1	Bi-directional air-sea exchange and accumulation of POPs (PAHs, PCBs, OCPs and
2	PBDEs) in the nocturnal marine boundary layer
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15	Abstract
16	As a consequence of long-range transported pollution air-sea exchange can become a major
17	source of persistent organic pollutants in remote marine environments. The vertical gradients
18	in air of 14 species i.e., 4 parent polycyclic aromatic hydrocarbons (PAHs), 3 polychlorinated
19	biphenyls (PCBs), 3 organochlorine pesticides (OCPs) and 2 polybrominated diphenylethers
20	(PBDEs) in the gas-phase were quantified at a remote coastal site in the southern Aegean Sea
21	in summer. Most vertical gradients were positive ( $\Delta c/\Delta z > 0$ ) indicating downward (net
22	depositional) flux. Significant upward (net volatilisational) fluxes were found for 3 PAHs,
23	mostly during day-time, and for 2 OCPs, mostly during night-time, as well as for 1 PCB and 1
24	PBDE during part of the measurements. While phenanthrene was deposited, fluoranthene
25	(FLT) and pyrene (PYR) seem to undergo flux oscillation, hereby not following a day/night

26 cycle. Box modelling confirms that volatilisation from the sea surface has significantly

27 contributed to the night-time maxima of OCPs. Fluxes were quantified based on Eddy 28 covariance. Deposition fluxes ranged  $-28.5 - +1.8 \ \mu g \ m^{-2} \ d^{-1}$  for PAHs and  $-3.4 - +0.9 \ \mu g \ m^{-2}$ 29  $d^{-1}$  for halogenated compounds. Dry particle deposition of FLT and PYR did not contribute 30 significantly to the vertical flux.

31

### 32 **1. Introduction**

33 The marine atmospheric environment is a receptor for persistent organic pollutants (POPs) 34 which are advected from primary and secondary sources on land. This is a concern as these 35 substance bioaccumulate along marine food chains (e.g., Lipiatou and Saliot, 1991; Borgå et 36 al., 2001). Primary sources do not exist in the marine environment, except for polycyclic 37 aromatic hydrocarbons (PAHs, ship engines). Long-range transport from urban and industrial 38 sources on land are the predominant sources of PAHs and polychlorinated biphenyls (PCBs) 39 in the global oceans (Atlas and Giam, 1986) and in the Mediterranean (Mandalakis et al., 40 2005; Tsapakis and Stephanou, 2005; Tsapakis et. al, 2006; Iacovidou et al., 2009; Mulder et 41 al., 2015).

42 However, the sea surface itself can turn into a secondary source of POPs provided 43 concentrations build up in surface waters, fed by riverine or atmospheric deposition input. 44 Such studies are still rare. Re-volatilisation was observed for hexachlorocyclohexane (HCH) 45 and PAHs, not only in coastal waters (Lohmann et al., 2011), but also in the open sea 46 (Jantunen and Bidleman, 1995; Lakaschus et al., 2002) including the Mediterranean (Castro-Jiménez et al., 2012; Mulder et al., 2014). After long-term accumulation of declining 47 48 emissions (even after phase-out), reversal of air-sea exchange may result at some point, as 49 indicated by global modelling for organochlorine pesticides (OCPs; Stemmler and Lammel, 50 2009). The seasonality of on-going emissions on the other hand may trigger a seasonal 51 reversal of air-sea exchange, as indicated for retene, a PAH emitted from biomass burning in 52 the Mediterranean (summer maximum; Mulder et al., 2014). Similarly, PAHs emitted in fossil fuel combustion in residential heating (winter maximum) may re-volatilise seasonally from
the sea surface in receptor areas.

The direction of diffusive air-surface exchange flux of organics can be identified by comparing the fugacities and can be quantified based on the Whitman two-film model (Bidleman and Connell, 1995; Schwarzenbach et al., 2003) or micro-meteorological techniques. The latter have so far only rarely been used to quantify air-water (Perlinger et al., 2005; Rowe and Perlinger, 2012; Sandy et al., 2012; Wong et al., 2012) or air-soil (Parmele et al., 1972; Majewski et al., 1993; Kurt-Karakus et al., 2006) gas exchange fluxes.

We studied the vertical fluxes of POPs at sea surface level with a gradient method at a remote coastal site in the eastern Mediterranean. The measurements were done in the context of a coordinated multi-site campaign on POP cycling in the region (Lammel et al., 2015). The POP concentration in surface seawater was determined, too, such that the direction of air-sea exchange could be addressed by a second method.

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#### 67 **2.1 Site and sampling**

68 The site selected for atmospheric measurements was Selles Beach, at the northern coast of Crete, 35.2°N/25.4°E, very close (4 km) to the Finokalia observatory. This is a remote site, 69 70 some 70 km east of major anthropogenic emissions (Iraklion, a city of 100000 inhabitants 71 with airport and industries; Mihalopoulos et al., 1997; Kouvarakis et al., 2000). The 72 Mediterranean region includes urban and industrial areas and is adjacent to source regions 73 (i.e. western, central and eastern Europe). Exposure of the study area to long-range 74 transported pollution from central and eastern Europe is highest in summer (Lelieveld et al., 75 2002).

Organic substances were collected 3-13 July in the gaseous and particulate atmospheric phases using low volume samplers ( $F \approx 2.3 \text{ m}^3 \text{ h}^{-1}$ , Leckel LVS, PM<sub>10</sub> inlet) equipped with quartz fibre filter (QFF, Whatman QMA 47 mm, baked at 320°C prior to usage) and 2

polyurethane foam (PUF) plugs (Molitan, density 0.030 g cm<sup>-3</sup>, 5.5 cm diameter, total depth 79 80 10 cm, cleaned by extraction in acetone and dichloromethane, 8 h each) in series. Two of these samplers collected gases and particles at different heights (inlets at  $z_1 = 1.05$  and  $z_2 =$ 81 2.8 m), about 0.5 m apart in the horizontal. According to the Monin-Obukhov similarity 82 83 theory of turbulent transport in the surface layer (see section S1.3), vertical concentration 84 profiles are expected to be logarithmic, while - due to the vertically non-linear behaviour of 85 the eddy diffusivity – the resulting vertical flux is *per definitionem* constant. For a given 86 surface source (sink) of gases or particles corresponding negative (positive) vertical 87 concentration gradients  $(\partial c/\partial z)$  will be maximal close to the source (sink). Therefore, over 88 aerodynamically smooth surfaces, the lower inlet height should be preferably in the order of a 89 few tenths of a meter, while the distance to the upper inlet height, should be maximized to 90 yield large (and consequently statistically significant) vertical concentration differences. 91 However, the choice for the upper inlet height is limited by the horizontal extension of the so-92 called "fetch", i.e. the up-wind surface homogeneity (in terms of orography, structure, and 93 vegetation), which should be at least  $100 \times z_2$  (e.g. Foken, 2008). In the case of our study, the 94 choice of the lower inlet height  $(z_1=1.05 \text{ m})$  is just due to the design of the aerosol sampler 95 which does not allow sampling below 1.05 m above ground, while the upper inlet height  $(z_2=2.80 \text{ m})$  accounts for the limited surface homogeneity (200 m) of the Selles Beach site. 96 97 Day-time (9-20 h EEDST) and night-time (21-8 h EEDST) sampling was conducted from 2 98 July in the evening until 13 July 2012 in the evening. During part of the measurements, from

6 July in the evening until 13 July 2012 in the evening. During part of the measurements, from replica of gaseous samples (PUF plugs only) at  $z_1$ . For the concentration at  $z_1$ ,  $c_{z1}$ , replica concentrations (mean of 2 measurements) were used whenever possible. The samplers were placed on a rocky beach. The horizontal distance between the samplers and the water was  $\approx 3$ m, while the vertical distance between the rock and water surfaces was 0.1-0.3 m, varying due to tide and waves. After exposure, filters and PUFs were packed in Al foil and zip-bags,stored and transported in a cool box to the laboratory.

106 Free dissolved contaminants in seawater were sampled using silicone rubber (SR) sheets 107 (Altec, Great Britain) as passive water samplers (PWS). Quantification of trace organics from 108 PWS is sensitive and validated (Rusina et al., 2010). Uncertainties in results obtained by 109 application of partition based passive samplers are believed to range around a factor of two 110 depending on the level of experience of the laboratory (Allan et al., 2009). Different aspects 111 of uncertainty are discussed in Lohmann et al. (2012). At two localities, distanced 0.8 and 2.2 112 km west of Selles Beach, each two SR PWS were deployed in parallel. Each sampler consisted of six sheets (55  $\times$  90  $\times$  0.5 mm). Before exposure SR sheets were cleaned by 113 114 Soxhlet extraction in ethyl acetate (96 h) followed by methanol (48 h, shaken), and spiked by 115 a mix of 15 performance reference compounds (PRCs; D<sub>10</sub>-biphenyl and 13 PCB congeners 116 not occurring in the environment) according to the procedure (Booij et al., 2002). Samplers 117 were deployed 3 July – 2 August 2012 in water mounted on stainless steel wire holders at 1 m 118 depth using buoy and rope. After exposure, samplers were stored and transported in original 119 vials and brought in a cool box to the laboratory.

Daily mean temperature was 28.2 (22.4-34.5)°C and wind velocity was 4.8 (0.6-7.7) m s<sup>-1</sup>
(hourly data). No precipitation occurred. The meteorological situation is described in the
Supplementary information (SI), S2.1.

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# 124 **2.2 Meteorological parameters and vertical flux calculations**

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Boundary layer (BL) depth is needed for interpretation of the variation of the concentrations
in air. BL depth data are taken from simulations of the Lagrangian dispersion model
FLEXPART, version 9 (Stohl et al., 1998). These were run in forward direction, and based on
analysed wind fields (ECMWF, 0.5° resolution). The model BL height is calculated according

to Vogelezang and Holtslag (1996) using the critical Richardson number. According to wind
direction during sampling we allocate BL depths at upwind locations well off shore (70-100
km) or inland (≈20 km), respectively, as the relevant BL depth for interpretation of
atmospheric concentrations at the coastal site. The mean BL depth during sampling intervals
is used.

135 For characterization of the local meteorological conditions, continuous measurements (5 min 136 averages) of air temperature, relative humidity, wind speed and wind direction were accom-137 plished by three automatic weather stations (model WMT520; Vaisala, Helsinki, Finland) 138 which have been placed at the beach in  $\approx 200 \text{ m}$  distance (2) and  $\approx 100 \text{ m}$  inland (1), 139 respectively, from the sampling location. For characterization of the atmospheric surface 140 layer's thermodynamic stratification, vertical profiles of wind speed, wind direction, air tem-141 perature and relative humidity were determined by continuous measurements at four levels 142 (0.34, 0.70, 1.45, and 3.00 m above ground). Data was recorded by 2D ultrasonic wind 143 sensors (model WMT701; Vaisala, Helsinki, Finland) and aspirated temperature and relative 144 humidity sensors (model MP103A; Rotronic, Bassersdorf, Switzerland) in 10 s intervals, 145 which were averaged to 30 min means for further data processing. For determination of key 146 micrometeorological quantities (e.g., sensible heat flux, friction velocity; see SI, S1.3), fast 147 response measurements of the 3D wind vector and air temperature have been performed by a 148 3D ultrasonic anemometer (CSAT-3, Campbell Scientific Inc., Logan, USA) on a small mast, 149 4 m above ground and about 7 m ESE of the profile mast. Corresponding data were 150 continuously recorded with a sampling frequency of 20 Hz by a suitable logger (model 151 CR3000; Campbell Scientific Inc., Logan, USA). Key micrometeorological quantities were 152 derived from fast response 3D wind and air temperature data (20 Hz) according to the eddy 153 covariance (EC) method; 20 Hz data were processed by the TK3 algorithm (Mauder and 154 Foken, Department of Micrometeorology, University of Bayreuth, Germany), and the results were averaged every 30 minutes. Only periods with wind direction between  $270^{\circ}$  and  $40^{\circ}$ 155

(i.e., onshore winds) were considered to calculate vertical fluxes of gaseous organics (moredetails in the SI, S2.1).

158 The turbulent vertical gaseous organics flux,  $F_c$  (ng m<sup>-2</sup> s<sup>-1</sup>), has been calculated according to 159 the aerodynamic method as the product of the vertical difference of concentration,  $\Delta c_z$  (ng m<sup>-1</sup> 160 <sup>3</sup>), and the turbulent transfer velocity,  $v_{tr}$  (m s<sup>-1</sup>):

161 
$$F_{\rm c} = -v_{\rm tr} \Delta c_z = -v_{\rm tr} [c(z_2) - c(z_1)]$$
 (1)

162

where  $z_2$  and  $z_1$  are the heights of inlets of gaseous organics' sampling (1.05 m and 2.80 m, see 2.1, above). The transfer velocity is a measure of the vertical turbulent (eddy) diffusivity. As long as the vertical concentration gradient is statistically significant, and the choice of the upper inlet height accounts for the homogeneity of the up-wind so-called fetch (see above), the resulting flux, calculated from the transfer velocity and the vertical concentration gradient (see eq. (1)), is the vertical turbulent net flux of the corresponding gas, representative for the fetch area and equal to the overall deposition flux (if  $c(z_2) - c(z_1) > 0$ ).

170 Details of the underlying formulation and the calculation scheme are given in the SI, S1.3.

171

### 172 **2.3 Chemical analysis**

For organic analysis all samples were extracted with dichloromethane during  $\approx 1$  h in an automatic extractor (Büchi B-811). Surrogate extraction standards (D<sub>8</sub>-naphthalene, D<sub>10</sub>phenanthrene, D<sub>12</sub>-perylene, PCB30, PCB185, <sup>13</sup>C BDEs 28, 47, 99, 100, 153, 154, 183 and 209) were spiked on each PUF and QFF prior to extraction. The volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation was achieved on a silica gel column. Samples were analyzed using a GC-MS (gas chromatograph coupled with a mass spectrometer) Agilent 7890 coupled to Agilent 7000B with a J&W

180 Scientific fused silica column DB-5MSUI (60 m  $\times$  0.25 mm  $\times$  0.25 µm) for 2-4-ring PAHs 181 (naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), 182 phenanthrene anthracene (ANT), fluoranthene (PHE), (FLT), pyrene (PYR), benzo(a)anthracene (BAA), and chrysene (CHR). Terphenyl was used as injection standard. 183 The temperature program was 80°C, 15°C min<sup>-1</sup> to 180°C, 5°C min<sup>-1</sup> to 310°C. The injection 184 185 volume was 1 µL in splitless mode at 280°C, with He used as a carrier gas at constant flow of 186  $1.5 \text{ mL min}^{-1}$ .

A sulphuric acid modified silica gel column was used for the PCB/OCP and PBDE cleanup. Samples were analyzed using a GC-MS/MS Agilent 7890 coupled to Agilent 7000B with a SGE HT-8 column (60 m × 0.25 mm × 0.25  $\mu$ m) for  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, o, p'and p, p'-DDE, -DDD and –DDT, penta- and hexachlorobenzene (PeCB, HCB). PCB 121 was used as injection standard for chlorinated substances. The temperature program was 80°C (1 min hold), 40°C min<sup>-1</sup> to 200°C, 5°C min<sup>-1</sup> to 305°C. The injection volume was 3  $\mu$ L in splitless mode at 280°C, with He used as a carrier gas at constant flow of 1.5 mL min<sup>-1</sup>.

PBDEs were analysed using GC-HRMS (gas chromatography with high resolution mas spectrometry) on a Restek RTX-1614 column (15 m × 0.25 mm × 0.1  $\mu$ m). The resolution was set to > 10000 for BDE 28–183, and > 5000 for BDE 209. <sup>13</sup>C BDEs 77 and 138 were used as injection standards. The MS was operated in EI+ mode at the resolution of >10000. The temperature program was 80°C (1 min hold), then 20°C min<sup>-1</sup> to 250°C, followed by 1.5°C min<sup>-1</sup> to 260°C and 25°C min<sup>-1</sup> to 320°C (4.5 min hold). The injection volume was 3  $\mu$ L in splitless mode at 280°C, with He used as a carrier gas at constant flow of 1 mL min<sup>-1</sup>.

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Recovery of native analytes varied between 72 and 102% for PAHs, between 88 and 103% for PCBs, and between 75 and 98% for OCPs. The results for PAHs, OCPs and PCBs were not recovery corrected. For PBDEs, isotopic dilution method was used, the average recoveries ranged 78-128%. 206 The mean of 4 field blank values was subtracted from the air sample values. Values below the 207 mean + 3 standard deviations of the field blank values were considered to be <LOQ. Field 208 blank values of most analytes in air samples were below the instrument limit of quantification (ILOO), which corresponded to 6-34 pg m<sup>-3</sup> for PAHs, 7-23 pg m<sup>-3</sup> for PCB and OCPs and 209 0.003-0.04 pg m<sup>-3</sup> for PBDEs (SI, Table S2). Higher LOQs were determined for analytes in 210 gaseous air samples, namely 0.18 and 0.50 ng  $m^{-3}$  for FLN and PHE, and typically 28 pg  $m^{-3}$ 211 for HCB. In the particulate phase a higher LOQ resulted for PHE, i.e. 170 pg m<sup>-3</sup>. The 212 213 breakthrough in PUF samples was estimated, and as a consequence, NAP, FLN, HCB and 214 PeCB results are not considered as the sampled air volume (typically  $\approx 25 \text{ m}^3$  for PUFs) 215 expectedly lead to breakthrough under the prevailing temperatures (Melymuk et al., 2016).

216 Free dissolved water concentrations of analytes in PWS were calculated from amounts 217 accumulated in SRs using the exponential uptake model described in Smedes (2007). The 218 required sampling rates were estimated by fitting performance reference compounds 219 dissipation data from sampler to the model described by Booij and Smedes, 2010. ILOQ corresponded to 0.5-4.2 pg  $L^{-1}$  for PAHs (but 9 pg  $L^{-1}$  for NAP), 0.05-0.5 pg  $L^{-1}$  for PCB and 220 OCPs and 0.0003-0.037 pg  $L^{-1}$  for PBDEs (SI, Table S2). Site specific LOQs were 1–10 pg  $L^{-1}$ 221 <sup>1</sup> for PAHs (but 400 pg  $L^{-1}$  for NAP), 0.1-0.8 pg  $L^{-1}$  for PCB, 0.1–1.4 pg  $L^{-1}$  for OCPs (but 2.8 222 pg L-1 for  $\alpha$ -HCH) and 0.01–0.11 pg L<sup>-1</sup> for PBDEs (but 0.59 pg L<sup>-1</sup> for BDE209). 223

224

### 225 2.4 Vertical gradients of trace organics' concentration in air

Air-sea gas exchange can be studied by determining the vertical concentration gradients oftrace gases in air (Doskey et al., 2004; Else et al., 2008).

228 Three standard deviations of field blank concentrations are considered as the absolute 229 uncertainty of concentration measurements, c, and twice that much as the uncertainty of 230 concentration differences,  $\Delta c_z$ . Values of concentrations and vertical concentration differences (gradients) not exceeding these thresholds are considered insignificant. This applied for a
large fraction of gradients, namely OCP (34 out of 70), PCB (27 out of 44), PBDE (4 out of
5), and PAHs (17 out of 46) (Table S3).

234

### 235 **2.5 Air-water fugacity ratio**

The direction of diffusive air-sea gas exchange can be derived from the fugacity ratio calculation, based on the Whitman two-film model (Bidleman and McConnell, 1995). The fugacity ratio,  $f_a/f_w$ , is calculated as:

239

240 
$$f_a/f_w = c_a R T_a / (c_w H_{Tw,salt})$$
 (2)

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with gas-phase concentration  $c_a$  (ng m<sup>-3</sup>), dissolved aqueous concentration  $c_w$  (ng m<sup>-3</sup>), 242 universal gas constant R (Pa m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>), and both sea surface temperature (SST or  $T_w(K)$ ) 243 and salinity corrected Henry's law constant H<sub>Tw.salt</sub> (Pa m<sup>3</sup> mol<sup>-1</sup>; see S1.1 for details), and air 244 245 temperature T<sub>a</sub> (K). T<sub>a</sub> was adopted from the on-site measurement (see above). c<sub>w</sub> is derived 246 as the average of the results at two localities, 2 replicas each (see above, 2.1). SST data, 247 measured on the sampling day and in the area, were downloaded from respective database 248 (see S1.4 for details). Air and water sampling was not totally in phase: sampling in air was 249 over 12 days (2-13 July), while SR exposure was during 28 days (3-30 July) i.e., collection 250 was done 10 days after air sample collection. Consequently, for those substances which are 251 quickly equilibrated (within a few days) in PWS i.e., HCH and 3-ring PAHs, no simultaneous 252 measurement in air and water was done (see section 2.1). Although the seawater 253 concentrations of HCH and 3-ring PAHs might have been stable over 28 days, no such 254 evidence exists and we refrain from relating the fugacities. Values 0.3 < FR < 3.0 are conservatively considered to not safely differ from phase equilibrium, as propagating from the 255 256 uncertainty of the Henry's law constant, H<sub>Tw,salt</sub>, and measured concentrations and 257 temperature changes during sampling (e.g., Bruhn et al., 2003; Castro-Jiménez et al., 2012). 258 Substance property data are taken from the literature (SI, Table S1). This conservative 259 uncertainty margin is also adopted here, while  $f_a/f_w > 3.0$  indicates net deposition and  $f_a/f_w$ 260 <0.3 net volatilisation.

261

#### 262 **2.6 Non-steady state 2-box model**

The air-sea mass exchange flux of several OCPs and PAHs are simulated by a non-steady 263 264 state zero-dimensional model of intercompartmental mass exchange (Lammel, 2004; Mulder 265 et al., 2014) in order to test the hypothesis that the diurnal variation of contaminant 266 concentrations in air during a period of on-shore advection of one air mass is explained by the 267 combination of volatilisation from the sea surface and atmospheric mixing depth, while 268 advection (long-range transport) is less significant (horizontal homogeneity of air mass; Lammel et al., 2003). This 2-box model predicts concentrations by integration of two coupled 269 270 ordinary differential equations that solve the mass balances for the two compartments, namely 271 the atmospheric marine BL and seawater surface mixed layer. Processes considered in air are 272 dry (particle) deposition, removal from air by reaction with the hydroxyl radical, and air-sea 273 mass exchange flux (dry gaseous deposition), while in seawater export (settling) velocity, 274 deposition flux from air, air-sea mass exchange flux (volatilisation), and degradation (as first 275 order process) are considered. Input parameters are listed in the SM, Table S3.

276

## 277 **3. Results and discussion**

278 **3.1 Day/night variation of concentrations in air** 

279 4 PAHs (ACE, PHE, FLT, PYR), 3 OCPs ( $\alpha$ - and  $\gamma$ -HCH, p,p'-DDE), 3 PCB congeners 280 (PCB28, -52 and -101) and 2 PBDE congeners (BDE47 and -99) were quantified in gas-phase 281 samples, while the other species were found <LOQ in all or most samples (Fig. 1a, 2a, Table 282 1a, b). This is a consequence of limited air sample volume ( $\approx 25 \text{ m}^3$ ). PAHs and PBDEs were 283 also found in the particulate phase. The levels observed (Table 1a) are at the lower end of 284 what had been reported from marine, rural and remote sites in the region in the previous  $\approx 15$ 285 years, in particular with regard to the chlorinated species (Kamarianos et al., 2002; 286 Mandalakis and Stephanou, 2002; Tsapakis and Stephanou, 2005; Cetin and Odabasi, 2008; 287 Halse et al., 2011; Lammel et al., 2010 and 2011; Castro-Jiménez et al., 2012; Berrojalbiz et 288 al., 2014; Mulder et al., 2014 and 2015). To our best knowledge, the DDE levels are the 289 lowest reported from the region. This confirms the remote character of the site. Influence of 290 local sources, not expected at this remote site (Iacovidou et al., 2009), is sometimes indicated 291 by an anti-correlation between wind speed and atmospheric concentration. At Selles Beach, 292 dilution by higher wind speed is indeed indicated for one contaminant, ACE (by significant 293 anti-correlation, p < 0.05 confidence level, t-test). This is expected, because of its short 294 atmospheric lifetime.

295 BL depths ranged 160-500 m during night-time and 270-760 m during day-time (mean of 296 sampling intervals i.e., 11 h). Day/night variation of contaminants' atmospheric 297 concentrations, often related to mixing and local sources, was not obvious: For PAHs the 298 mean ratio of day/night concentrations (gaseous only), c<sub>day</sub>/c<sub>night</sub>, was 0.67 (0.54-0.85) for ACE, while  $c_{day}/c_{night}$  ranged wider, 0.25-3.35, for PHE, FLT and PYR, with mean values of 299 300  $c_{dav}/c_{night} = 1.41-1.53$ . Also for PBDEs  $c_{dav}/c_{night} > 1$  is found (1.20 and 1.37). The low value 301 for ACE can be explained by its short photochemical lifetime (Keyte et al., 2013).  $c_{dav}/c_{night} >$ 302 1 was previously observed for PAHs at the same site and explained by temperature driven 303 volatilisation from surfaces overcompensating for photochemistry (Lee et al., 1998; Tsapakis 304 and Stephanou, 2007). For chlorinated substances, we find mean  $c_{day}/c_{night} < 1$ , namely 0.56-305 0.66 for HCH isomers, and 0.68-0.94 for PCBs and DDE, while the individual values range 306 widely, 0.04-4.8. However, there was a clear day/night, with mostly night-time maxima of both PAHs (Fig. 1a) and chlorinated species (Fig. 1b) during a period of continuous on-shore 307

308 winds, 6-10 July. Apparently, contaminants' concentrations were influenced by BL depth, as 309 indicated by anti-correlation with PAHs and OCPs (except DDE; significant for  $\alpha$ -HCH on 310 the p < 0.05 confidence level, t-test). This results in night-time accumulation. Diel variation, 311 apart from mixing, is related to advection and air-sea mass exchange and studied in more 312 detail in Section 3.2.

313

## 314 **3.2 Diffusive air-sea exchange**

315 The variation of air concentrations (with nighttime maxima) during a period of northerly flow 316 without change of air mass is predicted using the 2-box model (Section 2.6). For PCB28, -52, 317 FLT and BDE47 air concentrations are qualitatively well captured (Fig. 2). These are 318 maintained by dry gaseous deposition alone (PCB52, FLT) or by oscillating fluxes (HCB, 319 PCB28: upward, Fig. 2; PYR: mostly downward, Fig. S4a). The model predicted fluxes are in good agreement with the observed values (Section 3.3, Table S5) except for each one day-320 321 time sampling interval of FLT and BDE47 (upward fluxes), and for one day-time interval of 322 PCB28 (downward flux; in total 4 agreements, 3 disagreements). The modelling results 323 support that (during advection of one air mass) the diel variation of contaminant 324 concentrations in air and, particularly, the night-time accumulation was explained by the 325 combination of volatilisation from the sea surface and atmospheric mixing depth. 326 Volatilisation from the sea surface has significantly contributed to the night-time maxima of 327 HCB (upward flux, Fig. 2) and PCB28 (Fig. 2), as well as of PYR during 1 night (Fig. S4a; 328 Table S5). This, to our knowledge, had never been observed before.

f<sub>w</sub> is derived from the mean concentrations in seawater at two locations (see SI, Table S6, for individual data). The comparison of air-water fugacity ratios (Section 2.5) suggests for the measurement period, 2-13 July 2012, net deposition (prevailing downward fluxes,  $f_a/f_w > 3$ ) of gaseous FLT, PYR, BDE47 and –99, net volatilization (prevailing upward fluxes ,  $f_a/f_w < 0.3$ ) of gaseous PCB28 and -101 and close to phase equilibrium (0.3 <  $f_a/f_w < 3$ ) for *p,p* '-DDE, and PCB52 (Table 2). These results are the same as determined based on passive air sampling
at several locations along the shore at and near Selles Beach (Lammel et al., 2015).

The direction of DDE and PCB fluxes derived from fugacity calculations is consistent with what was indicated by the correlation of air concentrations and BL depth during on-shore winds (SI, S2.5).

339

340 **3.3 Vertical concentration gradients in air** 

341 PAH vertical gradients mostly indicated deposition,  $\Delta c/\Delta z > 0$ , found in 28 cases (14 during 342 day, 14 during night), while negative gradients were found in 10 cases (8 during day, 2 during 343 night). The vertical gradient of PAHs was insignificant in 17 cases. When volatilisation was 344 observed (3-5 July for FLT and PYR, 6-9 July for ACE)  $\Delta c/\Delta z$  tended to be clearly lower 345 during day-time, indicating that volatilisation of PAHs from the sea surface was stronger 346 during day-time. This could be explained by a higher fugacity from seawater, f<sub>w</sub>, which 347 increases with H<sub>Tw.salt</sub> (see above, 2.5), which, in turn, increases with sea surface temperature, T<sub>w</sub>. Similarly, for the halogenated substances, significant positive gradients,  $\Delta c/\Delta z > 0$ , 348 349 indicating deposition were more frequent than significant negative gradients i.e., 37 cases (15 350 PCBs, 22 OCPs, 30 during day, 7 during one night only) and 20 cases (2 PCBs, 17 OCPs, 1 351 PBDE, 5 during day, 15 during night), respectively. For these substance classes, a vertical 352 gradient was insignificant in 65 cases (according to the measurement uncertainties). During at 353 least some nights of the period 6-10 July night-time maxima of HCH, and PCB52 in air 354 coincided with negative vertical gradients, i.e. emissions from the sea surface. Diel variation 355 of PCB52 air-sea exchange flux direction is well reflected by the model (Fig. S4b). This 356 trend is most significant for the HCH isomers for which a stronger volatilisation flux from the 357 sea surface is found during the nights than during day time ( $\Delta c/\Delta z < 0$ ), or even deposition during day-time ( $\Delta c/\Delta z > 0$  on 6 and 9 July). Hence, volatilisation from the sea surface may 358

359 have contributed to and may even have caused the night-time maxima of the atmospheric 360 concentrations of HCH and PCB52 (see above and Table 1a): The diel variation of air 361 temperature was small i.e., day-time mean was typically 0.5-1.5 K warmer than night-time 362 mean temperature. Even somewhat lower upward fluxes, F<sub>c</sub>, of HCH during night than during day, caused by a slightly lower sea surface temperature, may have caused  $c_{day}/c_{night} < 1$  in 363 364 combination with the day/night variation of the BL depth (by average 50% deeper for day-365 time sampling periods). PBDE day-time maxima may indicate local volatilisation from soil, 366 enhanced during day-time. Again, this is consistent with the positive correlation of air 367 concentrations with BL depth (above). Only one BDE concentration gradient was significant, 368 which was volatilisational and during day-time (Fig. 1b, Table 1b). Fluctuating PCB fluxes 369 are in line with the observation that PCBs were close to phase equilibrium in the Aegean in 370 2006 (Berrojalbiz et al., 2014). Summarizing, average significant day-time vertical gradients, 371  $\Delta c/\Delta z$ , of all contaminants exceeded average significant night-time gradients, except for FLT 372 and PYR.

373 The direction of the gradient, hence, of air-sea exchange is found to have changed for ACE, 374 PYR and the HCH isomers on a half-day basis (sequential sampling periods), for FLT during 375 less than 2 days (Table S4). Changing directions of net air-sea mass exchange had been 376 observed in the region along a ship cruise for OCPs, PCBs and one alkylated PAH, 377 dimethylphenanthrene (Castro-Jiménez et al., 2012; Berrojalbiz et al., 2014) in 2006 and for 378 FLT and PYR in 2010 (Mulder et al., 2014). Fast fluctuation of the direction of air-sea 379 exchange throughout large parts of the year had been found for one alkylated PAH, retene, in 380 the sea region following biomass burning emissions (based on box modelling; Mulder et al., 381 2014). Earlier, in 2000-02 air-sea exchange of PAHs was found depositional for all members 382 (Tsapakis et al., 2006).

383 These observations of an increasing number of pollutants attaining phase equilibrium and bi-384 directional flux may indicate a long-term trend from deposition towards 'reversal', i.e. 385 volatilisation of these pollutants in the marine environment of the eastern Mediterranean and, more general, of receptor seas regions, located in the outflow of regions emitting long-lived 386 387 semivolatile pollutants, such as most POPs. For substances close to phase equilibrium (attained in a long-term trend) the direction of air-sea exchange may change with a high 388 389 frequency, as found here. Implicitly, dry deposition is difficult to budget. However, 390 fluctuation may also occur in response to seasonal trends: In summer 2010 FLT and PYR 391 were found close to phase equilibrium in the eastern Mediterranean, while retene (RET) was 392 found mostly volatilisational. A model simulation had revealed that seasonal primary 393 emissions and subsequent deposition of RET (from open fires in the region) are triggering 394 seasonal flux reversal, which over many weeks, however, is fluctuating with a high frequency 395 (< 24 h). (Mulder et al., 2014) Obviously, longer observations are needed to assess the 396 prevailing vertical flux direction. Extrapolation of the observations to annual fluxes is not 397 justified, as day/night fluctuations may be part of a more complex temporal pattern. The 398 seawater surface as secondary source of pollution should be assessed based on flux 399 measurements during several seasons and over longer time periods.

400

## 401 **3.4 Quantification of vertical fluxes of gaseous contaminants**

402 Vertical fluxes,  $F_c$ , can be quantified for periods with transfer velocity,  $v_{tr}$ , determined, which 403 varied between 3.3 and 8.4 cm s<sup>-1</sup>, by average it was  $5.3\pm1.9$  cm s<sup>-1</sup>. The time coverage of this 404 parameter was 70%, however, i.e., satisfying time coverage of sampling intervals was 405 achieved during 14 out of 20 sampling intervals, 11 days (by average 5.5 cm s<sup>-1</sup>) and 3 nights 406 (by average 3.5 cm s<sup>-1</sup>) (Figures 1a, 2c, Table S5).

The fluxes of PAHs could be determined based on 8 periods of day-time and 2 periods of night-time sampling. 15 PAH fluxes were downward ( $F_c = -3.6\pm7.0 \ \mu g \ m^{-2} \ d^{-1}$ ), 8 upward (ranging  $F_c = 0.8\pm0.6 \ \mu g \ m^{-2} \ d^{-1}$ ) and insignificant ( $|F_c| < (0.7\pm0.7) \ \mu g \ m^{-2} \ d^{-1}$ ) in 13 cases. 410 Both directions were observed for 3 species, while the flux of PHE was downward (by 411 average  $F_c = -7.3 \ \mu g \ m^{-2} \ d^{-1}$ ) whenever significant (Table S5a). With

412

413 
$$v_{dep} = -F_c / c_g$$
 (3)

414

this corresponded to a mean deposition velocity for gaseous PHE of  $v_{dep} = 0.0043\pm0.0031$  cm s<sup>-1</sup>, still significantly deviating from zero (1 standard deviation criterion, based on measurement at  $z_1 = 1.05$  m). Even 3-ring PAHs' deposition is dominated by the particulate phase and a wide range has been reported (0.001-10 cm s<sup>-1</sup>; Zhang et al., 2015), also based on measurements in the region (Tasdemir and Esen, 2009). During the first days of the campaign FLT and PYR were volatilised, later deposited, too.

For 11 periods of day-time and 2 of night-time sampling the fluxes of 8 halogenated substances were downward in 12 cases ( $F_c = -0.58\pm0.87 \ \mu g \ m^{-2} \ d^{-1}$ ), upward in 6 cases ( $F_c = 0.30\pm0.31 \ \mu g \ m^{-2} \ d^{-1}$ ; these were 0.11-0.25 for  $\gamma$ -hexachlorocyclohexane (HCH) and 0.91  $\mu g \ m^{-2} \ d^{-1}$  for BDE47) and insignificant in 15 cases ( $|F_c| \leq 0.19\pm0.45 \ \mu g \ m^{-2} \ d^{-1}$ ) (Table S5b). The fluxes corresponded to mean deposition velocities not distinguishable from zero e.g., 0.020\pm0.032 \ cm \ s^{-1} for  $\alpha$ -HCH and 0.011\pm0.015 \ cm \ s^{-1} for PCB28 (1 standard deviation criterion).

428 Air-sea exchange fluxes had been estimated earlier based on measurements in air and 429 seawater in the Aegean Sea and application of the 2-film model for PAHs in 2001-02 430 (Tsapakis et al., 2006) and in spring 2006 for PAHs, HCB and PCBs (Castro-Jiménez et al., 431 2012). Hereby, the flux is calculated proportional to a substance specific mass transfer 432 coefficient, kol, strongly dependent on wind velocity and sea surface temperature (Jurado et al., 2004; Mandalakis et al., 2005). For both PCBs and PAHs widely varying k<sub>ol</sub> values have 433 been estimated (Gigliotti et al., 2002; Mandalakis et al., 2005). The corresponding mean  $F_c$  (5 434 435 sampling periods, just 1 in the case of ACE; Table S5) found in our study, 2012, has the same direction but exceeds by more than one and two orders of magnitude, respectively, the
previous findings for PHE (downward) and FLT (downward in 2001-02, upward in 2006). For
PYR the opposite direction (now upward, downward in 2001-02 and 2006) is found. The flux
direction found for the PCBs is unchanged compared to the 2006 measurements, then found
close to phase equilibrium (Berrojalbiz et al., 2014).

441

## 442 **3.5 Particulate phase concentrations and total deposition**

443 Only PAHs and PBDEs were found exceeding LOQ in the particulate phase. Their day-night 444 variation was minimal (Table S3a, b), by average  $c_{dav}/c_{night} = 0.90-1.18$  for particulate PAHs, 445 1.03 and 1.07 for the PBDEs. This supports the perception that particulate PAH is not 446 attacked by the hydroxyl radical, but 'shielded' by the particle matrix (e.g. Zhou et al., 2012). 447 The same had been observed previously at the same site (Tsapakis and Stephanou, 2007). Effective photochemistry can also be excluded for particulate PBDEs for the same reason. 448 449 While  $c_{dav}/c_{night} = 1.20$  and 1.37 for gaseous PBDEs suggests volatilisation from ground 450 during the day, the absence of  $c_{day}/c_{night} > 1$  for the particulate phase may indicate that the 451 species are not in gas-particle phase equilibrium. This has been pointed out based on previous 452 PBDE measurements in the region (Cetin and Odabasi, 2008). However, the data set 453 discussed here is limited and gas-particle partitioning was not the subject of this study.

Total deposition is the sum of dry and wet deposition, the latter not being significant in the Mediterranean in summer, because of small amount of precipitation. Dry deposition is the sum of particle deposition and diffusive depositional fluxes (part of air-sea exchange, see 3.2). The dry particle deposition flux, F<sub>p dep</sub>, can be estimated based on

458

$$459 F_{p dep} = -v_{dep} c_p (4)$$

460

with v<sub>dep</sub> being determined by particle size and wind speed and c<sub>p</sub> determined close to the sea 461 462 surface. Dry particle deposition to the sea surface is most efficient under high wind speeds (Williams, 1982). The mass median diameter of PAHs at remote sites has been mostly found 463 464 in the submicrometer range (Lipiatou and Saliot, 1991), also during the measurements 465 reported here (own, unpublished data measured simultaneously). For particles of 0.5 µm aerodynamic size  $v_{dep} \approx 0.1$  cm s<sup>-1</sup> can be expected for the mean wind velocity at Selles 466 Beach, i.e. 5 m s<sup>-1</sup> (Slinn and Slinn, 1980). Adopting  $v_{dep} = 0.1$  cm s<sup>-1</sup> would suggest  $F_{p dep} \approx -$ 467 0.023, -0.016 and -0.010  $\mu$ g m<sup>-2</sup> d<sup>-1</sup> for PHE, FLT and PYR (c<sub>p</sub> = 0.26, 0.19 and 0.11 ng m<sup>-3</sup>, 468 469 respectively, mean of the same 5 day-time sampling intervals in the period 3-10 July for which  $F_c$  was determined, Table S5a). This means that the contribution of  $F_{p \ dep}$  to dry 470 deposition of PHE was negligible ( $F_c \approx 1000 \times F_{p \text{ dep}}$ ;  $F_c = -26 \ \mu g \ m^{-2} \ d^{-1}$ ) and  $F_{p \text{ dep}}$  negligibly 471 compensated for net-volatilization of FLT and PYR in diffusive air-sea exchange ( $F_c = +0.91$ 472 and +0.79  $\mu$ g m<sup>-2</sup> d<sup>-1</sup> for FLT and PYR, respectively). The values of v<sub>dep</sub> integrated over the 473 474 entire size spectrum may differ considerably from values of v<sub>dep</sub> for MMD (Ruijgrok et al., 475 1995). Furthermore, the mass median diameter of the semivolatile PAHs FLT and PYR might 476 well be larger than 0.5 µm as a consequence of redistribution in the aerosol along transport. 477 However, even then, particle deposition is unlikely to have significantly compensated for net-478 volatilization, as even for particles grown to 1.5 µm F<sub>p dep</sub> would be higher by not more than a 479 factor of 10 (Slinn and Slinn, 1980). For PHE, FLT and PYR  $F_{p dep} = -0.021$ , -0.018 and -0.009 µg m<sup>-2</sup> d<sup>-1</sup>, respectively, were determined experimentally at Finokalia Observatory in 480 481 2001 (mean of 25 weeks between March and October; Tsapakis et al., 2006). This means that 482 within measurement uncertainties the particle deposition fluxes found in 2012 are the same 483 than one decade earlier, in both absolute and relative (3 PAH members) terms. These fluxes are also in agreement with what was estimated in the Aegean Sea in summer 2006, namely F<sub>p</sub> 484  $_{dep}$  = -0.010- -0.015 µg m<sup>-2</sup> d<sup>-1</sup> for the same PAHs based on assuming  $v_{dep} \approx 0.2$  cm s<sup>-1</sup> (Castro-485 486 Jiménez et al., 2012).

487 A similar calculation for the BDEs for one day-time sampling interval ( $c_p = 0.16$  and 0.20 ng 488 m<sup>-3</sup> for BDE47 and BDE99, respectively, 6 July for which  $F_c$  was determined, Table S5b) 489 suggests that the contribution of  $F_{p dep}$  to dry deposition of BDE47 was negligible, too ( $F_c \approx$ 490  $100 \times F_{p dep}$ ;  $F_c = +3.0 \ \mu g \ m^{-2} \ d^{-1}$ ), while no direct comparison can be made for BDE99 ( $|F_c|$ 

491  $\leq 3.8 \ \mu g \ m^{-2} \ d^{-1}$ ; Table S5b). Hereby,  $v_{dep} = 0.05 - 0.3 \ cm \ s^{-1}$  was adopted to account for mass

median diameters ranging 0.5-1.5 and mass transfer kinetic limitations for re-distribution
during long-range transport (Cetin and Odabasi, 2008; Luo et al., 2014; and in agreement with
own, unpublished data measured simultaneously in a short distance).

495 Significant vertical concentration differences in the particulate phase,  $\Delta c_p/\Delta z > 0$  and  $\Delta c_p/\Delta z$ 496 < 0, were found. Notably during one day-time and sequential night-time sampling (6-7 July) 497 and during day-time of 9 July all significant gradients determined for particulate phase 498 contaminants were negative, i.e. higher concentrations at the lower level, z<sub>1</sub> (PHE and FLT 499 each 1, PYR 2 cases; PBDEs each 1 case; Table S3), while the opposite gradient was found in 500 other nights and days. Marine aerosol contains organic matter (OM), mostly in the 501 accumulation mode, in particular over biological productive surface waters and under low 502 wind speeds (Gantt et al., 2011; Albert et al., 2012). A considerable part of OM is water 503 insoluble (O'Dowd et al., 2004; Facchini et al., 2008). Hence, the marine aerosol contains 504 traces of POPs, which previously were in either dissolved form or associated with suspended 505 OM. Vertical particle gradients may be sustained by turbulent diffusion (Pryor et al., 2008). 506 While average wind speed was highest during day-time of 9 July, it was average during 6-7 507 July. No fluxes can be derived from the gradients determined in this study, downward or 508 upward.

509

510 **4. Conclusions** 

The diurnal variation of contaminant concentrations in air at a remote coastal site in the Aegean Sea was explained by the combination of atmospheric mixing depth and volatilisation from the sea surface. Volatilisation from the sea surface has significantly contributed to the night-time maxima of (at least) HCB, HCH, PCB28, PCB52 and PYR. Apart from long-range transport across the Aegean Sea, local sources were indicated for PBDEs: PBDE cycling was characterized by volatilization and transport from the island during the day and deposition to the sea surface.

We successfully quantified the diffusive air-sea exchange flux of 4 3-4 ring PAHs (in the upper pg m<sup>-3</sup> concentration range), 3 OCPs, 3 PCBs and 2 PBDEs (in the lower pg m<sup>-3</sup> concentration range) at a remote coastal site using a gradient in combination with the eddy covariance technique. Many vertical gradients were insignificant and concentrations of other analytically targeted PAHs, PCBs, OCPs and PBDEs remained <LOQ. More substances could have been included using high-volume sampling, by which the sampled air volume could have been increased by one order of magnitude.

525 Both flux directions were observed (fluctuation) for the OCPs studied, as well as for 3 PAHs 526 (ACE, FLT, PYR) and 1 PCB (PCB52), not determined by the day-night cycle. Fluctuation of 527 more substances addressed might have been hidden by gaps in the time series of fluxes 528 (limited by the uncertainties of sampling and analysis) or the time resolution (limited by the 529 sensitivity of the analytical method). Hence, the mean flux direction on one hand side and 530 observations during part of the time of the trace substances may differ. E.g. volatilisation of 531 BDE47 (observed in 1 night only) may have been the exception. In general, longer 532 observations and across seasons of the flux is needed to assess dry deposition fluxes and the state of air-sea exchange of those anthropogenic trace substances, which have been 533 534 approaching phase equilibrium historically (Jantunen and Bidleman, 1995; Stemmler and Lammel, 2009; Berrojalbiz et al., 2014) or seasonally (Mulder et al., 2014). 535

536

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543

# 544 **Supporting Information**

545 Detailed methodological information (substance properties, analytical quality assurance 546 parameters, micrometeorological technique, two-box model) and results (meteorological 547 situation, transfer velocity, atmospheric concentration and flux data).

548

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- Table 1. Statistics of (a) concentrations at ground level,  $z_1 = 1.05$  m and (b) vertical gradients,
- $\Delta c_z$ , over  $\Delta z = 1.75$  m of gaseous PAHs and halogenated POPs. Mean ±standard deviation (n, min-max), ng m<sup>-3</sup>, except PBDEs: pg m<sup>-3</sup>). All data included (exceeding or below uncertainty thresholds), individual data: see Tables S3, S4. For mean and standard deviations values
- <LOQ were replaced by LOQ/2.
- a.

	all samples	night-time	day-time
ACE	0.091±0.021 (0.059–0.12)	0.11±0.006 (5, 0.11–0.12)	0.076±0.012 (5, 0.059–0.091)
PHE	1.28±0.89 (0.21-3.54)	1.00±0.52 (8, 0.21–1.46)	1.47±1.10 (10, 0.25–3.54)
FLT	0.35±0.26 (0.044–0.89)	0.29±0.24 (8, 0.046–0.76)	0.40±0.29 (10, 0.044–0.89)
PYR	0.23±0.20(0.09-0.86)	0.18±0.09 (6, 0.13–0.34)	0.28±0.25 (8, 0.09–0.86)
PCB 28	0.020±0.009 (0.006-0.037)	0.021±0.010 (5, 0.008–0.033)	0.020±0.009 (10, 0.006–0.037)
PCB 52	0.012±0.007 (0.003–0.024)	0.014±0.008 (6, 0.003–0.024)	0.011±0.005 (10, 0.003–0.023)
PCB101	0.008±0.002 (0.005-0.011)	0.009±0.002 (4, 0.006–0.011)	$0.006 \pm 0.001$ (5, $0.005 - 0.008$ )
α-HCH	0.038±0.021 (0.008-0.078)	0.056±0.013 (6, 0.039–0.076)	0.031±0.020 (10, 0.008–0.078)
<i>ү</i> -НСН	0.106±0.072 (0.007–0.245)	0.136±0.078 (8, 0.030–0.245)	0.089±0.067 (11, 0.007–0.242)
<i>p</i> , <i>p</i> '-DDE	0.007±0.004 (0.003-0.015)	0.008±0.003 (4, 0.006–0.012)	0.007±0.004 (8, 0.003–0.015)
BDE 47	0.327±0.119 (0.20-0.51)	0.265±0.046 (3, 0.228–0.317)	0.36±0.14 (5, 0.20–0.51)
BDE 99	0.218±0.062 (0.14-0.31)	0.195±0.024 (4, 0.161–0.214)	0.234±0.077 (5, 0.137–0.313)

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b.						
	all samples	night-time	day-time			
ACE	0.008±0.047 (-0.026-0.10)	-0.001±0.027 (4, -0.024–0.037)	0.019±0.072 (3, -0.026–0.10)			
PHE	1.24±2.10 (-0.047-7.35)	1.19±1.96 (4, -0.047–5.55)	1.29±2.32 (6, 0.009–7.35)			
FLT	0.19±0.43 (-0.46–0.95)	0.33±0.44 (6, -0.25–0.95)	0.073±0.40 (6, -0.46–0.73)			
PYR	0.081±0.21 (-0.42–0.45)	0.18±0.17 (6, 0.038–0.45)	0.004±0.22 (6, -0.42–0.32)			
PCB 28	0.024±0.046 (-0.013-0.155)	0.013±0.040 (7, -0.011-0.103)	0.032±0.050 (10, -0.013-0.155)			
PCB 52	0.016±0.036 (-0.011-0.120)	0.009±0.036 (7, -0.011-0.089)	0.020±0.038 (10, -0.004-0.120)			
PCB101	0.012±0.018 (-0.005-0.044)	0.007±0.019 (4, -0.005-0.035)	0.018±0.018 (4, -0.001–0.044)			
α-HCH	0.079±0.188 (-0.048-0.675)	0.025±0.131 (5, -0.048-0.258)	0.107±0.212 (10, -0.019–0.675)			
<i>ү</i> -НСН	0.107±0.273 (-0.159–0.890)	0.018±0.222 (7, -0.159-0.510)	0.164±0.297 (11, -0.073–0.890)			
p,p'-DDE	0.001±0.005 (-0.006-0.009)	0.002±0.004 (4, -0.001-0.007)	0.001±0.006 (5, -0.006–0.009)			
BDE 47	-0.229±0.072 (-0.2800.178)	n.d.	-0.229±0.072 (2, -0.2800.178)			
<b>BDE 99</b>	-0.042+0.017(-0.059-0.025)	-0.058(1)	-0.034+0.014(2 -0.044-0.025)			

	ca	c <sub>w</sub>	$f_a/f_w$
FLT	0.35	18.2	19
PYR	0.23	4.4	59
PCB 28	0.020	4.65	0.15
PCB 52	0.012	0.54	0.94
PCB 101	0.0076	0.84	0.34
p,p'-DDE	0.0072	0.84	0.76
BDE 47	0.33	0.15	2600
BDE 99	0.22	0.038	16140

Table 2. Concentrations in air (gaseous, ground level, z = 1.05 m, if >LOQ for most samples) (ng m<sup>-3</sup>, except PBDEs: pg m<sup>-3</sup>) and surface seawater (pg L<sup>-1</sup>) and fugacity ratios, f<sub>a</sub>/f<sub>w</sub>.

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- 740 Figure captions
- 741
- Fig. 1. Gaseous (a) PAH and (b) halogenated substances' concentrations at ground level,  $z_1 =$
- 1.05 m (upper), vertical concentration differences,  $\Delta c_z = c_{z2}-c_{z1}$ , over  $\Delta z = 1.75$  m (middle)
- and vertical fluxes,  $F_c = -v_{tr} \Delta c_z$  (positive = upward, negative = downward; lower). Only
- significant data (exceeding uncertainty thresholds) shown, gaps = no data.
- 746
- Fig. 2. Predicted (pink) and observed (black) concentrations (ng m<sup>-3</sup>) and predicted diffusive
- air-sea exchange fluxes,  $F_c$ , (lower: red upward and blue downward, ng m<sup>-2</sup> d<sup>-1</sup>) of selected
- contaminants, (a) HCB, (b) PCB28, (c) FLT and (d) BDE47 during 6-10 July 2012.
- 750

752 Fig. 1





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