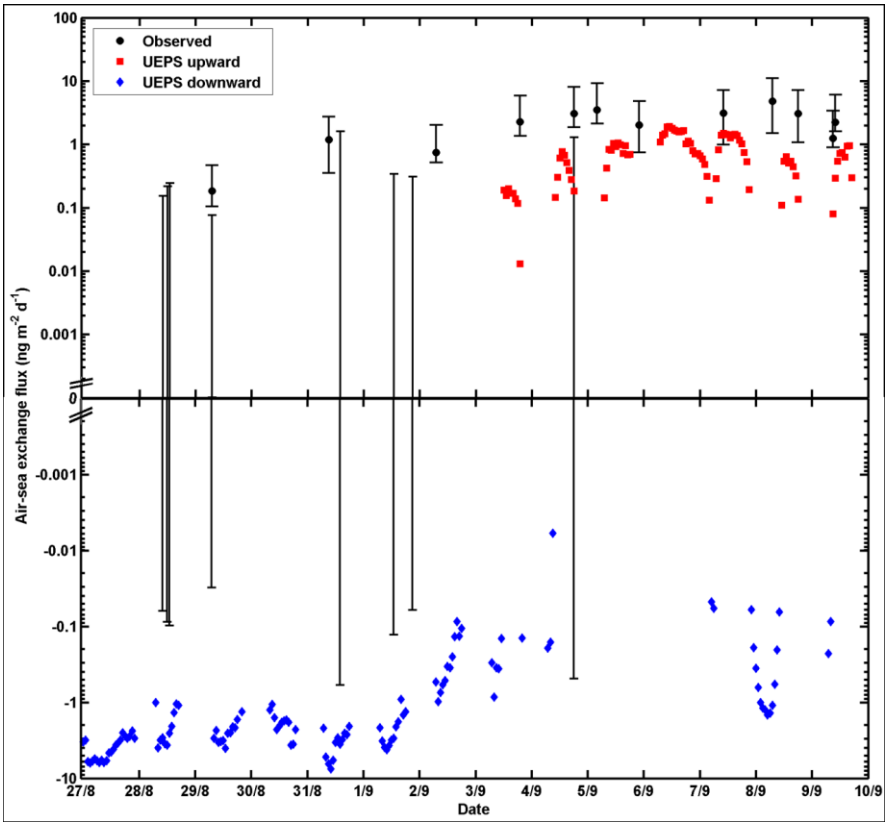
428

429 b.



430

431

432 **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. The particulate phase PAHs were concentrated in the size fraction < 0.25 μm a.e.d. The residence time in the troposphere is longest for particles around 0.2 μm of size, with ≈0.01 cm s^{-1} being a characteristic corresponding dry deposition velocity (Franklin et al., 2000), which translates into a residence time of ≈120 days in the MBL (depth of 1000 m; see Table S3) and deposition flux $F_{dep} = c \times v$ = 0.03-0.13 μg m^{-2} $year^{-1}$ for the individual PAHs associated with the particulate phase (c = 0.01-0.04 ng m^{-3}; Table 2b), such as BAP, and 0.80 and 0.35 μg m^{-2} $year^{-1}$, respectively, for the total flux of particulate phase PAHs in the ISS and SEM in summer, respectively. The flux will be higher in winter, because of the seasonality of the emissions.

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. For the wood burning marker RET it is found that the secondary source became significant in recent years: While the flux of secondary RET emissions (from surface seawaters) in the study area was 1.0 µg m^{-2} $year^{-1}$ (mean of years 2005-2010,_UEPS), the primary sources amounted to 3.1 µg m^{-2} $year^{-1}$. 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.

Acknowledgements

We thank the crew of RV Urania for scientific support during the cruise, and Giorgos Kouvarakis and Nikolas Mihalopoulos, University of Crete, Franz Meixner, MPIC, and Manolios Tsapakis, HCMR Gournes-Pediados, for discussion and providing meteorological data. This research was supported by the Granting Agency of the Czech Republic (GACR project No. P503/11/1230), by the European Commission (European Structural Funds project No. CZ.1.05/2.1.00/01.0001, CETOCOEN) and has been co-funded from the European Social Fund and the state budget of the Czech Republic.

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