

Some corrections and clarifications are still needed.

We would like to thank for careful re-reviewing and useful comments. We have addressed all comments below. In addition, we corrected an erroneous calculation (**Table 2**, see below).

Main text:

A few acronyms should still be defined. This is the case for the indices p and g of c, OM (it is first used in line 165, but only defined in line 184), Fem, and ISS (it is first used in line 267, but only defined in line 285).

done

Lines 62-65: In contrast to what is written in the reply, this paragraph was not rephrased. It should be.

thanks for reminding, this had indeed been forgotten, now done

Line 173: It is still unclear what the difference is between “cp” and “cTSP”.

now clarified

Line 235: Replace “supplementary material (SM)” by “SM”; “SM” is defined in line 70.

done

Lines 305-306 (**Table 2**): The basis for the calculation of time-weighted means in columns 2 and 4 ('this study') was incorrect (used the wrong sampling times of the individual samples: instead of the time weights 0.29-0.15-0.18-0.22-0.16 for 5 samples collected in the ISS 0.21-0.20-0.24-0.15-0.20 was used, and instead of the time weights 0.27-0.20-0.07-0.15-0.31 for another 5 samples collected in the SEM 0.20-0.19-0.21-0.23-0.18 was used). Now replaced by the means based on the correct sampling times of the individual samples, somewhat lower in Table 2, in the conclusions (lines 443-445) and in the abstract (line 17: total deposition flux of particulate PAHs was $0.3\text{-}0.5 \mu\text{g m}^{-2} \text{ year}^{-1}$, rather than ' $0.35\text{-}0.8 \mu\text{g m}^{-2} \text{ year}^{-1}$ ').

Lines 360-364, further in the main text, and also in the Supplementary Material: Figure captions should be below figures instead of above.

done

Supplementary Material:

Page 9, line 9: Replace “also SM Fig. S4a” by “also Fig. S4a”.

done

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

3 Marie D. Mulder^a, Angelika Heil^b, Petr Kukučka^a, Jana Klánová^a, Jan Kuta^a, Roman Prokeš^a,
4 Francesca Sprovieri^c, Gerhard Lammel^{a,d*}

5 ^a Masaryk University, Research Centre for Toxic Compounds in the Environment, Brno,
6 Czech Republic

7 ^b Helmholtz Research Centre Jülich, Institute for Energy & Climate Research, Jülich,
8 Germany

9 ^c CNR, Institute for Atmospheric Pollution Research, Rende, Italy

10 ^d Max Planck Institute for Chemistry, Mainz, Germany

11 * phone +420-54949-4106, fax +420-54949-2840, lammel@recetox.muni.cz

12

13 **Abstract**

14 Polycyclic aromatic hydrocarbons concentration in air of the central and eastern
15 Mediterranean in summer 2010 was 1.45 (0.30-3.25) ng m⁻³ (sum of 25 PAHs), with 8 (1-17)
16 % in the particulate phase, almost exclusively associated with particles <0.25 μm. The total
17 deposition flux of particulate PAHs was 0.3-0.5 μg m⁻² year⁻¹. The diffusive air-sea exchange
18 fluxes of fluoranthene and pyrene were mostly found net-depositional or close to phase
19 equilibrium, while retene was net-volatilisation in a large sea region. Regional fire activity
20 records in combination with box model simulations suggest that seasonal depositional input
21 of retene from biomass burning into the surface waters during summer is followed by an
22 annual reversal of air-sea exchange, while inter-annual variability is dominated by the
23 variability of the fire season. One third of primary retene sources to the sea region in the

24 period 2005-2010 returned to the atmosphere as secondary emissions from surface seawaters.
25 It is concluded that future negative emission trends or interannual variability of regional
26 sources may trigger the sea to become a secondary PAH source through reversal of diffusive
27 air-sea exchange.

28

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

31

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

34

35 **1. Introduction**

36 The marine atmospheric environment is a receptor for polycyclic aromatic hydrocarbons
37 (PAHs) which are advected from combustion sources on land (power plants, biomass
38 burning, road transport, domestic heating). Marine sources may be significant near transport
39 routes (ship exhaust). Long-range transport from urban and industrial sources on land are the
40 predominant sources of PAHs in the Mediterranean (Masclat et al., 1988; Tsapakis et. al,
41 2003 and 2006; Tsapakis and Stephanou, 2005a). A number of PAHs are semivolatile (vapour
42 pressures at 298 K in the range 10^{-6} - 10^{-2} Pa) and, hence partition between the gas and
43 particulate phases of the atmospheric aerosol, influenced by temperature, particulate phase
44 chemical composition and particle size (Keyte et al., 2013). Upon deposition to surface water
45 PAHs partition between the aqueous and particulate (colloidal and sinking) phases and may
46 bioaccumulate in marine food chains (Lipiatou and Saliot, 1991; Dachs et al., 1997; Tsapakis

47 et. al, 2003; Berrojalbiz et al., 2011). They were also found enriched in the sea-surface
48 microlayer relative to subsurface water (Lim et al., 2007; Guitart et al., 2010). Semivolatile
49 PAHs may be subject to re-volatilisation from the sea surface (reversal of air-sea exchange),
50 similar to chlorinated semivolatile organics (Bidleman and McConnell, 1995), in case high
51 concentrations in surface water would build up. This had been predicted by
52 multicompartmental modelling for 2-4 ring PAHs for polluted coastal waters and also the
53 open ocean (Greenfield and Davis, 2005; Lammel et al., 2009a) and was indeed observed in
54 coastal waters off the northeastern United States (Lohmann et al., 2011). Field studies in the
55 open sea found net-deposition to prevail whenever determined (e.g. Tsapakis et al., 2006;
56 Balasubramanian and He, 2010; Guitart et al., 2010; Castro-Jiménez et al., 2012; Mai, 2012).
57 However, some 3-4 ring parent PAHs, among them fluorene (FLN), fluoranthene (FLT) and
58 pyrene (PYR), were reported to be close to phase equilibrium in the Mediterranean, Black
59 and North seas (Castro-Jiménez et al., 2012; Mai, 2012), and net volatilisation of FLT and
60 PYR was observed in the open southeastern Mediterranean Sea in spring 2007 (Castro-
61 Jiménez et al., 2012).

62 The aim of [this study was to add insights on the cycling of PAHs in the Mediterranean in](#)
63 [summer, with a focus on](#) sources and phase partitioning in the aerosol.

65 2. Methods

66 2.1 Sampling

67 Gas and particulate phase air samples were taken during the RV Urania cruise, 27 August –
68 12 September 2010 (see Supplementary Material (SM), Fig. S1). The high volume sampler
69 (Digitel) was equipped with one glass fibre filter (GFF, Whatman) and one polyurethane

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Gelöscht: the measurements on board RV Urania was to investigate levels of organic pollutants in summer in Mediterranean air and gain insights about

Gelöscht: of these substances. This study is on the cycling of PAHs in the marine atmosphere

70 foam (PUF) plug (Gumotex Břeclav, density 0.030 g cm^{-3} , 50 mm diameter, cleaned by
71 extraction in acetone and dichloromethane, 8 h each, placed in a glass cartridge) in series.
72 Particle size was classified in the particulate phase using high-volume filter sampling ($F = 68$
73 $\text{m}^3 \text{ h}^{-1}$, model HVS110, Baghirra, Prague) and low-volume impactor sampling ($F = 0.54 \text{ m}^3 \text{ h}^{-1}$,
74 Sioutas 5-stage cascade, PM_{10} inlet, cutoffs 2.5, 1.0, 0.5, $0.25 \mu\text{m}$ of aerodynamic particle
75 size and back-up filter, impaction on quartz fibre filters (QFF), SKC Inc., Eighty Four, USA,
76 sampler Baghirra PM_{10-35}). In total 15 high-volume filter samples, exposed 8-36 h ($230\text{-}1060$
77 m^3 of air), and 3 low-volume impactor samples, exposed 5 d, were collected. Water sampling
78 was performed using the stainless steel ROSETTE active sampling device equipped with 24
79 Niskin bottles (volume of 10 l) deployed in water at 1.5 m depth for surface water sampling.

80

81 PAH sampling on GFF and in PUF can be subject to losses related to oxidation of sorbed
82 PAH by ozone (Tsapakis and Stephanou, 2003). This artifact is species-specific and the more
83 pronounced the higher the ozone concentration and the longer the sampling time. Among the
84 PAHs addressed benzo(a)pyrene and pyrene have been identified as particularly vulnerable to
85 oxidation. Based on such sampling artefact quantification studies (Tsapakis and Stephanou,
86 2003; Galarneau et al., 2006) and ozone levels (Table 1a) and sampling times (Table S1) we
87 expect that total PAHs are underestimated by up to 50% in the gas-phase and by up to 25% in
88 the particulate phase.

89 With the aim to characterize the potential influences of ship-bourne emissions on the
90 samples, passive air samplers with PUF disks (150 mm diameter, 15 mm thick, deployed in
91 protective chambers consisting of two stainless steel bowls; Klánová et al., 2008) were

92 exposed at 5 different locations on board during 16 days. The PAH levels of these samples
93 indicated that ship-based contamination was negligible.

94

95 **2.2 PAHs analyses and quality assurance**

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

101 The extract was fractionated on a silica column (5 g of silica 0.063 – 0.200 mm, activated 12
102 h at 150°C). The first fraction (10 mL n-hexane) containing aliphatic hydrocarbons was
103 discarded. The second fraction (20 mL dichloromethane) containing PAHs was collected and
104 then reduced by stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA)
105 concentrator unit and transferred into an insert in a vial. Terphenyl was used as syringe
106 standard, final volume was 200 µL. Gas-chromatography / mass spectrometric analysis was
107 performed on a 6890N GC equipped with a 60m x 0.25mm x 0.25µm DB5-MS column
108 (Agilent J&W, USA) coupled to 5973N MS (Agilent, USA). The MS was operated in
109 electron impact positive ion mode with selected ion recording (SIR). The targeted compounds
110 are the 16 EPA priority PAHs (i.e., naphthalene (NAP), acenaphthylene (ACY),
111 acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene
112 (FLT), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene
113 (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), indeno(123cd)pyrene (IPY),
114 dibenzo(ah)anthracene (DBA), benzo(ghi)perylene (BPE)), 10 more parent PAHs (i.e.,

115 benzo(ghi)fluoranthene (BGF), cyclopenta(cd)pyrene (CPP), triphenylene (TPH),
116 benzo(j)fluoranthene (BJF), benzo(k)fluoranthene (BKF), benzo(e)pyrene (BEP), perylene
117 (PER), dibenz(ac)anthracene (DCA), anthranthrene (ATT), and coronene (COR)), and one
118 alkylated PAH, retene (RET). The injection volume was 1 μ L. Terphenyl was used as internal
119 standard.

120 Field blank values, b , were gained from GFFs and PUFs manipulated in the field, as far as
121 possible identical to the samples, except without switching the high-volume sampler on. No
122 QFF field blank was taken for impactor sampling. As no PAHs were detected in the stages
123 corresponding to 2.5-10 μ m (all PAHs < limit of detection in all such samples), instead the
124 mean of values of the QFF substrates of the 2 uppermost impactor stages (in total 6) was
125 taken. The respective b value was subtracted from sample values. The limit of quantification
126 needs to take the accuracy of the blank level into account. In lack of a measure for the
127 variation of the field blank, the relative standard deviation (SD) of field blanks from earlier
128 field campaigns, (σ_c/b_c) , on a high-mountain site (high-volume sampling summer 2007, $n = 5$;
129 Lammel et al., 2009b) and in the Mediterranean (impactor sampling summer 2008, $n = 6$;
130 Lammel et al., 2010a) was used ($\sigma = (\sigma_c/b_c) \times b$). Identical samplers, sampling and analysis
131 protocols for all analytes had been applied. Values below the sum of the field blank value
132 (from this campaign) and 3 relative SDs of the field blank values (from the previous
133 campaigns) were considered <LOQ (limit of quantification, $LOQ = b + 3\sigma$). NAP and ACY
134 were excluded from the data set, because of the lack of blank values. The field blank values
135 of most other analytes were below instrument LOQ in high-volume PUF and GFF samples.
136 However, higher field LOQs, up to (6-25) pg m^{-3} (according to sampled volume of air)
137 resulted for ANT, PYR and RET, and up to (45-180) pg m^{-3} for ACE, FLN, PHE and FLT in

138 PUF. Field LOQs of PAHs in impactor QFF samples were below instrumental LOQ for most
139 substances, but in the range (8-15) pg m^{-3} for ACE, ANT, and FLT, $\approx 55 \text{ pg m}^{-3}$ for FLN, and
140 $120\text{-}140 \text{ pg m}^{-3}$ for NAP and PHE.

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

145 Water samples (2-2.5 L) were extracted immediately after their collection using solid phase
146 extraction on C_{18} Empore discs using a vacuum manifold device. Disks were stored closed in
147 glass vials in a freezer and transported to the processing laboratory, PAHs were eluted from
148 disks using 40 mL of dichloromethane. The above listed PAHs were analysed on GC/MS
149 (Agilent GC 6890N coupled to an Agilent single quadrupole MS 5973N operating in electron
150 impact ionisation mode). LOQ was 0.1 ng L^{-1} .

151

152 **Other trace constituents and meteorological parameters**

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

156

157 **2.3 Models of gas-particle partitioning**

158 The data set (15 high-volume samples of separate gas and particulate phase concentrations)
159 is used to test gas-particle partitioning models for semivolatile organics in terms of the
160 organics' mass size distribution and size dependent particulate matter (PM) composition. The

161 models assume different processes to determine gas-particle partitioning, i.e. an adsorption
 162 model (Junge-Pankow; Pankow, 1987), and two absorption models (i.e. K_{OA} models; Finizio
 163 et al., 1997; Harner and Bidleman, 1998). Absorption is into particulate [organic matter \(OM\)](#).
 164 Adsorption to soot is a significant gas--particle partitioning processes for PAHs, but no soot
 165 data or PM chemical composition data are available. We, therefore, refrain from testing dual
 166 adsorption and absorption models (e.g. Lohmann and Lammel, 2004). Particulate mass
 167 fraction, θ , and partitioning coefficient, K_p , are defined by the concentrations in the 2 phases:

168

$$169 \quad \theta = c_p / (c_p + c_g)$$

170

$$171 \quad K_p = c_p / (c_g \times c_{TSP}) = \theta / [(1 - \theta) \times c_{TSP}]$$

172

173 With [PAH particulate and gas-phase concentrations](#) c_p and c_g in units of ng m^{-3} , c_p
 174 representing the whole particle size spectrum, [concentration of](#) total suspended matter, c_{TSP} .

Gelöscht: concentration

175 Different models describe different processes to quantify differences in ad- and absorption
 176 between compounds. The Junge-Pankow model uses the vapour pressure of the sub-cooled
 177 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
 178 171 Pa cm for PAHs (Pankow, 1987). The aerosol particle surface concentration, S , was not
 179 measured and a typical value for maritime aerosols is adopted instead ($4.32 \times 10^{-7} \text{ cm}^{-1}$;
 180 Jaenicke, 1988). Harner and Bidleman, 1998, use the $\log K_{OA}$ and f_{OM} : $\log K_p = \log K_{OA} + \log$
 181 $f_{OM} - 11.91$; and Finizio et al., 1997, uses only the K_{OA} as predictor (data taken from Ma et al.,
 182 2010): $\log K_p = 0.79 \times \log K_{OA} - 10.01$. The range of the fraction of [OM](#) used here is based on
 183 Putaud et al., 2004 (16% lower limit) and Spindler et al., 2012 (45% upper limit).

Gelöscht: organic matter (

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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

$$190 \text{ FR} = f_a/f_w = C_aRT_a / (C_wH_{T_w,\text{salt}})$$

191

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

196

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

198

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

206 gas exchange flux (F_{aw} , $\text{ng m}^{-2} \text{ day}^{-1}$) is calculated according to the Whitman two-film model
207 (Bidleman and McConnell, 1995; Schwarzenbach et al., 2003):

208

$$209 \quad F_{aw} = k_{ol} (C_w - C_a RT_a / H_{Tw,salt})$$

210

211 with air-water gas exchange mass transfer coefficient k_{ol} (m h^{-1}), accounting for resistances
212 to mass transfer in both water (k_w , m h^{-1}) and air (k_a , m h^{-1}), defined as

213

$$214 \quad 1/k_{ol} = 1/k_w + RT_a / (k_a H_{Tw,salt})$$

215

216 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
217 the wind speed at 10 meter height above sea level (m s^{-1}), $D_{i,air}$ and $D_{H2O,air}$ are the
218 temperature dependent diffusivities of substance i and H_2O in air, and Sc_i and Sc_{CO2} are the
219 Schmidt numbers for substance i and CO_2 (see Bidleman and McConnell, 1995; Zhong et al.
220 2012; and references therein). U_{10} , T_a , T_w and air pressure are taken from the ship based
221 measurements.

222

223 **2.5 Non-steady state 2-box model**

224 The air-sea mass exchange flux of RET is simulated by a non-steady state zero-dimensional
225 model of intercompartmental mass exchange (Lammel, 2004). RET is selected, because of
226 the prevalence of one dominating source. This 2-box model predicts concentrations by
227 integration of two coupled ordinary differential equations that solve the mass balances for the
228 two compartments, namely the atmospheric marine boundary layer (MBL) and seawater

229 surface mixed layer. Processes considered in air are dry (particle) deposition, removal from
230 air by reaction with the hydroxyl radical, and air-sea mass exchange flux (dry gaseous
231 deposition), while in seawater export (settling) velocity, deposition flux from air, air-sea
232 mass exchange flux (volatilisation), and degradation (as 1st order process) are considered. All
233 input parameters are listed in the [SM](#), Table S2.

Gelöscht: supplementary material (SM)

234 Atmospheric depositions related to emissions from open fires are assumed to provide the
235 only source for seawater RET. These are available as daily time series for the East
236 Mediterranean domain (28-45°N, 8-30°E) through the fire-related PM_{2.5} emissions as
237 provided by the Global Fire Assimilation System (GFASv1.0; Kaiser et al., 2012) in
238 combination with an emission factor (207 mg RET in PM_{2.5} (kg fuel burnt)⁻¹; Schmidl et al.,
239 2008). The fire emissions are averaged over the domain and assumed to disperse within the
240 MBL only. This is justified due to the assumed underestimation of the fire related emissions
241 and ignorance of other (emission) sources. The 2-box model is run for the years 2005-2010,
242 for the east Mediterranean domain (28-45°N, 8-30°E) with a 1 h time resolution. [Air-sea](#)
243 [mass exchange fluxes, \$F_{em}\$](#) , in the range $(0.30 \pm 1.46) \text{ ng m}^{-2} \text{ h}^{-1}$ (positive defined upward) are
244 simulated (using the initially estimated parameter set, Table S2). GFAS uses global satellite
245 observations of fire radiative power to estimate daily dry matter combustion rates and fire
246 emission fluxes. The GFAS system partly corrects for observational gaps (e.g. due to cloud
247 cover) and detects fires in all biomes, except for very small fires (lower detection limit of
248 around 100-1000 m² effective fire area).

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249

250 **2.6 Analysis of long-range advection of air**

251 Distributions of potential sources can be identified by inverse modelling using
252 meteorological input data (Stohl et al., 2003; Eckhardt et al., 2007). So-called retroplumes
253 are generated using operational weather prediction model data and a Lagrangian particle
254 dispersion model, FLEXPART (Stohl et al., 1998, 2005). Hereby, 50000 virtual particles per
255 hour were 'released' and followed backwards in time for 5 days. The model output is a 3-D
256 distribution of residence time.

257

258 **3. Results and discussion**

259 **3.1 PAH concentrations in air and seawater**

260 The mean total (i.e., sum of gaseous and particulate) $\Sigma 25$ PAHs concentration is 1.45 ng m^{-3}
261 (time-weighted; 1.54 with values $< \text{LOQ}$ replaced by $\text{LOQ}/2$, see Table 1a), and ranged from
262 $0.30\text{-}3.25 \text{ ng m}^{-3}$. The spatial variability of PAH levels in the Mediterranean is large,
263 determined by long-range advection (Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006).
264 The levels found in this study in the southeastern Mediterranean are for most substances
265 lower than found earlier (Table 2). In the [Jonian Sea and Sicily region \(ISS\)](#) some PAHs are
266 found somewhat higher than previously measured i.e., FLT and PYR (in the gas-phase) and
267 BAP and PER (in the particulate phase). Due to a sampling artefact BAP and other
268 particulate phase PAHs could be underestimated by up to 25% (aforementioned, section 2.1).
269 The seasonality of emissions and the variability of advection or advection in combination
270 with different cruise routes being influenced differently by coastal or ship emission plumes
271 can have a large influence and may explain these differences. On the other hand, the duration
272 of temporal averaging atmospheric concentrations was similar across the various studies.
273 Diagnostic ratios ($\text{BAA}/(\text{BAA}+\text{CHR})$, $\text{FLT}/(\text{FLT}+\text{PYR})$; Dvorská et al., 2011) in some of the

Gelöscht: ISS

274 samples (No. 2, 4, 7, 8, and 15) reflect the influence of traffic and industrial sources. We
275 investigated the potential source distribution of individual samples collected along the cruise
276 (section 2.6) and found that indeed maxima of PAH concentrations corresponded with air
277 masses having resided over large urban areas, and, vice versa, low concentrations
278 corresponded with air masses without apparent passage of such areas (illustrated in Fig. S4).
279 This finding is supported by the ozone data i.e., 53 (47-65) ppbv during influence from urban
280 areas but 37 (33-62) ppbv otherwise.

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

Gelöscht: Ionian Sea and Sicily region (ISS)

285 Most PAH concentrations in surface seawater were <LOQ, while FLT, PYR and RET were
286 quantified in at least part of the samples (Table 1b). These observed seawater contamination
287 levels are comparable to levels found in the region 2 and 1 decades ago (Lipiatou et al.,
288 1997; Tsapakis et al., 2003). The concentrations near Crete (samples No. 7 and 8a) are very
289 similar to those found in fall 2001 and winter-spring 2002 (Tsapakis et al., 2006; FLT = 0.15
290 (0.11-0.21) ng L⁻¹, PYR = 0.12 (0.07-0.17) ng L⁻¹).

291

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

297 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)

298

299 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)

300

301 Table 2 Gaseous (a) and particulate (b) concentrations in air (time-weighted mean (min-
302 max), ng m⁻³) of selected PAHs compared to other studies in the Ionian Sea and Sicily region
303 (ISS) and in the southeastern Mediterranean (SEM). For calculation of means values <LOQ
304 were replaced by LOQ/2. RV = research vessel cruise.

305 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 et al., 2012	this study	Castro-Jiménez et al., 2012	Tsapakis et al. 2006	Tsapakis & Stephanou 2005a
FLN	0.16 (<0.027– 0.34)	2.25 (1.27– 5.65)	0.071 (<0.050– 0.40)	0.69 (0.36– 1.23)	1.05 (0.15– 1.67)	1.8 (0.2–5.7)
PHE	0.52 (0.14– 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	0.040 (<0.021– 0.10)	0.37 (0.18– 0.55)	0.039 (<0.013– 0.22)	0.20 (0.16– 0.30)	0.61 (0.12– 1.31)	0.9 (0.1–4.5)
FLT	0.14 (0.053– 0.31)	0.05 (0.02– 0.07)	0.10 (0.061– 0.37)	0.007 (0.003– 0.011)	0.82 (0.12– 1.69)	1.8 (0.07–6.0)
PYR	0.14 (0.058– 0.56)	0.04 (0.02– 0.06)	0.12 (0.044– 0.29)	0.006 (0.003– 0.009)	0.65 (0.14– 0.97)	0.9 (0.1–2.8)
CHR	0.012 (0.0071– 0.021)	0.09 (0.03– 0.23)	0.014 (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 PAH s	1.0	9.8	0.7	4.9	8.1	12.9

306

307 b)

ISS		SEM		
RV	RV June 2006, August- May 2007	RV August- September	RV June 2006, May	Finokalia November 2000-

	September 2010		2010	2007	February 2002
	this study	Castro-Jiménez et al., 2012	this study	Castro- Jiménez et al., 2012	Tsapakis & Stephanou 2005a
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	0.0054 (<0.0018– 0.025)	0.013 (0.006– 0.023)	0.0026 (<0.0006– 0.0080)	0.018 (0.004– 0.046)	0.03 (0.003–0.1)
CHR	0.018 (0.0030– 0.076)	0.04 (0.01– 0.08)	0.0079 (0.0033– 0.020)	0.043 (0.012– 0.101)	0.1 (0.02–0.3)
BBF	0.023	0.029 (0.012– 0.046)	0.011	0.033 (0.010– 0.056)	0.04 (<0.001–0.2)

	(<0.0018– 0.010)	0.045)	(0.0042– 0.033)	0.060)	
BKF	0.012 (<0.0018– 0.057)	0.015 (0.005– 0.027)	0.0047 (0.0018– 0.015)	0.089 (0.005– 0.333)	0.04 (<0.001–0.2)
BAP	0.013 (<0.0009– 0.072)	0.009 (0.04– 0.016)	0.0046 (<0.0011– 0.0098)	0.034 (0.005– 0.081)	0.02 (0.01–0.05)
BJF	0.018 (<0.0018– 0.079)	0.015 (0.014– 0.016)	0.0072 (0.0023– 0.031)	0.010 (0.008– 0.011)	-
BEP	0.019 (<0.0018– 0.088)	0.03 (0.02– 0.05)	0.0082 (0.0035– 0.025)	0.046 (0.017– 0.093)	0.04 (0.01–0.1)
PER	0.0023 (<0.00096 –0.011)	0.002 (0.0005– 0.004)	0.00075 (<0.0006– 0.0021)	0.026 (0.0001– 0.068)	0.004 (<0.001– 0.01)
IPY	0.015 (<0.00096 –0.094)	0.018 (0.006– 0.032)	0.0016 (<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)	0.0041 (<0.00052– 0.020)	0.081 (0.012– 0.210)	0.03 (0.010–0.09)
Sum of 15 PAH s	0.09	1.06	0.05	0.54	0.54

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

309 ⁽²⁾ 24h per month between Feb 2000 and Feb 2002

310

311 **3.2 Gas-particle partitioning**

312 Only a small mass fraction of the total, $\theta = 0.08$, is found in the particulate phase, confirming
313 earlier findings from remote sites in the region (Tsapakis and Stephanou, 2005a; Tsapakis et
314 al., 2006; Table 3c). The particulate mass fraction, θ , of four semivolatile PAHs varied
315 considerably along the cruise track (see SM Fig. S2). θ is thought to be strongly influenced
316 by temperature and doubling per 13 K cooling was found in a Mediterranean environment
317 (Lammel et al., 2010b) apart from PM composition. We refrain from an exploration of the
318 vapour pressure (p_L^0) dependence of θ (or K_p): A low time resolution implies lack of
319 representativeness of the temperature measurement for the phase change (Pankow and
320 Bidleman, 1992). Furthermore, non-equilibrium conditions cannot be excluded (but are
321 likely as a consequence of time resolution; Hoff et al., 1998), and supporting physical and
322 chemical aerosol parameters, necessary to relate to, are lacking. For similar temperatures
323 higher θ values had been observed at sites on the region influenced by urban and industrial
324 sources (Mandalakis et al., 2002; Tsapakis and Stephanou, 2005b; Akyüz and Çabuk, 2010),
325 which is probably related to the influence of higher organic and soot PM mass fractions. Gas-
326 particle partitioning models (Table 3) underpredict θ , except the Finizio et al., 1997, model
327 for one substance, TPH. θ predicted by the Junge-Pankow (JP) model comes closest. A
328 number of semivolatile PAHs could not be included in this test of gas-particle partitioning
329 models as concentrations in either the gas-phase (CPP, BBF, BJF), or the particulate phase
330 (FLT, PYR, BBN) did not exceed LOQ or no insufficient input data were available (BBF).

331 The neglect of adsorption to soot, not covered by the gas-particle partitioning models tested,
 332 may explain at least part of the underprediction (Lohmann and Lammel, 2004). Due to the
 333 lack of organic and elemental carbon data an extended examination is not possible.

334 In size-segregated samples particulate PAH mass was almost exclusively found in the size
 335 fraction $<0.25 \mu\text{m}$ aerodynamic diameter (AD) ($<\text{LOQ}$ in the other stages, except 0.002 ng
 336 m^{-3} CPP in the size fraction corresponding to $0.5\text{-}1.0 \mu\text{m}$; S2.1, Table S4). Most particulate
 337 phase PAHs, 40%, have been found associated with particles $<0.5\mu\text{m}$ out of 5 size ranges in
 338 the marine background aerosol of the sea region (coast of Crete, November 1996 – June
 339 1997; Kavouras and Stephanou, 2002). At continental sites in central and southern Europe
 340 mass median diameters of PAHs were found to be in the accumulation range, mostly $0.5\text{-}1.4$
 341 μm (Schnelle et al., 1995; Kiss et al., 1998; Lammel et al., 2010b and 2010c), but also a
 342 second, coarse mode was found (up to $2.4 \mu\text{m}$; Chrysikou et al., 2009).

343

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

348 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

349

350 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

351

352 3.3 Fugacity ratio and air-sea exchange flux

353 Fugacity ratios (Fig. 1a) and vertical fluxes (Fig. 1b) could be quantified for FLT, PYR and

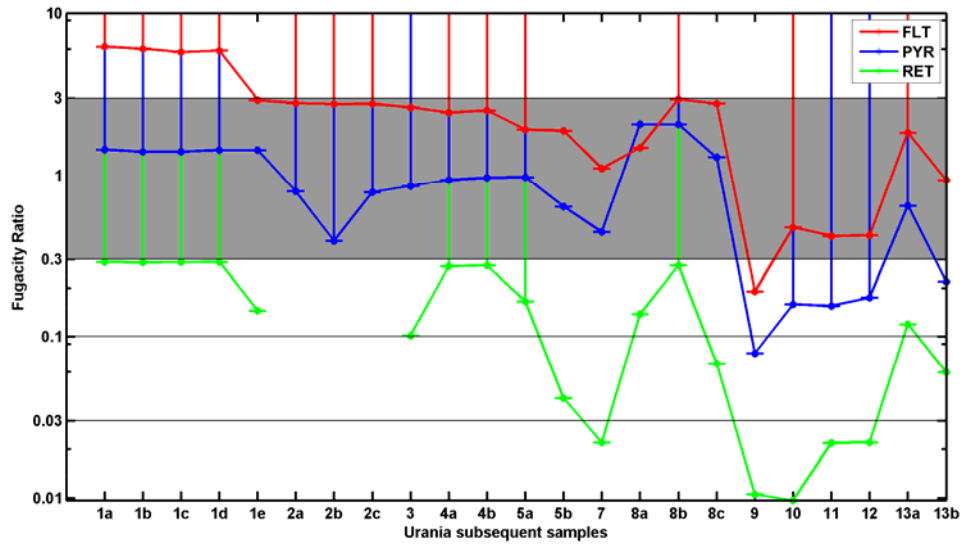
354 RET. The uncertainty window of $FR = f_a/f_w = 0.3 - 3.0$ is based on the uncertainty of $H_{Tw,salt}$.

355 Values $FR > 3.0$ indicate net deposition, $FR < 0.3$ indicate net volatilisation. For RET both

356 water and air concentrations of sample No. 2 were <LOQ. Transfer coefficients were $k_w \ll$

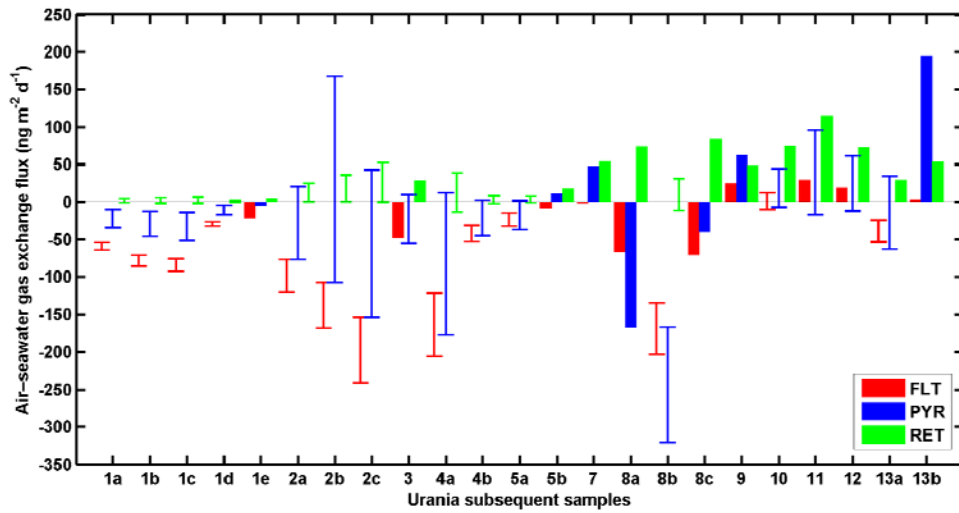
357 k_a .

358 a.



359

360 b.



361

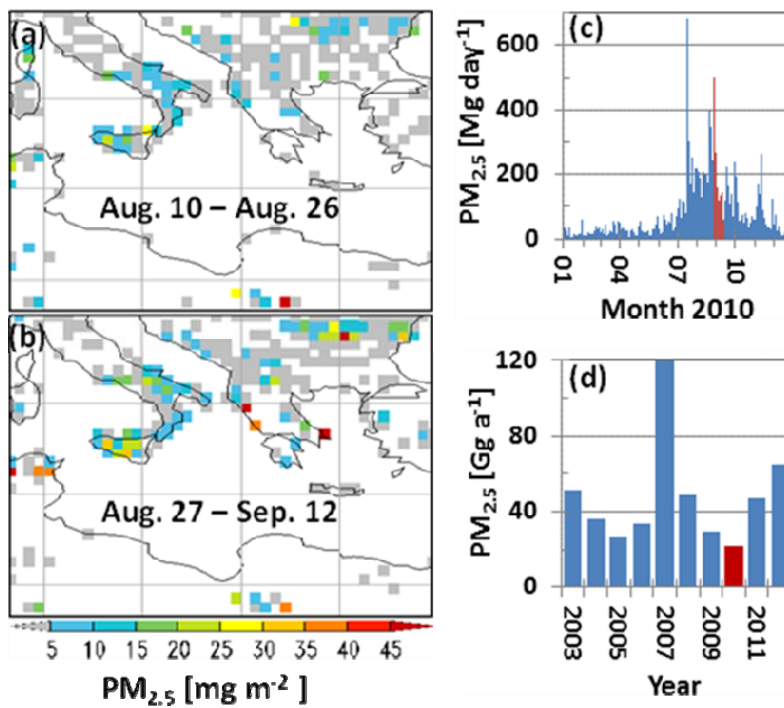
362 [Fig. 1. Air-sea exchange, \(a\) fugacity ratios \$FR = f_a/f_w\$ \(volatilisation \$> 3\$, deposition \$< 0.3\$,](#)
 363 [grey area insignificant deviation from phase equilibrium\) and \(b\) flux \$F_{aw}\$ \(\$\text{ng m}^{-2} \text{d}^{-1}\$,](#)
 364 [volatilisation \$> 0\$, deposition \$< 0\$ \) of FLT, PYR and RET along the cruise of RV Uria. Error](#)

365 | [bars indicate sea water concentration \$C_w < \text{LOQ}\$. The x-axis depicts the correspondence of](#)
366 | [sequential pairs of air samples \(1-13\) and water samples \(a-e\).](#)

367

368 FLT and PYR were found to be close to phase equilibrium, with most of the FR values within
369 the uncertainty range, one sample (No. 1) indicating deposition of FLT and one or two (No. 9
370 and 13) indicating volatilisation of FLT and PYR, respectively. In comparison with earlier
371 observations of FLT and PYR air-sea exchange in the SEM in 2001-02 and 2007 (Tsapakis et
372 al., 2006; Castro-Jiménez et al., 2012) and considering spatial and temporal variabilities no
373 trend, in particular no reversal of air-sea exchange is indicated. This comparison is detailed
374 in the SM, S2.2.1. RET, however, is found net-volatilisation throughout most of the cruise
375 (Fig. 1). Among the highest fluxes ($> 50 \text{ ng m}^2 \text{ d}^{-1}$) are some samples with very low FR,
376 < 0.03 . Fugacity of RET from water is supported by its Henry's law coefficient (11 Pa m^3
377 mol^{-1} at 298 K) which is higher than for CHR ($0.53 \text{ Pa m}^3 \text{ mol}^{-1}$) and FLT ($2.0 \text{ Pa m}^3 \text{ mol}^{-1}$).
378 RET is commonly considered as biomarker for coniferous wood combustion (Ramdahl,
379 1983). A decrease in wildfires could explain the suspected RET volatilisation. Integrated over
380 the domain and the year 2010, fires released 7.2 PJ fire radiative energy, which translates into
381 around 22.2 Gg of $\text{PM}_{2.5}$ emitted (Fig. 2). Compared to the $\text{PM}_{2.5}$ emissions of the years 2003
382 to 2012, the year 2010 had the lowest emissions, equivalent to 46% of the 2003-2012 mean,
383 and only 18% of the peak emissions of the year 2007 (Fig. 2d). As typical for the East
384 Mediterranean region, the fire season in 2010 started by the end of June and ended by early
385 October. The Urania cruise measurements took place between 27.8. and 12.9., i.e. towards
386 the end of the main burning season (Fig. 2c). During the first half of the Urania cruise,
387 widespread fire activity was observed in the entire domain, with most intense fires occurring

388 in Southern Italy, Sicilia and along the East coast of the Adriatic and the Ionian Sea (notably
 389 in Albania and Greece) (Fig. 2a).
 390



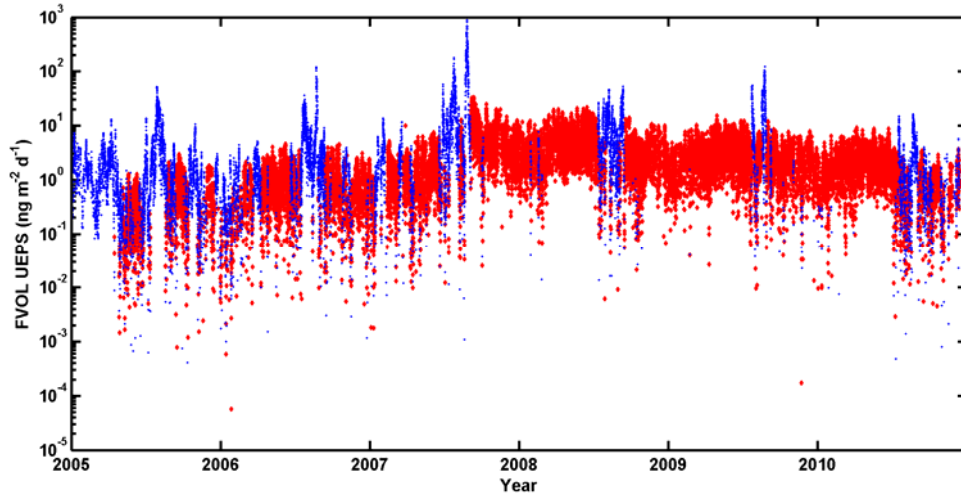
391
 392 [Fig. 2. Spatial pattern of fire-related PM_{2.5} emissions \(Global Fire Assimilation System](#)
 393 [GFASv1.0; Kaiser et al., 2012\) for the East Mediterranean \(28-45°N/8-30°E\). \(a\) time](#)
 394 [integral of August 10-26, \(b\) time integral of August 27 - September 12, 2010, given as sum](#)
 395 [over each period in mg m⁻². Areas with no observed fire activity are displayed in white.](#)
 396 [Temporal pattern of domain-integrated \(c\) daily total PM_{2.5} emissions over 2010 \(c\) and](#)
 397 [yearly total PM_{2.5} emissions over 2003 to 2012. Labeled in red is \(c\) the the period of the](#)
 398 [Urania cruise \(27 August – 11 September 2010\) \(d\) and the year 2010.](#)
 399

400 The hypothesis that seasonal depositional input of RET into the surface waters during the fire
401 season (summer) triggers reversal of diffusive air-sea exchange, at least in the year 2010, are
402 tested by box model (sections 2.5 and S1.3) runs. Two scenarios are considered, an 'Initially
403 Estimated Parameter Set' (IEPS) representing mean values for environmental parameters, and
404 an 'Upper Estimate Parameter Set' (UEPS) which represents realistic environmental
405 conditions favouring seawater pollution (SM, Table S3). Simulated diffusive air-sea
406 exchange flux, F_{aw} , during 2005-2010 initialised by the UEPS is shown in Fig. 3a and by the
407 IEPS in the SM, Fig. S3, and during the observations (cruise of RV Urania, 27.8.-9.9.2010)
408 initialised by the UEPS in Fig. 3b.

409 The model confirms the hypothesis that seasonal depositional input of RET into the surface
410 waters during the fire season (July-September, typically in the range $F_{aw} = 10^{-2}$ - 10^1 ng m⁻² d⁻¹
411 ¹ under IEPS) is followed by a period of prevailing flux reversal, typically $F_{aw} = 10^{-2}$ - 10^0 ng
412 m⁻² d⁻¹, which in the years 2008-10 started in October and lasted until the onset of the fire
413 season, but eventually started later in the years 2005-07 (at least under IEPS). The
414 volatilisation flux is predicted smaller in magnitude than the net-deposition flux during the
415 fire season, but correspondingly, i.e. higher after intense fire seasons. The high RET
416 volatilisation flux, indicated by measured C_a and C_w , seems to be dominated by biomass
417 burning in the region in the previous fire season. F_{aw} is predicted highly fluctuating, also
418 during the observational period (Fig. 3b). Even under UEPS the model is underpredicting F_{aw}
419 (Fig. 3b). The sensitivity to input uncertainties (SM S1.2) may explain part of the
420 underestimate, but not up to one order of magnitude. Neglected RET sources to seawater,
421 such as riverine input may explain part of the discrepancy.

422

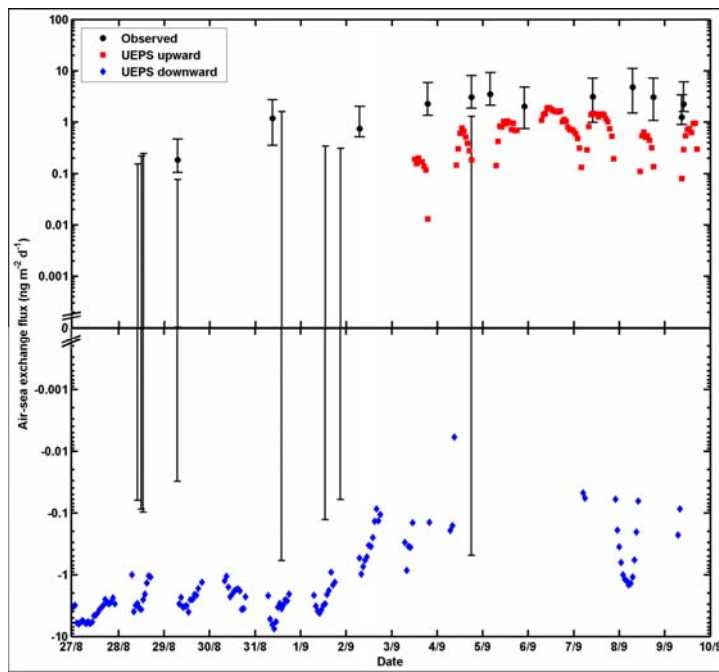
423 a.



424

425

426 b.



427

428 [Fig. 3. Diffusive air-sea exchange flux, \$F_{aw}\$, of RET \(\$\text{ng m}^{-2} \text{d}^{-1}\$; downward in blue and](#)
429 [upward in red\) using the upper estimate parameter set \(UEPS\) for the Eastern Mediterranean](#)
430 [\(28-45°N/8-30°E\) \(a.\) model predicted for 1.1.2005-31.12.2010 and \(b.\) model predicted and](#)
431 [observed \(black\) for 27.8.-9.9.2010. Hourly mean data filtered against off-shore winds \(see](#)
432 [text\). Error bars including both signs of \$F_{aw}\$ reflect \$C_w < \text{LOQ}\$.](#)

433

434 **4. Conclusions**

435

436 PAH pollution of the atmospheric Mediterranean environment was below previous
437 observations at the beginning of the decade (2001-02; Tsapakis and Stephanou, 2005a;
438 Tsapakis et al., 2006), also considering possible losses during sampling. This might reflect
439 emission reductions. The particulate phase PAHs were concentrated in the size fraction <
440 $0.25 \mu\text{m AD}$. The residence time in the troposphere is longest for particles around $0.2 \mu\text{m}$ of
441 size, with $\approx 0.01 \text{ cm s}^{-1}$ being a characteristic corresponding dry deposition velocity (Franklin
442 et al., 2000), which translates into a residence time of ≈ 120 days in the MBL (depth of 1000
443 m; see Table S3) and deposition flux $F_{\text{dep}} = c \times v = 0.03\text{-}0.06 \mu\text{g m}^{-2} \text{ year}^{-1}$ for the individual
444 PAHs associated with the particulate phase ($c = 0.01\text{-}0.02 \text{ ng m}^{-3}$; Table 2b), such as BAP,
445 and 0.5 and $0.3 \mu\text{g m}^{-2} \text{ year}^{-1}$, respectively, for the total flux of particulate phase PAHs in the
446 ISS and SEM in summer, respectively. The flux will be higher in winter, because of the
447 seasonality of the emissions.

448 Three gas-particle partitioning models were tested and found to underpredict the particulate
449 mass fraction in most of the samples (four PAHs i.e., BAA, TPH, CHR and BBF). Although
450 input parameters were incomplete these results confirm the earlier insight that additional

451 processes on the molecular level need to be included, beyond adsorption (Junge-Pankow
452 model) and absorption in OM (K_{oa} models), namely both adsorption and absorption
453 (Lohmann and Lammel, 2004) or even a complete description of molecular interactions
454 between sorbate and PM matrix (Goss and Schwarzenbach, 2001).

455 Simulations with a non-steady state 2-box model confirm the hypothesis that seasonal
456 depositional input of RET from biomass burning into the surface waters during summer is
457 followed by a period of flux reversal. The volatilisation flux is smaller in magnitude than the
458 net-deposition flux during the previous months, but correspondingly, i.e. higher after intense
459 fire seasons. Future negative emission trends or interannual variability of regional sources
460 may trigger the sea to become a secondary PAH source through reversal of diffusive air-sea
461 exchange. For the wood burning marker RET it is found that the secondary source became
462 significant in recent years: While the flux of secondary RET emissions (from surface
463 seawaters) in the study area was $1.0 \mu\text{g m}^{-2} \text{ year}^{-1}$ (mean of years 2005-2010, UEPS), the
464 primary sources amounted to $3.1 \mu\text{g m}^{-2} \text{ year}^{-1}$. Because of non-diffusive emission from the
465 sea surface, such as aerosol suspension from sea spray and bubble bursting (Woolf, 1997;
466 Qureshi et al., 2009; Albert et al., 2012), the true volatilisation may have exceeded the
467 diffusive flux significantly.

468

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477

478 **References**

479 Akyüz, M., Çabuk, H.: Gas-particle partitioning and seasonal variation of polycyclic
480 aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. *Sci. Total Environ.*,
481 2010, 408, 5550-5558.

482 Albert, M.F.M.A., Schaap, M., Manders, A.M.M., Scannell, C., O'Dowd, C.D., de Leeuw, G.:
483 Uncertainties in the determination of global sub-micron marine organic matter emissions,
484 *Atmos. Environ.*, 2012, 57, 289-300.

485 Balasubramanian, R., He, J.: Fate and transfer of persistent organic pollutants in a
486 multimedia environment. In: Zereini, F., Wiseman, C.L.S. (eds) *Urban airborne
487 particulate matter: origins, chemistry, fate and health impacts*. Springer, Heidelberg, pp.
488 277-307, 2010.

489 Berrojalbiz, N., Dachs, J., Ojeda, M.J., Valle, M.C., Castro Jiménez, J., Wollgast, J., Ghiani,
490 M., Hanke, G., Zaldivar, J.M.: Biogeochemical and physical controls on concentrations of
491 polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black
492 Seas, *Glob. Biogeochem. Cycles*, 2011, 25, GB4003.

493 Bidleman, T.F., McConnell, L.L.: A review of field experiments to determine air–water gas-
494 exchange of persistent organic pollutants. *Sci. Total Environ.*, 1995, 159, 101-107.

495 Bruhn, R., Lakaschus, S., McLachlan, M.S.: Air/sea gas exchange of PCBs in the southern
496 Baltic sea. *Atmos. Environ.*, 2003, 37, 3445–3454.

497 Castro-Jiménez, J., Berrojalbiz, N., Wollgast, J., Dachs, J.: Polycyclic aromatic hydrocarbons
498 (PAHs) in the Mediterranean Sea: Atmospheric occurrence, deposition and decoupling
499 with settling fluxes in the water column. *Environ. Pollut.*, 2012, 166, 40-47.

500 Chrysikou, L.P., Gemenetzi, P.G., Samara, C.A.: Wintertime size distributions of polycyclic
501 aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochlorine
502 pesticides (OCPs) in the urban environment: Street- vs. rooftop-level measurements.
503 *Atmos. Environ.*, 2009, 43, 290-300.

504 Dachs, J., Bayona, J.M., Raoux, C., Albaiges, J.: Spatial, vertical distribution and budget of
505 polycyclic aromatic hydrocarbons in the western Mediterranean seawater. *Environ. Sci.
506 Technol.*, 1997, 31, 682-688.

507 Dvorská, A., Lammel, G., Klánová, J.: Use of diagnostic ratios for studying source
508 apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over central
509 Europe. *Atmos. Environ.*, 2011, 45, 420-427.

510 Eckhardt, S., Breivik, K., Manø, S., Stohl, A.: Record high peaks in PCB concentrations in
511 the Arctic atmosphere due to long-range transport of biomass burning emissions, *Atmos.*
512 *Chem. Phys.*, 2007, 7, 4527–4536.

513 Finizio, A., Mackay, D., Bidleman, T.F., Harner, T.: Octanol-air partition coefficient as a
514 predictor of partitioning of semi-volatile organic chemicals to aerosols. *Atmos. Environ.*,
515 1997, 31, 2289-2296.

516 Franklin, J., Atkinson, R., Howard, P.H., Orlando, J.J., Seigneur, C., Wallington, T.J.,
517 Zetzsch, C.: Quantitative determination of persistence in air. In: *Criteria for persistence*
518 *and long-range transport of chemicals in the environment* (Klečka, G., Boethling, B.,
519 Franklin, J., Grady, L., Graham, D., Howard, P.H., Kannan, K., Larson, R.J., Mackay, D.,
520 Muir, D., van de Meent, D., eds.), SETAC Press, Pensacola, USA, pp. 7-62, 2000.

521 Galarneau, E., Bidleman, T.F., Blanchard, P.: Modelling the temperature-induced blow-off
522 and blow-on artefacts in filter-sorbent measurements of semivolatile substances. *Atmos.*
523 *Environ.*, 2006, 40, 4258-4268.

524 Goss, K.U., Schwarzenbach, R.P.: Linear free energy relationships used to evaluate
525 equilibrium partitioning of organic compounds. *Environ. Sci. Technol.*, 2001, 35, 1–9.

526 Greenfield, B.K., Davis, J.A.: A PAH fate model for San Francisco Bay, *Chemosphere*, 2005,
527 6, 515-530.

528 Guitart, C., Garcá-Flor, N., Miquel, J.C., Fowler, S.W., Albaiges, J.: Effect of accumulation
529 PAHs in the sea surface microlayer on their coastal air-sea exchange, *J. Mar. Systems*,
530 2010, 79, 210-217

531 Harner, T., Bidleman, T.F.: Octanol–air partition coefficient for describing particle-gas
532 partitioning of aromatic compounds in urban air. *Environ Sci Technol.*, 1998, 32, 1494 –
533 1502.

534 Hoff, E.M., Brice, K.A., Halsall, C.J.: Non-linearities in the slope of Clausius-Clapeyron
535 plots for semivolatile organic compounds. *Environ. Sci. Technol.*, 1998, 32, 1793–1798.

536 Jaenicke, R.: Aerosol physics and chemistry. In: *Numerical Data and Functional*
537 *Relationships in Science and Technology*, ed. G. Fischer, vol. 4, pp. 391-457, Springer,
538 Berlin, 1988.

539 Kaiser, J.W., Heil, A., Andreae, M.O., Benedetti, A., Chubarova, N., Jones, L., Morcrette,
540 J.J., Razinger, M., Schultz, M.G., Suttie, M., van der Werf, G.R.: Biomass burning

541 emissions estimated with a global fire assimilation system based on observed fire
542 radiative power. *Biogeosci.*, 2012, 9, 527-554.

543 Karickhoff, S.W.: Semiempirical estimation of sorption of hydrophobic pollutants on natural
544 sediments and soils. *Chemosphere*, 1981, 10, 833-849.

545 Kavouras, I.G., Stephanou, E.G.: Particle size distribution of organic primary and secondary
546 aerosol constituents in urban, background marine, and forest atmosphere. *J. Geophys.*
547 *Res.*, 2002, 107, 4069.

548 Keyte, I.J., Harrison, R.M., Lammel, G.: Chemical reactivity and long-range transport
549 potential of polycyclic aromatic hydrocarbons – a review, *Chem. Soc. Rev.*, 2013, 42,
550 9333-9391.

551 Kiss, G., Varga-Puchony, Z., Rohrbacher, G., Hlavay, J.: Distribution of polycyclic aromatic
552 hydrocarbons on atmospheric aerosol particles of different sizes, *Atmos. Res.*, 1998, 46,
553 253-261.

554 Klánová, J., Čupr, P., Kohoutek, J., Harner, T., 2008. Assessing the influence of
555 meteorological parameters on the performance of polyurethane foam-based passive air
556 samplers, *Environ. Sci. Technol.* 42, 550-555.

557 Lammel, G.: Effects of time-averaging climate parameters on predicted multicompartmental
558 fate of pesticides and POPs. *Environ. Pollut.*, 2004, 128, 291-302.

559 Lammel, G., Sehili, A.M., Bond, T.C., Feichter, J., Grassl, H.: Gas/particle partitioning and
560 global distribution of polycyclic aromatic hydrocarbons – a modelling approach.
561 *Chemosphere*, 2009a, 76, 98-106.

562 Lammel, G., Klánová, J., Kohoutek, J., Prokeš, R., Ries, L., Stohl, A.: Observation and origin
563 of organochlorine pesticides, polychlorinated biphenyls and polycyclic aromatic
564 hydrocarbons in the free troposphere over central Europe. *Environ. Pollut.*, 2009b, 157,
565 3264-3271.

566 Lammel G., Klánová J., Ilić P., Kohoutek J., Gasić B., Kovacić I., Lakić N., Radić R.:
567 Polycyclic aromatic hydrocarbons on small spatial and temporal scales – I. Levels and
568 variabilities, *Atmos. Environ.*, 2010a, 44, 5015-5021.

569 Lammel, G., Klánová, J., Ilić, P., Kohoutek, J., Gasić, B., Kovacić, I., Škrdlíková, L.:
570 Polycyclic aromatic hydrocarbons on small spatial and temporal scales – II. Mass size
571 distributions and gas-particle partitioning, *Atmos. Environ.*, 2010b, 44, 5022-5027.

572 Lammel, G., Novák, J., Landlová, L., Dvorská, A., Klánová, J., Čupr, P., Kohoutek, J.,
573 Reimer, E., Škrdlíková, L.: Sources and distributions of polycyclic aromatic
574 hydrocarbons and toxicity of polluted atmosphere aerosols. In: Urban Airborne
575 Particulate Matter: Origins. Chemistry. Fate and Health Impacts (Zereini, F., Wiseman,
576 C.L.S., eds.), Springer, Berlin, pp. 39-62, 2010c.

577 Lei, Y.D., Chankalal, R., Chan, A., Wania, F.: Supercooled liquid vapor pressures of the
578 polycyclic aromatic hydrocarbons. *J. Chem. Eng. Data*, 2002, 47, 801–806.

579 Lim, L., Wurl, O., Karuppiyah, S., Obbard, J.P.: Atmospheric wet deposition of PAHs to the
580 sea-surface microlayer, *Mar. Poll. Bull.*, 2007, 54, 1212-1219.

581 Lipiatou, E., Saliot, A.: Fluxes and transport of anthropogenic and natural polycyclic
582 aromatic-hydrocarbons in the western Mediterranean Sea. *Mar. Chem.*, 1991, 32, 51-71.

583 Lipiatou, E., Tolosa, I., Simó, R., Bouloubassi, I., Dachs, J., Marti, S., Sicre, M.A., Bayona,
584 J.M., Grimalt, J.O., Saliot, A., Albaiges J.: Mass budget and dynamics of polycyclic
585 aromatic hydrocarbons in the Mediterranean Sea, *Deep Sea Res. II*, 1997, 44, 881-905.

586 Liss, P.S., Slater, P.G.: Flux of gases across air–sea interface. *Nature*, 1974, 247, 181-184.

587 Lohmann, R., Lammel G.: Adsorptive and absorptive contributions to the gas particle
588 partitioning of polycyclic aromatic hydrocarbons: State of knowledge and recommended
589 parameterization for modelling. *Environ. Sci. Technol.*, 2004, 38, 3793-3803.

590 Lohmann, R., Dapsis, M., Morgan, E.J., Dekany, E., Luey, P.J.: Determining airwater
591 exchange spatial and temporal trends of freely dissolved PAHs in an urban estuary using
592 passive polyethylene samplers. *Environ. Sci. Technol.*, 2011, 45, 2655-2662.

593 Lüers, F., ten Hulscher, T.E.M.: Temperature effect on the partitioning of polycyclic aromatic
594 hydrocarbons between natural organic carbon and water. *Chemosphere*, 1996, 33, 643-
595 657.

596 Ma, Y.G., Lei, Y.D., Xiao, H., Wania, F., Wang, W.H.: Critical review and recommended
597 values for the physical-chemical property data of 15 polycyclic aromatic hydrocarbons at
598 25°C. *J. Chem. Eng. Data*, 2010, 55, 819-825

599 Mai, C.: Atmospheric deposition of organic contaminants into the North Sea and the western
600 Baltic Sea, PhD thesis, University of Hamburg, Hamburg, Germany, 444 pp., URL:
601 http://www.chemie.uni-hamburg.de/bibliothek/diss2012_/DissertationMai.pdf, 2012.

602 Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G.: Gas-particle concentrations and
603 distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of
604 Athens (Greece). *Atmos. Environ.*, 2002, 36, 4023-4035.

605 Masclet, P., Pistikopoulos, P., Beyne, S., Mouvier, G. : Long range transport and gas/particle
606 distribution of polycyclic aromatic hydrocarbons at a remote site in the Mediterranean
607 Sea, *Atmos. Environ.*, 1988, 22, 639-650.

608 Pankow, J.F.: Review and comparative analysis of the theory of partitioning between the
609 gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.*, 1987, 21, 2275-
610 2283.

611 Pankow, J.F., Bidleman, T.F.: Interdependence of the slopes and intercepts from log-log
612 correlations of measured gas-particle partitioning and vapor pressure. I. Theory and
613 analysis of available data. *Atmos. Environ.*, 1992, 26A, 1071-1080.

614 Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J.F., Goyet, C.,
615 Moutin, T., Prieur, L.: Integrated survey of elemental stoichiometry (C, N, P) from the
616 western to eastern Mediterranean Sea. *Biogeosci.*, 2011, 8, 883-899.

617 Putaud, J.P., Raes, F., van Dingenen, R., Brüggemann, E., Facchini, M.C., Decesari, S.,
618 Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N.,
619 Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tørseth,
620 K., Wiedensohler, A.: A European aerosol phenomenology-2: chemical characteristics of
621 particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos.*
622 *Environ.*, 2004, 38, 2579-2595.

623 Qureshi, A., MacLeod, M., Hungerbühler, K.: Modeling aerosol suspension from soils and
624 oceans as sources of micropollutants to air. *Chemosphere*, 2009, 77, 495-500.

625 Ramdahl, T.: Retene — a molecular marker of wood combustion in ambient air. *Nature*,
626 1983, 306, 580 - 582.

627 Rowe, C.L., Mitchelmore, C.L., Baker, J.E.: Lack of biological effects of water
628 accommodated fractions of chemically-and physically-dispersed oil on molecular,
629 physiological, and behavioral traits of juvenile snapping turtles following embryonic
630 exposure. *Sci. Total Environ.*, 2009, 407, 5344-5355.

631 Schmidl, C., Bauer, H., Dattler, A., Hitzemberger, R., Weissenböck, G.: Chemical
632 characterisation of particle emissions from burning leaves. *Atmos. Environ.*, 2008, 42,
633 9070–9079.

634 Schnelle, J., Jänsch, J., Wolf, K., Gebefügi, I., Kettrup, A.: Particle size dependent
635 concentrations of polycyclic aromatic hydrocarbons (PAH) in the outdoor air.
636 *Chemosphere*, 1995, 31, 3119-3127.

637 Schwarzenbach, R.P., Gschwend, P.M. Imboden, D.M.: *Environmental Organic Chemistry*.
638 2nd ed., Wiley, Hoboken, USA, 2003.

639 Spindler, G., Gnauk, T., Grüner, A., Iinuma, Y., Müller, K., Scheinhardt, S., Herrmann, H.:
640 Site-segregated characterization of PM₁₀ at the EMEP site Melpitz (Germany) using a
641 five-stage impactor: a six year study. *J. Atmos. Chem.*, 2012, 69, 127-157.

642 Stohl, A., Hitzemberger, M., Wotawa, G.: Validation of the Lagrangian particle dispersion
643 model FLEXPART against large scale tracer experiments. *Atmos. Environ.*, 1998, 32,
644 4245-4264.

645 Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager,
646 H., Wilhelm, S., Arnold, F., Cooper, O.: A backward modeling study of intercontinental
647 pollution transport using aircraft measurements. *J. Geophys. Res.*, 2003, 108, 4370,
648 doi:10.1029/2002jd002862.

649 Stohl, A., Forster, C., Frank, A., Seibert, P., Wotawa, G.: Technical Note: The Lagrangian
650 particle dispersion model FLEXPART version 6.2. *Atmos. Chem. Phys.*, 2005, 5, 2461-
651 2474.

652 Tsapakis, M., Stephanou, E.G.: Collection of gas and particle semi-volatile organic
653 compounds: Use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons
654 degradation during high-volume air sampling. *Atmos. Environ.*, 2003, 37, 4935-4944.

655 Tsapakis, M., Stephanou, E.G.: Polycyclic aromatic hydrocarbons in the atmosphere of the
656 Eastern Mediterranean. *Environ. Sci. Technol.*, 2005a, 39, 6584-6590.

657 Tsapakis, M., Stephanou, E.G.: Occurrence of gaseous and particulate polycyclic aromatic
658 hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect
659 on the gas/particle concentration and distribution. *Environ. Poll.*, 2005b, 133, 147-156.

660 Tsapakis, M., Stephanou, E.G, Karakassis, I.: Evaluation of atmospheric transport as a non-
661 point source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern
662 Mediterranean, *Mar. Chem.*, 2003, 80, 283-298.

663 Tsapakis, M., Apostolaki, M., Eisenreich, S., Stephanou, E.G: Atmospheric deposition and
664 marine sedimentation fluxes of polycyclic aromatic hydrocarbons in the Eastern
665 Mediterranean Basin, *Environ. Sci. Technol.*, 2006, 40, 4922-4927.

666 Woolf, D.K.: Bubbles and their role in gas exchange, in: *Sea Surface and Global Change*
667 (Liss, P.S., Duce, R.A., eds.), Cambridge University Press, Cambridge, UK, pp. 173-206,
668 1997.

669 Zhong, G., Xie, Z., Möller, A., Halsall, C., Caba, A., Sturm, R., Tang, J., Zhang, G.,
670 Ebinghaus, R.: Currently used pesticides, hexachlorobenzene and
671 hexachlorocyclohexanes in the air and seawater of the German Bight (North Sea).
672 *Environ. Chem.*, 2012, 9, 405-414.

673