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Atmospheric Chemistry and Physics Discussions

Bi-directional air-sea exchange and accumulation of POPs (PAHs, PCBs, OCPs and PBDEs) in the nocturnal marine boundary layer

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Abstract

As a consequence of long-range transported pollution air-sea exchange can become a major source of persistent organic pollutants in remote marine environments. The vertical gradients in air of 14 species i.e., 4 parent polycyclic aromatic hydrocarbons (PAHs), 3 polychlorinated biphenyls (PCBs), 3 organochlorine pesticides (OCPs) and 2 polybrominated diphenylethers (PBDEs) in the gas-phase were quantified at a remote coastal site in the southern Aegean Sea in summer. Most vertical gradients were positive ($\Delta c/\Delta z > 0$) indicating downward (net depositional) flux. Significant upward (net volatilisational) fluxes were found for 3 PAHs, mostly during day-time, and for 2 OCPs, mostly during night-time, as well as for 1 PCB and 1 PBDE during part of the measurements. While phenanthrene was deposited, fluoranthene (FLT) and pyrene (PYR) seem to undergo flux oscillation, hereby not following a day/night cycle. Box modelling confirms that volatilisation from the sea surface has significantly

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Atmospheric Chemistry and Physics Discussions

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

1. Introduction

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

However, the sea surface itself can turn into a secondary source of POPs provided concentrations build up in surface waters. Such studies are still rare. Re-volatilisation was observed for hexachlorocyclohexane (HCH) and PAHs, not only in coastal waters (Lohmann et al., 2011), but also in the open sea (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 emissions (even after phase-out), reversal of air-sea exchange may result at some point, as indicated by global modelling for organochlorine pesticides (OCPs; Stemmler and Lammel, 2009). The seasonality of on-going emissions on the other hand may trigger a seasonal reversal of air-sea exchange, as indicated for retene, a PAH emitted from biomass burning in the Mediterranean (summer maximum; Mulder et al., 2014).

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Atmospheric Chemistry and Physics Discussions

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.

2.1 Site and sampling

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, some 70 km east of major anthropogenic emissions (Iraklion, a city of 100000 inhabitants with airport and industries; Mihalopoulos et al., 1997; Kouvarakis et al., 2000). The Mediterranean region includes urban and industrial areas and is adjacent to to source regions (i.e. western, central and eastern Europe). Exposure of the study area to long-range transported pollution from central and eastern Europe is highest in summer (Lelieveld et al., 2002).

Organic substances were collected 3-13 July in the gaseous and particulate atmospheric phases using low volume samplers ($F \approx 2.3$ m³ h^{-1}, Leckel LVS, PM_{10} inlet) equipped with quartz fibre filter (QFF, Whatman QMA 47 mm, baked at 320°C prior to usage) and 2

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Atmospheric Chemistry and Physics Discussions

polyurethane foam (PUF) plugs (Molitan, density 0.030 g cm^{-3}, 5.5 cm diameter, total depth 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 = 2.8 m), about 0.5 m apart in the horizontal. Day-time (9-20 h EEDST) and night-time (21-8 h EEDST) sampling was conducted from 2 July in the evening until 13 July 2012 in the evening. During part of the measurements, from 6 July in the morning until 10 July 2012 in the evening, a third sampler was used to collect 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 ≈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.

Free dissolved contaminants in seawater were sampled using silicone rubber (SR) sheets (Altec, Great Britain) as passive water samplers (PWS). Quantification of trace organics from PWS is sensitive and validated (Rusina et al., 2010). Uncertainties in results obtained by application of partition based passive samplers are believed to range around a factor of two depending on the level of experience of the laboratory (Allan et al., 2009). Different aspects of uncertainty are discussed in Lohmann et al. (2012). At two localities, distanced 0.8 and 2.2 km west of Selles Beach, each two SR PWS were deployed in parallel. Each sampler consisted of six sheets (55 × 90 × 0.5 mm). Before exposure SR sheets were cleaned by Soxhlet extraction in ethyl acetate (96 h) followed by methanol (48 h, shaken), and spiked by a mix of 15 performance reference compounds (PRCs; D_{10}-biphenyl and 13 PCB congeners not occurring in the environment) according to the procedure (Booij et al., 2002). Samplers were deployed 3 July – 2 August 2012 in water mounted on stainless steel wire holders at 1 m

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
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Published: 1 February 2016

depth using buoy and rope. After exposure, samplers were stored and transported in original 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^{-1} (hourly data). No precipitation occurred. The meteorological situation is described in the Supplementary information (SI), S2.1.

2.2 Meteorological parameters and vertical flux calculations

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.

For characterization of the local meteorological conditions, continuous measurements (5 min averages) of air temperature, relative humidity, wind speed and wind direction were accomplished by three automatic weather stations (model WMT520; Vaisala, Helsinki, Finland) which have been placed at the beach in ≈200 m distance (2) and ≈100 m inland (1), respectively, from the sampling location. For characterization of the atmospheric surface layer's thermodynamic stratification, vertical profiles of wind speed, wind direction, air temperature and relative humidity were determined by continuous measurements at four levels (0.34, 0.70, 1.45, and 3.00 m above ground). Data was recorded by 2D ultrasonic wind sensors (model WMT701; Vaisala, Helsinki, Finland) and aspirated temperature and relative

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
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Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

humidity sensors (model MP103A; Rotronic, Bassersdorf, Switzerland) in 10 s intervals, which were averaged to 30 min means for further data processing. For determination of key micrometeorological quantities (e.g., sensible heat flux, friction velocity; see SI, S1.3), fast response measurements of the 3D wind vector and air temperature have been performed by a 3D ultrasonic anemometer (CSAT-3, Campbell Scientific Inc., Logan, USA) on a small mast, 4 m above ground and about 7 m ESE of the profile mast. Corresponding data were continuously recorded with a sampling frequency of 20 Hz by a suitable logger (model CR3000; Campbell Scientific Inc., Logan, USA). Key micrometeorological quantities were derived from fast response 3D wind and air temperature data (20 Hz) according to the eddy covariance (EC) method; 20 Hz data were processed by the TK3 algorithm (Mauder and Foken, Department of Micrometeorology, University of Bayreuth, Germany), and the results were averaged every 30 minutes. Only periods with wind direction between 270° and 40° (i.e., onshore winds) were considered to calculate vertical fluxes of gaseous organics (more details in the SI, S2.1).

The turbulent vertical gaseous organics flux, F_c (ng m^{-2} s^{-1}), has been calculated according to the aerodynamic method as the product of the vertical difference of concentration, Δc_z (ng m^{-3}), and the turbulent transfer velocity, v_{tr} (m s^{-1}):

$$F_c = - v_{tr} \Delta c_z = - v_{tr} [c(z_2) - c(z_1)]$$

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

2.3 Chemical analysis

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

153 For organic analysis all samples were extracted with dichloromethane during ≈1 h in an
154 automatic extractor (Büchi B-811). Surrogate extraction standards (D_8-naphthalene, D_{10}-
155 phenanthrene, D_{12}-perylene, PCB30, PCB185, ^{13}C BDEs 28, 47, 99, 100, 153, 154, 183 and
156 209) were spiked on each PUF and QFF prior to extraction. The volume was reduced after
157 extraction under a gentle nitrogen stream at ambient temperature, and fractionation was
158 achieved on a silica gel column. Samples were analyzed using a GC-MS (gas chromatograph
159 coupled with a mass spectrometer) Agilent 7890 coupled to Agilent 7000B with a J&W
160 Scientific fused silica column DB-5MSUI (60 m × 0.25 mm × 0.25 µm) for 2-4-ring PAHs
161 (naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN),
162 phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR),
163 benzo(a)anthracene (BAA), and chrysene (CHR).Terphenyl was used as injection standard.
164 The temperature program was 80°C, 15°C min^{-1} to 180°C, 5°C min^{-1} to 310°C. The injection
165 volume was 1 µL in splitless mode at 280°C, with He used as a carrier gas at constant flow of
166 1.5 mL min^{-1}.
167 A sulphuric acid modified silica gel column was used for the PCB/OCP and PBDE cleanup.
168 Samples were analyzed using a GC-MS/MS Agilent 7890 coupled to Agilent 7000B with a
169 SGE HT-8 column (60 m × 0.25 mm × 0.25 µm) for *α*-HCH, *β*-HCH, *γ*-HCH, *δ*-HCH, *o,p'*-
170 and *p,p´*-DDE, -DDD and –DDT, penta- and hexachlorobenzene (PeCB, HCB). PCB 121 was
171 used as injection standard for chlorinated substances. The temperature program was 80°C (1
172 min hold), 40°C min^{-1} to 200°C, 5°C min^{-1} to 305°C. The injection volume was 3 µL in
173 splitless mode at 280°C, with He used as a carrier gas at constant flow of 1.5 mL min^{-1}.
174 PBDEs were analysed using GC-HRMS (gas chromatography with high resolution mas
175 spectrometry) on a Restek RTX-1614 column (15 m × 0.25 mm × 0.1 µm). The resolution
176 was set to > 10000 for BDE 28–183, and > 5000 for BDE 209. ^{13}C BDEs 77 and 138 were
177 used as injection standards. The MS was operated in EI+ mode at the resolution of >10000.
178 The temperature program was 80°C (1 min hold), then 20°C min^{-1} to 250°C, followed by

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
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Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

179 1.5°C min^{-1} to 260°C and 25°C min^{-1} to 320°C (4.5 min hold). The injection volume was 3 µL
180 in splitless mode at 280°C, with He used as a carrier gas at constant flow of 1 mL min^{-1}.
181
182 Recovery of native analytes varied between 72 and 102% for PAHs, between 88 and 103%
183 for PCBs, and between 75 and 98% for OCPs. The results for PAHs, OCPs and PCBs were
184 not recovery corrected. For PBDEs, isotopic dilution method was used, the average recoveries
185 ranged 78-128%.
186 The mean of 4 field blank values was subtracted from the air sample values. Values below the
187 mean + 3 standard deviations of the field blank values were considered to be <LOQ. Field
188 blank values of most analytes in air samples were below the instrument limit of quantification
189 (ILOQ), which corresponded to 6-34 pg m^{-3} for PAHs, 7-23 pg m^{-3} for PCB and OCPs and
190 0.003-0.04 pg m^{-3} for PBDEs (SI, Table S2). Higher LOQs were determined for analytes in
191 gaseous air samples, namely 0.18 and 0.50 ng m^{-3} for FLN and PHE, and typically 28 pg m^{-3}
192 for HCB. In the particulate phase a higher LOQ resulted for PHE, i.e. 170 pg m^{-3}. The
193 breakthrough in PUF samples was estimated, and as a consequence, NAP, FLN, HCB and
194 PeCB results are not considered as the sampled air volume (typically ≈25 m³ for PUFs)
195 expectedly lead to breakthrough under the prevailing temperatures (Melymuk et al., 2016).
196 Free dissolved water concentrations of analytes in PWS were calculated from amounts
197 accumulated in SRs using the exponential uptake model described in Smedes (2007). The
198 required sampling rates were estimated by fitting performance reference compounds
199 dissipation data from sampler to the model described by Booij and Smedes, 2010. ILOQ
200 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
201 OCPs and 0.0003-0.037 pg L^{-1} for PBDEs (SI, Table S2). Site specific LOQs were 1–10 pg L^{-}
202 ^{1} 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
203 pg L-1 for α-HCH) and 0.01–0.11 pg L^{-1} for PBDEs (but 0.59 pg L^{-1} for BDE209).
204

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
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Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

205 **2.4 Vertical gradients of trace organics' concentration in air**

206 Air-sea gas exchange can be studied by determining the vertical concentration gradients of
207 trace gases in air (Doskey et al., 2004; Else et al., 2008).
208 Three standard deviations of field blank concentrations are considered as the absolute
209 uncertainty of concentration measurements, c, and twice that much as the uncertainty of
210 concentration differences, Δc_z. Values of concentrations and vertical concentration differences
211 (gradients) not exceeding these thresholds are considered insignificant. This applied for a
212 large fraction of gradients, namely OCP (34 out of 70), PCB (27 out of 44), PBDE (4 out of
213 5), and PAHs (17 out of 46) (Table S3).
214
215 **2.5 Air-water fugacity ratio**
216 The direction of diffusive air-sea gas exchange can be derived from the fugacity ratio
217 calculation, based on the Whitman two-film model (Bidleman and McConnell, 1995**)**. The
218 fugacity ratio, f_a/f_w, is calculated as:
219
220 $f_a/f_w = c_a R T_a / (c_w H_{Tw,salt})$
221
222 with gas-phase concentration c_a (ng m^{-3}), dissolved aqueous concentration c_w (ng m^{-3}),
223 universal gas constant R (Pa m^3 mol^{-1} K^{-1}), sea surface temperature (SST), T_w, and both T_w
224 and salinity corrected Henry's law constant $H_{Tw,salt}$ (Pa m^3 mol^{-1}; see S1.1 for details), and air
225 temperature T_a (K). T_a was adopted from the on-site measurement (see above). c_w is derived
226 as the average of the results at two localities, 2 replicas each (see above, 2.1). SST data,
227 measured on the sampling day and in the area, were downloaded from respective database
228 (see S1.4 for details). Air and water sampling was not totally in phase: sampling in air was
229 over 12 days (2-13 July), while SR exposure was during 28 days (3-30 July) i.e., collection
230 was done 10 days after air sample collection. Consequently, for those substances which are

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
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Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

231 quickly equilibrated (within a few days) in PWS i.e., HCH and 3-ring PAHs, no simultaneous
232 measurement in air and water was done (see section 2.1). Although the seawater
233 concentrations of HCH and 3-ring PAHs might have been stable over 28 days, no such
234 evidence exists and we refrain from relating the fugacities. Values $0.3 < FR < 3.0$ are
235 conservatively considered to not safely differ from phase equilibrium, as propagating from the
236 uncertainty of the Henry's law constant, $H_{Tw,salt}$, and measured concentrations and
237 temperature changes during sampling (e.g., Bruhn et al., 2003; Castro-Jiménez et al., 2012).
238 Substance property data are taken from the literature (SI, Table S1). This conservative
239 uncertainty margin is also adopted here, while $f_a/f_w > 3.0$ indicates net deposition and f_a/f_w
240 <0.3 net volatilisation.
241
242 **2.6 Non-steady state 2-box model**
243 The air–sea mass exchange flux of several OCPs and PAHs are simulated by a non-steady
244 state zero-dimensional model of intercompartmental mass exchange (Lammel, 2004; Mulder
245 et al., 2014) in order to test the hypothesis that the diurnal variation of contaminant
246 concentrations in air during a period of on-shore advection of one air mass is explained by the
247 combination of volatilisation from the sea surface and atmospheric mixing depth, while
248 advection (long-range transport) is less significant (horizontal homogeneity of air mass;
249 Lammel et al., 2003). This 2-box model predicts concentrations by integration of two coupled
250 ordinary differential equations that solve the mass balances for the two compartments, namely
251 the atmospheric marine BL and seawater surface mixed layer. Processes considered in air are
252 dry (particle) deposition, removal from air by reaction with the hydroxyl radical, and air-sea
253 mass exchange flux (dry gaseous deposition), while in seawater export (settling) velocity,
254 deposition flux from air, air-sea mass exchange flux (volatilisation), and degradation (as first
255 order process) are considered. Input parameters are listed in the SM, Table S3.
256

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

3. Results and discussion

3.1 Day/night variation of concentrations in air

4 PAHs (ACE, PHE, FLT, PYR), 3 OCPs (α- and γ-HCH, *p,p'*-DDE), 3 PCB congeners (PCB28, -52 and -101) and 2 PBDE congeners (BDE47 and -99) were quantified in gas-phase samples, while the other species were found <LOQ in all or most samples (Fig. 1a, 2a, Table 1a, b). This is a consequence of limited air sample volume (≈25 m³). PAHs and PBDEs were also found in the particulate phase. The levels observed (Table 1a) are at the lower end of what had been reported from marine, rural and remote sites in the region in the previous ≈15 years, in particular with regard to the chlorinated species (Kamarianos et al., 2002; Mandalakis and Stephanou, 2002; Tsapakis and Stephanou, 2005; Cetin and Odabasi, 2008; Halse et al., 2011; Lammel et al., 2010 and 2011; Castro-Jiménez et al., 2012; Berrojalbiz et al., 2014; Mulder et al., 2014 and 2015). To our best knowledge, the DDE levels are the lowest reported from the region. This confirms the remote character of the site. Influence of local sources, not expected at this remote site (Iacovidou et al., 2009), is sometimes indicated by an anti-correlation between wind speed and atmospheric concentration. At Selles Beach, dilution by higher wind speed is indeed indicated for one contaminant, ACE (by significant anti-correlation, $p < 0.05$ confidence level, t-test). This is expected, because of its short atmospheric lifetime.

BL depths ranged 160-500 m during night-time and 270-760 m during day-time (mean of sampling intervals i.e., 11 h). Day/night variation of contaminants' atmospheric concentrations, often related to mixing and local sources, was not obvious: For PAHs the mean ratio of day/night concentrations $c_{day}/c_{night} = 0.67$ for ACE, while it was $c_{day}/c_{night} = 1.4$-1.55 for PHE, FLT and PYR. Also for PBDEs $c_{day}/c_{night} > 1$ is found (1.20 and 1.37). The low value for ACE can be explained by its short photochemical lifetime (Keyte et al., 2013). $c_{day}/c_{night} > 1$ was previously observed for PAHs at the same site and explained by temperature

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
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Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

driven volatilisation from surfaces overcompensating for photochemistry (Lee et al., 1998; Tsapakis and Stephanou, 2007). For chlorinated substances, we find $c_{day}/c_{night} < 1$, namely 0.56-0.66 for HCH isomers, and 0.68-0.95 for PCBs and DDE. However, there was a clear day/night, with mostly night-time maxima trend during a period of continuous on-shore winds, 6-10 July (Fig. 1). Apparently, contaminants' concentrations were influenced by BL depth, as indicated by anti-correlation with PAHs and OCPs (except DDE; significant for α-HCH on the $p < 0.05$ confidence level, t-test). This, apart from mixing, is related to advection and air-sea mass exchange and studied in more detail in Section 3.5.

3.2 Diffusive air-sea exchange

The variation of air concentrations (with nighttime maxima) during a period of northerly flow without change of air mass is predicted using the 2-box model (Section 2.6). For PCB28, -52, FLT and BDE47 air concentrations are qualitatively well captured (Fig. 2, S4). These are maintained by dry gaseous deposition alone (PCB52, FLT) or by oscillating fluxes (HCB, PCB28: mostly upward, PYR: mostly downward; Fig. S5). The model predicted fluxes are in good agreement with the observed values (Section 3.3, Table S5) except for each one day-time sampling interval of FLT and BDE47 (upward fluxes), and for one day-time interval of PCB28 (downward flux; in total 4 agreements, 3 disagreements). The modelling results support that (during advection of one air mass) the diurnal variation of contaminant concentrations in air was explained by the combination of volatilisation from the sea surface and atmospheric mixing depth. Volatilisation from the sea surface has significantly contributed to the night-time maxima of HCB and PCB28, as well as of PYR during 1 night (night-time upward fluxes; Table S5). This, to our knowledge, had never been observed before.

f_w 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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
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Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

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).

3.3 Vertical concentration gradients in air

PAH vertical gradients mostly indicated deposition, $\Delta c/\Delta z > 0$, found in 28 cases (14 during day, 14 during night), while negative gradients were found in 10 cases (8 during day, 2 during night). The vertical gradient of PAHs was insignificant in 17 cases. When volatilisation was observed (3-5 July for FLT and PYR, 6-9 July for ACE) $\Delta c/\Delta z$ tended to be clearly lower during day-time, indicating that volatilisation of PAHs from the sea surface was stronger during day-time. This could be explained by a higher fugacity from seawater, f_w, which increases with $H_{Tw,salt}$ (see above, 2.5), which, in turn, increases with sea surface temperature, T_w. Similarly, for the halogenated substances, significant positive gradients, $\Delta c/\Delta z > 0$, indicating deposition were more frequent than significant negative gradients i.e., 37 cases (15 PCBs, 22 OCPs, 30 during day, 7 during one night only) and 20 cases (2 PCBs, 17 OCPs, 1 PBDE, 5 during day, 15 during night), respectively. For these substance classes, a vertical gradient was insignificant in 65 cases (according to the measurement uncertainties). During at least some nights of the period 6-10 July night-time maxima of HCH, and PCB52 in air coincided with negative vertical gradients, i.e. emissions from the sea surface. This trend is most significant for the HCH isomers for which a stronger volatilisation flux from the sea

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

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

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

359 These observations of an increasing number of pollutants attaining phase equilibrium and bi-
360 directional flux may indicate a long-term trend from deposition towards 'reversal', i.e.
361 volatilisation of these pollutants in the marine environment of the eastern Mediterranean and,
362 more general, of receptor seas regions, located in the outflow of regions emitting long-lived
363 semivolatile pollutants, such as most POPs. For substances close to phase equilibrium
364 (attained in a long-term trend) the direction of air-sea exchange may change with a high
365 frequency, as found here. However, fluctuation may also occur in response to seasonal trends:
366 In summer 2010 FLT and PYR were found close to phase equilibrium in the eastern
367 Mediterranean, while retene (RET) was found mostly volatilisational. A model simulation had
368 revealed that seasonal primary emissions and subsequent deposition of RET (from open fires
369 in the region) are triggering seasonal flux reversal, which over many weeks, however, is
370 fluctuating with a high frequency (< 24 h). (Mulder et al., 2014) Obviously, longer
371 observations are needed to assess the prevailing vertical flux direction. Extrapolation of the
372 observations to annual fluxes is not justified, as day/night fluctuations may be part of a more
373 complex temporal pattern. The seawater surface as secondary source of pollution should be
374 assessed based on flux measurements during several seasons and over longer time periods.
375

376 **3.4 Quantification of vertical fluxes of gaseous contaminants**

377 Vertical fluxes, F_c, can be quantified for periods with transfer velocity, v_{tr}, determined, which
378 varied between 3.3 and 8.4 cm s^{-1}, by average it was 5.3±1.9 cm s^{-1}. The time coverage of this
379 parameter was 70%, however, i.e., satisfying time coverage of sampling intervals was
380 achieved during 14 out of 20 sampling intervals, 11 days (by average 5.5 cm s^{-1}) and 3 nights
381 (by average 3.5 cm s^{-1}) (Figures 1a, 2c, Table S5).
382 The fluxes of PAHs could be determined based on 8 periods of day-time and 2 periods of
383 night-time sampling. 15 PAH fluxes were downward (F_c = -3.6±7.0 µg m^{-2} d^{-1}), 8 upward
384 (ranging F_c = 0.8±0.6 µg m^{-2} d^{-1}) and insignificant ($|F_c| < (0.7\pm0.7)$ µg m^{-2} d^{-1}) in 13 cases.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

Both directions were observed for 3 species, while the flux of PHE was downward (by average F_c = -7.3 µg m^{-2} d^{-1}) whenever significant (Table S5a). With

$$v_{dep} = -F_c / c_g,$$

this corresponded to a mean deposition velocity for gaseous PHE of v_{dep} = 0.0043±0.0031 cm s^{-1}, still significantly deviating fom zero. Even 3-ring PAHs' deposition is dominated by the particulate phase and a wide range has been reported (0.001-10 cm s^{-1}; 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±0.87 µg m^{-2} d^{-1}), upward in 6 cases (F_c = 0.30±0.31 µg m^{-2} d^{-1}; these were 0.11-0.25 for γ-hexachlorocyclohexane (HCH) and 0.91 µg m^{-2} d^{-1} for BDE47) and insignificant in 15 cases ($|F_c| \lesssim$ 0.19±0.45 µg m^{-2} d^{-1}) (Table S5b). The fluxes corresponded to mean deposition velocities not distinguishable from zero e.g., 0.020±0.032 cm s^{-1} for α-HCH and 0.011±0.015 cm s^{-1} for PCB28.

Air-sea exchange fluxes had been estimated earlier based on measurements in air and seawater in the Aegean Sea and application of the 2-film model for PAHs in 2001-02 (Tsapakis et al., 2006) and in spring 2006 for PAHs, HCB and PCBs (Castro-Jiménez et al., 2012). Hereby, the flux is calculated proportional to a substance specific mass transfer coefficient, k_{ol}, 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_{ol} values have been estimated (Gigliotti et al., 2002; Mandalakis et al., 2005). The corresponding mean F_c (5 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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

411 PYR the opposite direction (now upward, downward in 2001-02 and 2006) is found. The flux
412 direction found for the PCBs is unchanged compared to the 2006 measurements, then found
413 close to phase equilibrium (Berrojalbiz et al., 2014).
414
415 **3.5 Particulate phase concentrations and total deposition**
416 Only PAHs and PBDEs were found exceeding LOQ in the particulate phase. Their day-night
417 variation was minimal (Table S3a, b), by average c_{day}/c_{night} = 0.90-1.18 for particulate PAHs,
418 1.03 and 1.07 for the PBDEs. This supports the perception that particulate PAH is not
419 attacked by the hydroxyl radical, but 'shielded' by the particle matrix (e.g. Zhou et al., 2012).
420 The same had been observed previously at the same site (Tsapakis and Stephanou, 2007).
421 Effective photochemistry can also be excluded for particulate PBDEs for the same
422 reasonWhile c_{day}/c_{night} = 1.20 and 1.37 for gaseous PBDEs suggests volatilisation from ground
423 during the day, the absence of $c_{day}/c_{night} > 1$ for the particulate phase may indicate that the
424 species are not in gas-particle phase equilibrium. This has been pointed out based on previous
425 PBDE measurements in the region (Cetin and Odabasi, 2008). However, the data set
426 discussed here is limited and gas-particle partitioning was not the subject of this study.
427 Total deposition is the sum of dry and wet deposition, the latter not being significant in the
428 Mediterranean in summer. Dry deposition is the sum of particle deposition and diffusive
429 depositional fluxes (part of air-sea exchange, see 3.2). The dry particle deposition flux, $F_{p\ dep}$,
430 can be estimated based on
431
432 $$F_{p\ dep} = -v_{dep}\ c_p$$
433
434 with v_{dep} being determined by particle size and wind speed. Dry particle deposition to the sea
435 surface is most efficient under high wind speeds (Williams, 1982). The mass median diameter
436 of PAHs at remote sites has been mostly found in the submicrometer range (Lipiatou and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

437 Saliot, 1991), also during the measurements reported here (own, unpublished data measured
438 simultaneously). For particles of 0.5 µm aerodynamic size v_{dep} ≈ 0.1 cm s^{-1} can be expected
439 for the mean wind velocity at Selles Beach, i.e. 5 m s^{-1}. Actually, v_{dep} is not very sensitive to
440 wind speed for this particle size range. (Slinn and Slinn, 1980) Adopting v_{dep} = 0.1 cm s^{-1}
441 would suggest $F_{p\ dep}$ ≈ -0.023, -0.016 and -0.010 µg m^{-2} d^{-1} for PHE, FLT and PYR (c_p = 0.26,
442 0.19 and 0.11 ng m^{-3}, respectively, mean of the same 5 day-time sampling intervals in the
443 period 3-10 July for which F_c was determined, Table S5a). This means that the contribution of
444 $F_{p\ dep}$ to dry deposition of PHE was negligible ($F_{p\ dep}$ ≈ 1000 × $F_{p\ dep}$; F_c = -26 µg m^{-2} d^{-1}) and
445 $F_{p\ dep}$ negligibly compensated for net-volatilization of FLT and PYR in diffusive air-sea
446 exchange (F_c = +0.91 and +0.79 µg m^{-2} d^{-1} for FLT and PYR, respectively). The mass median
447 diameter of the semivolatile PAHs FLT and PYR might well be larger than 0.5 µm as a
448 consequence of redistribution in the aerosol along transport. However, even then, particle
449 deposition could not have significantly compensated for net-volatilization, as for 1 µm
450 particles $F_{p\ dep}$ would be higher by approximately a factor of 3 (Slinn and Slinn, 1980). For
451 PHE, FLT and PYR $F_{p\ dep}$ = -0.021, -0.018 and -0.009 µg m^{-2} d^{-1}, respectively, were
452 determined experimentally at Finokalia Observatory in 2001 (mean of 25 weeks between
453 March and October; Tsapakis et al., 2006). This means that within measurement uncertainties
454 the particle deposition fluxes found in 2012 are the same than one decade earlier, in both
455 absolute and relative (3 PAH members) terms. These fluxes are also in agreement with what
456 was estimated in the Aegean Sea in summer 2006, namely $F_{p\ dep}$ = -0.010- -0.015 µg m^{-2} d^{-1}
457 for the same PAHs based on assuming v_{dep} ≈ 0.2 cm s^{-1} (Castro-Jiménez et al., 2012).
458 A similar calculation of for the BDEs for one day-time sampling interval (c_p = 0.16 and 0.20
459 ng m^{-3} for BDE47 and BDE99, respectively, for day-time 6 July for which F_c was determined,
460 Table S5b) suggests that the contribution of $F_{p\ dep}$ to dry deposition of BDE47 was negligible,
461 too ($F_{p\ dep}$ ≈ 100 × $F_{p\ dep}$; F_c = +3.0 µg m^{-2} d^{-1}), while no direct comparison can be made for

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

462 BDE99 ($|F_c| \lesssim 3.8$ µg m^{-2} d^{-1}; Table S5b). Hereby, v_{dep} = 0.3 cm s^{-1} was adopted to account
463 for mass median diameters close to 1 µm near the sources and mass transfer kinetic
464 limitations for re-distribution during long-range transport (Cetin and Odabasi, 2008; Luo et
465 al., 2014; and in agreement with own, unpublished data measured simultaneously in a short
466 distance).
467 Significant vertical concentration differences in the particulate phase, $\Delta c_p/\Delta z > 0$ and $\Delta c_p/\Delta z$
468 < 0, were found. Notably during one day-time and sequential night-time sampling (6-7 July)
469 and during day-time of 9 July all significant gradients determined for particulate phase
470 contaminants were negative, i.e. higher concentrations at the lower level, z_1 (PHE and FLT
471 each 1, PYR 2 cases; PBDEs each 1 case; Table S3), while the opposite gradient was found in
472 other nights and days. Apart from particle sources at the ground (not relevant here), vertical
473 particle gradients may be sustained by turbulent diffusion (Pryor et al., 2008). While average
474 wind speed was highest during day-time of 9 July, it was average during 6-7 July. No fluxes
475 can be derived from the gradients determined in this study, downward or upward.
476
477 **4. Conclusions**
478 The diurnal variation of contaminant concentrations in air at a remote coastal site in the
479 Aegean Sea was explained by the combination of atmospheric mixing depth and volatilisation
480 from the sea surface. Volatilisation from the sea surface has significantly contributed to the
481 night-time maxima of PCB28. Apart from long-range transport across the Aegean Sea, local
482 sources were indicated for PBDEs: PBDE cycling was characterized by volatilization and
483 transport from the island during the day and deposition to the sea surface.
484 We successfully quantified the diffusive air-sea exchange flux of 4 3-4 ring PAHs (in the
485 upper pg m^{-3} concentration range), 3 OCPs, 3 PCBs and 2 PBDEs (in the lower pg m^{-3}
486 concentration range) at a remote coastal site using a gradient in combination with the eddy

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

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.

Both flux directions were observed (fluctuation) for the OCPs studied, as well as for 3 PAHs (ACE, FLT, PYR) and 1 PCB (PCB52), not determined by the day-night cycle. Fluctuation of more substances might have been hidden by the method's uncertainties. Hence, the mean flux direction on one hand side and observations during part of the time of the trace substances may differ. E.g. volatilisation of BDE47 (observed in 1 night only) may have been the exception. In general, longer observations and across seasons of the flux is needed to assess the state of air-sea exchange of those anthropogenic trace substances, which have been approaching phase equilibrium historically (Jantunen and Bidleman, 1995; Stemmler and Lammel, 2009; Berrojalbiz et al., 2014) or seasonally (Mulder et al., 2014).

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

References
Allan, I.J., Booij, K., Paschke, A., Vrana, B., Mills, G.A., and Greenwood, R.: Field performance of seven passive sampling devices for monitoring of hydrophobic substances. Environ. Sci. Technol., 43, 5383-5390, 2009.

Atlas, E., and Giam, C.S.: Sea-air exchange of high-molecular weight synthetic organic compounds. In: The role of air-sea exchange in geochemical cycles (Buat-Ménard, P., ed.), NATO ASI Ser. Vol. C185, Reidel, Dordrecht, the Netherlands, pp. 295-329, 1986

Berrojalbiz, N., Castro-Jiménez, J., Mariani, G., Wollgast, J., Hanke, G., and Dachs, J.: Atmospheric occurrence, transport and deposition of polychlorinated biphenyls and hexachlorobenzene in the Mediterranean and Black Seas. Atmos. Chem. Phys., 14, 8947-8959, 2014.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

524 Bidleman, T.F., and McConnell, L.L.: A review of field experiments to determine air–water
525 gas-exchange of persistent organic pollutants. Sci. Total Environ., 159, 101-107, 1995.
526 Booij, K., and Smedes, F.: An improved method for estimating in situ sampling rates of
527 nonpolar passive samplers. Environ. Sci. Technol., 44, 6789–6794, 2010.
528 Borgå, K., Gabrielsen, G.W., and Skaare, J.U.: Biomagnification of organochlorines along a
529 Barents Sea food chain. Environ. Pollut., 113, 187-198, 2001.
530 Bruhn, R., Lakaschus, S., and McLachlan, M.S.: Air/sea gas exchange of PCBs in the
531 southern Baltic sea. Atmos. Environ., 37, 3445–3454, 2003.
532 Castro-Jiménez, J., Berrojalbiz, N., Wollgast, J., and Dachs, J.: Polycyclic aromatic
533 hydrocarbons (PAHs) in the Mediterranean Sea: Atmospheric occurrence, deposition and
534 decoupling with settling fluxes in the water column. Environ. Pollut., 166, 40-47, 2012.
535 Cetin, B., and Odabasi, M.: Atmospheric concentrations and phase partitioning of
536 polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. Chemosphere, 71, 1067-1078,
537 2008.
538 Doskey, P.V., Kotamarthi, V.R., Fukui, Y., Cook, D.R., Breitbeil, F.W., and Wesely, M.L.:
539 Air-surface exchange of peroxyacetyl nitrate at a grassland site. J. Geophys. Res., 109,
540 D10310, 2004.
541 Else, B.G.T., Papakyriakou, T.N., Granskog, M.A., and Yackel, J.J.: Observations of sea
542 surface f_{CO2} distributions and estimated air–sea CO_2 fluxes in the Hudson Bay region
543 (Canada) during the open water season. J. Geophys. Res., 113, C08026, 2004.
544 Gigliotti, C.L., Brunciak, P.A., Dachs, J., Glenn, T.R., Nelson, E.D., Totten, L.A., and
545 Eisenreich, S.J.: Air-water exchange of polycyclic aromatic hydrocarbons in
546 theNewYork-NewJersey, USA, harbor estuary. Environ. Toxicol. Chem., 21, 235-244,
547 2002.
548 Halse, A.K., Schlabach, M., Eckhardt,, S., Sweetman, A.J., Jones, K.C., and Breivik, K.:
549 Spatial variability of POPs in European background air. Atmos. Chem. Phys., 11, 1549–
550 1564, 2011.
551 Jantunen, L.M., and Bidleman, T.F.: Reversal of the air-water gas-exchange direction of
552 hexachlorocyclohexanes in the Bering and Chukchi Seas: 1993 vs. 1988, Environ. Sci.
553 Technol., 29, 1081-1089, 1995.
554 Kamarianos, A., Karamanlis, X., and Galoupi, E.: Pollution of coastal areas of N. Greece by
555 organochlorine pesticides and polychlorinated biphenyls (PCBs). In: Proceedings of the
556 1st Environmental Conference of Macedonia, 1–4 March 2002, Thessaloniki, Greece, pp.
557 116–121, 2002.
558 Keyte I.J., Harrison R.M., and Lammel G.: Chemical reactivity and long-range transport
559 potential of polycyclic aromatic hydrocarbons – a review. Chem. Soc. Rev., 42, 9333-
560 9391, 2013.
561 Kouvarakis, G., Tsigaridis, K., Kanakidou, M., and Mihalopoulos, N.: Temporal variations of
562 surface regional background ozone over Crete Island in the southeast Mediterranean. J.
563 Geophys. Res., 105, 4399-4407, 2000.
564 Kurt-Karakus, P.B., Bidleman, T.F., Staebler, R.M., and Jones, K.C.: Measurement of DDT
565 fluxes from a historically treated agricultural soil in Canada, Environ. Sci. Technol., 40,
566 4578-4585, 2006.
567 Lakaschus, S., Weber, K., Wania, F., and Schrems, O.: The air-sea equilibrium and time trend
568 of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica,
569 Environ. Sci. Technol., 36, 138– 145, 2002.
570 Lammel, G., Brüggemann, E., Müller, K., and Röhrl, A.: On the horizontal homogeneity of
571 mass-related aerosol properties, Environ. Monitoring Assessment, 84, 265-273, 2003.
572 Lammel, G., Klánová, J., Ilić, P., Kohoutek, J., Gasić, B., Kovacić, I., Lakić, N., and Radić,
573 R.: Polycyclic aromatic hydrocarbons on small spatial and temporal scales – I. Levels and
574 variabilities. Atmos. Environ., 44, 5015-5021, 2010.

575 Lammel, G., Klánová, J., Erić, L., Ilić, P., Kohoutek, J., and Kovacić, I.: Sources of
576 organochlorine pesticides in an urban Mediterranean environment: Volatilisation from
577 soil, J. Environ. Monit., 13, 3358–3364, 2011.
578 Lammel, G., Audy, O., Besis, A., Efstathiou, C., Eleftheriadis, K., Kohoutek, J., Kukučka, P.,
579 Mulder, M.D., Přibylová, P., Prokeš, R., Rusina, T., Samara, C., Sofuoglu, A., Sofuoglu,
580 S.C., Tasdemir, Y., Vassilatou, V., Voutsa, D., and Vrana B.: Air and seawater pollution
581 and air-sea exchange of persistent organic pollutants in the Aegean Sea: spatial trends of
582 PAHs, PCBs, OCPs and PBDEs. Environ. Sci. Pollut. Res., 22, 11301-11313, 2015.
583 Lee, R.G.M., Hung, H., Mackay, D., and Jones, K.C. : Measurement and modeling of the
584 diurnal cycling of atmospheric PCBs and PAHs. Environ. Sci. Technol., 32, 2172-2179,
585 1998.
586 Lipiatou, E., Saliot, A. : Fluxes and transport of anthropogenic and natural polycyclic
587 aromatic-hydrocarbons in the western Mediterranean Sea. Mar. Chem., 32, 51-71. , 1991.
588 Lohmann, R., Dapsis, M., Morgan, E.J., Dekany, E., and Luey, P.J.: Determining air-water
589 exchange spatial and temporal trends of freely dissolved PAHs in an urban estuary using
590 passive polyethylene samplers. Environ. Sci. Technol., 45, 2655-2662, 2011.
591 Lohmann, R., Booij, K., Smedes, F., and Vrana, B.: Use of passive sampling devices for
592 monitoring and compliance checking of POP concentrations in water. Environ. Sci. Pollut.
593 Res., 19, 1885–95, 2012.
594 Luo, P., Ni, H.G., Bao, L.J., Li, S.M., and Zeng, E.Y.: Size distribution of airborne particle-
595 bound polybrominated diphenyl ethers and its implications for dry and wet deposition.
596 Environ. Sci. Technol., 48, 13793-13799, 2014.
597 Majewski, M.S., Desjardins, R., Rochette, P., Pattey, E., Seiber, J., and Glotfelty, D.E.: Field
598 comparison of an eddy accumulation and an aerodynamic-gradient system for measuring
599 pesticide volatilization fluxes. Environ. Sci. Technol., 27, 121-128, 1993.
600 Mandalakis, M., and Stephanou, E.G.: Study of atmospheric PCB concentrations over eastern
601 Mediterranean Sea. J. Geophys. Res., 107, 4716, 2002.
602 Mandalakis, M., Apostolaki, M., Stephanou, E.G., and Stavrakakis, S.: Mass budget and
603 dynamics of polychlorinated biphenyls in the east Mediterranean Sea. Glob. Biogeochem.
604 Cycles, 19, GB3018, 2005.
605 Melymuk, L., Bohlin-Nizzetto, P., Prokeš, R., Kukučka, P., and Klánová, J.: Sampling
606 artifacts in active air sampling of semivolatile organic contaminants: Comparing
607 theoretical and measured artifacts and evaluating implications for monitoring networks.
608 Environ. Pollut. doi:10.1016/jenvpol.2015.12.015, 2016.
609 Mihalopoulos, N., Stephanou, E., Pilitsidis, S., Kanakidou, M., and Bousquet, P.:
610 Atmospheric aerosol composition above the Eastern Mediterranean region. Tellus B, 49,
611 314-326, 1997.
612 Mulder, M.D., Heil, A., Kukučka, P., Klánová, J., Kuta, J., Prokeš, R., Sprovieri, F., and
613 Lammel, G.: Air-sea exchange and gas-particle partitioning of polycyclic aromatic
614 hydrocarbons in the Mediterranean. Atmos. Chem. Phys., 14, 8905–8915, 2014.
615 Mulder, M.D., Heil, A., Kukučka, P., Kuta, J., Přibylová, P., Prokeš, R., and Lammel, G.:
616 Long-range atmospheric transport of PAHs, PCBs, OCPs and PBDEs to the central and
617 eastern Mediterranean 2010. Atmos. Environ., 111, 51-59, 2015.
618 Parmele, L.H., Lemon, E.R., and Taylor, A.W.: Micrometeorological measurement of
619 pesticide vapor flux from bare soil and corn under field conditions. Water Air Soil Pollut.,
620 1, 433-451, 1972.
621 Perlinger, J.A., Tobias, D.E., Morrow, P.S., and Doskey, P.V.: Evaluation of novel techniques
622 for measurement of air-water exchange or persistent bioaccumulative toxicants in Lake
623 Superior. Environ. Sci. Technol., 39, 8411-8419, 2005.

624 Rowe, M.D., and Perlinger, J.A.: Micrometeorological measurement of hexachlorobenzene
625 and polychlorinated biphenyl compound air-water gas exchange in Lake Superior and
626 comparison to model predictions. Atmos. Chem. Phys., 12, 4607-4617, 2012.
627 Rusina, T., Smedes, F., Kobližková, M., and Klánová, J.: Calibration of silicone rubber
628 passive samplers: experimental and modeled relations between sampling rate and
629 compound properties. Environ. Sci. Technol., 44, 362-367, 2010a.
630 Rusina, T., Smedes, F., and Klanova, J.: Diffusion coefficients of polychlorinated biphenyls
631 and polycyclic aromatic hydrocarbons in polydimethylsiloxane and low-density
632 polylethylene polymers. J. Appl. Polymer Sci., 116, 1803-1810, 2010b.
633 Sandy, A.L., Guo, J., Miskewitz, R.J., McGillis, W.R., and Rodenburg, L.A.: Fluxes of
634 polychlorinated biphenyls volatilizing from the Hudson River, New York measured using
635 micrometeorological approaches. Environ. Sci. Technol., 46, 885-891, 2012.
636 Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M.: Environmental Organic
637 Chemistry, 2nd ed., Wiley, Hoboken, USA, 2003.
638 Slinn, S.A., and Slinn, W.G.N.: Predictions for particle deposition on natural waters. Atmos.
639 Environ., 14, 1013-1016, 1980.
640 Smedes, F.: Monitoring of chlorinated biphenyls and polycyclic aromatic hydrocarbons by
641 passive sampling in concert with deployed mussels. In: Passive sampling techniques in
642 Environmental Monitoring (Comprehensive Analytical Chemistry Vol. 48; Greenwood,
643 R., Mills, G., Vrana, B., eds.), pp. 407–448, Elsevier, Amsterdam, the Netherlands, 2007.
644 Stemmler, I., and Lammel, G.: Cycling of DDT in the global oceans 1950-2002: World ocean
645 returns the pollutant. Geophys. Res. Lett., 36, L24602, 2009.
646 Stohl, A., Hittenberger, M., and Wotawa, G.: Validation of the Lagrangian particle dispersion
647 model FLEXPART against large scale tracer experiments. Atmos. Environ., 32, 4245-
648 4264, 1998.
649 Tasdemir, Y., and Esen, F.: Dry deposition fluxes and deposition velocities of PAHs at an
650 urban site in Turkey, Atmos. Environ., 41, 1288-1301, 2007.
651 Tsapakis, M., and Stephanou, E.G.: Polycyclic aromatic hydrocarbons in the atmosphere of
652 the Eastern Mediterranean. Environ. Sci. Technol., 39, 6584-6590, 2005.
653 Tsapakis, M., and Stephanou, E.G.: Diurnal cycle of PAHs, nitro-PAHs and oxy-PAHs in a
654 high oxidation capacity marine background atmosphere. Environ. Sci. Technol., 41, 8011-
655 8017, 2007.
656 Tsapakis M., Apostolaki, M., Eisenreich, S., and Stephanou, E.G.: Atmospheric deposition
657 and marine sediment fluxes of polycyclic aromatic hydrocarbons in the east
658 Mediterranean Basin. Environ. Sci. Technol. 40, 4922-4927, 2006.
659 UNEP-GEMS - United Nations Environment Programme Global Environment Monitoring
660 System: Water Programme, annual report, Geneva, 2006.
661 Vogelezang, D.H.P., and Holtslag, A.A.M.: Evaluation and model impacts of alternative
662 boundary-layer height formulations. Bound. Layer Met., 81, 245–269, 1996.
663 Williams, R.M.: A model for the dry deposition of particles to natural water surfaces. Atmos.
664 Envion., 16, 1933-1938, 1982.
665 Wong, F., Jantunen, L.M., Papakyriakou, T., Staebler, R.M., Stern, G.A., and Bidleman, T.F.:
666 Comparison of micrometeorological and two-film estimates of air-water gas exchange for
667 α-hexachlorocyclohexane in the Canadian Archipelago. Environ. Sci. Pollut. Res., 19,
668 1908-1914, 2012.
669 Zhang, L.M., Cheng, I., Wu, Z.Y., Harner, T., Schuster, J., Charland, J.P., Muir, D., and
670 Parnis, J.M.: Dry deposition of polycyclic aromatic compounds to various land covers in
671 the Athabasca oil sands region. J. Adv. Model. Earth Syst., 7, 1339-1350, 2015.
672 Zhou, S., Lee, A.K.Y., McWhinney, R.D., and Abbatt, J.P.D.: Burial effects of organic
673 coatings on the heterogeneous reactivity of particle-borne benzo(a)pyrene (BaP) towards
674 ozone. J. Phys. Chem. A, 116, 7050-7055, 2012.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

Table 1. Statistics of (a) concentrations at ground level, z_1 = 1.05 m and (b) vertical gradients, Δc_z, over Δz = 1.75 m of gaseous PAHs and halogenated POPs. Mean ±standard deviation (n, min-max), ng m^{-3}, except PBDEs: pg m^{-3}). 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±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)
γ-HCH	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)
p,p'-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)

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)
γ-HCH	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 (-0.280–-0.178)	n.d.	-0.229±0.072 (2, -0.280–-0.178)
BDE 99	-0.042±0.017 (-0.059–0.025)	-0.058 (1)	-0.034±0.014 (2, -0.044–-0.025)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

684 Table 2. Concentrations in air (gaseous, ground level, z = 1.05 m, if >LOQ for most samples)
685 (ng m^{-3}, except PBDEs: pg m^{-3}) and surface seawater (pg L^{-1}) and fugacity ratios, f_a/f_w.

	c_a	c_w	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

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Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

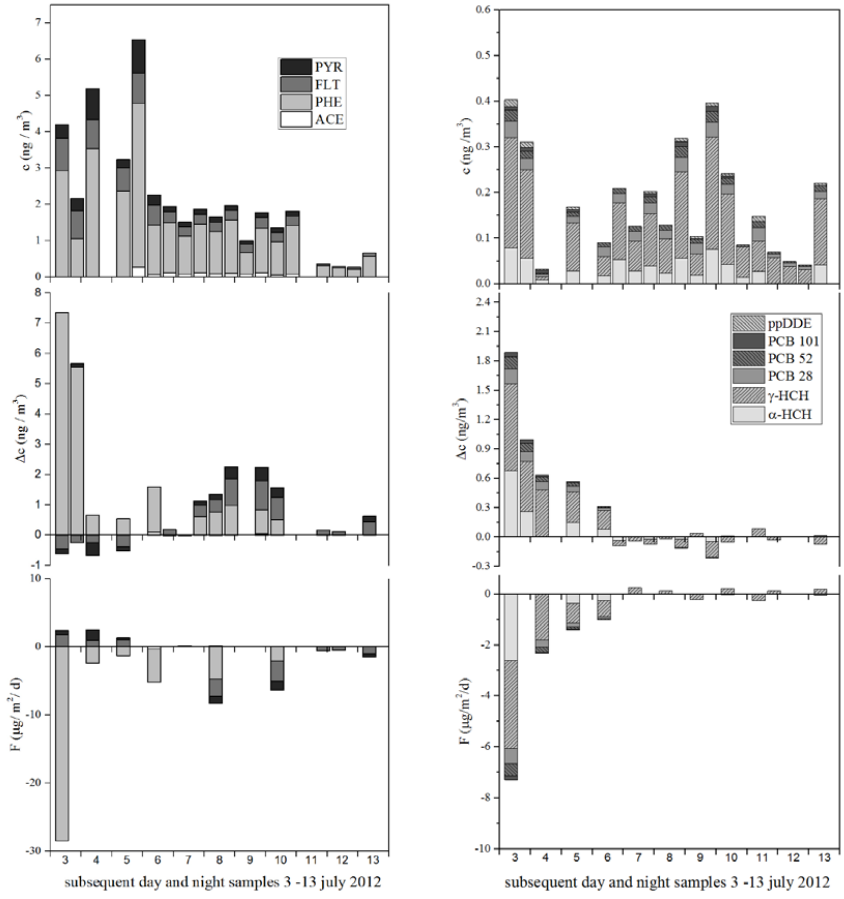
Atmospheric Chemistry and Physics Discussions

687 Figure captions
688
689 Fig. 1. Gaseous (a) PAH and (b) halogenated substances' concentrations at ground level, z_1 =
690 1.05 m (upper), vertical concentration differences, $\Delta c_z = c_{z2}-c_{z1}$, over Δz = 1.75 m (middle)
691 and vertical fluxes, $F_c = -v_{tr}\,\Delta c_z$ (positive = upward, negative = downward; lower). Only
692 significant data (exceeding uncertainty thresholds) shown, gaps = no data.
693
694 Fig. 2. Predicted and observed concentrations of selected contaminants, (a) PCB28, (b) FLT
695 and (c) BDE47 during 6-10 July 2012.
696

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

697 Fig. 1
698 a. b.



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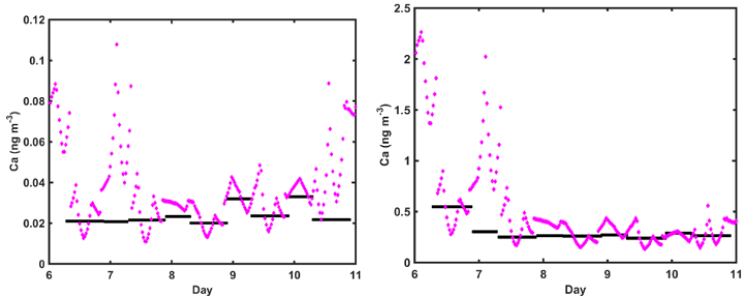
Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-926, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 1 February 2016

Atmospheric Chemistry and Physics Discussions

701 Fig. 2.
702 a. b.



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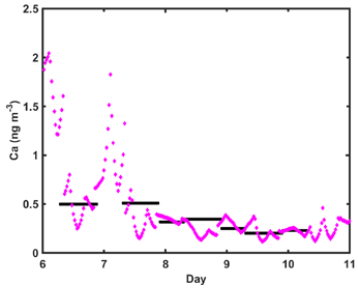
704 c.



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