Responses to Reviewers' Comments
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Manuscript Title: Bi-directional air-sea exchange and accumulation of POPs (PAHs, PCBs, OCPs and PBDEs) in the nocturnal marine boundary layer

Authors: Gerhard Lammel, Franz X. Meixner, Branislav Vrana, Christos Efstathiou, Jiři Kohoutek, Petr Kukučka, Marie D. Mulder, Petra Přibylová, Roman Prokeš, Tatsiana P. Rusina, Guo-Zheng Song, Manolis Tsapakis

We would like to thank the reviewers for their thoughtful reading, comments and questions, which considerably helped to improve this manuscript. We have addressed all comments below and have indicated the corresponding modifications in the revised version of the manuscript. All the changes are tracked in the manuscript. The line numbers mentioned in our responses to the comments refer to those in the submitted manuscript (please see attached).

Anonymous Referee #2
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This study presents bi-directional fluxes of a number of POPs generated from gradient measurements made at a remote coastal site. Such data are needed for improving our understanding of the sources and fates of POPs over ocean surfaces, although the measurements could cover longer periods and for more POPs species with highvolume sampling. A box chemistry model is also used to explain the observed data and to improving the understanding of the air-surface exchange processes. The paper is generally well written and only some minor comments are provided below.
Line 211 and lines 182-185: Briefly explain if the insignificant gradients were caused by uncertainties in the measurement, or they represent the situation that fluxes were minimal.
Small fluxes cannot be distinguished from measurement uncertainties. The criterion to identify gradients is given in the text.

Line 391 and line 399: two contradictory statements. "0.0043 cm/s, significantly deviating from zero", and "0.020 cm/s, not distinguishable from zero".
Refers to the ranges spanned by a number of flux measurements specified in the text. These were 0.0043±0.0031 cm s^{-1} and 0.020±0.032 cm s^{-1}, respectively. The criterion to identify distinguishability is now identified in the text. The new text reads: "0.0043±0.0031 cm s^{-1}, still significantly deviating from zero (1 standard deviation criterion)." and "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 (1 standard deviation criterion)."

Lines 427-428: "wet deposition not significant" - because of small amount of precipitation, or particle size range?
Small amount of precipitation. Now specified.

Lines 439-440: delete the statement. Vd is sensitive to friction velocity (and wind speed) over any surface (see Zhang and He, 2014, ACP 14, 3729-3737).
Will be done

Line 449-450: should not compare a single size since any particle species covers a size range (i.e., a size distribution). A representative size does not mean it has a representative deposition velocity (see Ruijgrok et al., 1997, Tellus 47B 587-601).

Yes, thank you for pointing this out. As the difference between gaseous and particulate deposition fluxes (at the site during the measurements) was ≈3 orders of magnitude, the estimate made still leads to the same qualitative statement. This discussion will be correspondingly extended in the revised version. New text will read: "Furthermore, values of v_{dep} integrated over the entire size spectrum may differ considerably from values of v_{dep} for MMD (Ruijgrok et al., 1995). However, even then, particle deposition is unlikely to have significantly compensated for net-volatilization, as even for particles grown to 1.5 µm $F_{p\ dep}$ would be higher by not more than a factor of 10 (Slinn and Slinn, 1980)."

Ruijgrok, W., Davidson, C.I., and Nicholson, K.W.: Dry deposition of particles – implications and recommendations for mapping of deposition over Europe. Tellus B, 47, 587-601, 1995.

Same case for Line 463. Also 0.3 cm/s seems to be on the high end for submicron particles.
Yes, should account for more uncertainty. However and again, as the difference between gaseous and particulate deposition fluxes was ≈2 orders of magnitude in this case, the estimate made still leads to the same qualitative statement. The correspondingly modified text will read: "Hereby, v_{dep} = 0.05-0.3 cm s^{-1} was adopted to account for mass median diameters ranging 0.5-1.5 µm..."

Proofread the paper for fixing the editorial issues, e.g., Line 71 "to to"; line 73 "the highest"; line 458 "of for".
Will be done

Anonymous Referee #3
This paper described a study of the gas and particle deposition flux of POPs over the marine boundary layer based on vertical gradient measurements. The results indicate both upward and downward fluxes of POPs occurred, and the direction of the fluxes changed frequently for some POPs. Emissions of POPs were driven by volatilization from the sea during daytime and nighttime for some POPs. Long-term measurements are needed to validate the results and apply them to modeling studies. This paper is suitable for publication after addressing the comments below.
Line 34: This sentence is not necessarily specific to the marine atmospheric environment; continental atmospheres are also impacted by land sources and contaminated soil emissions of POPs.
True, but will be left unchanged, as the statement itself is correct and nothing is or is intended to be said about continental atmospheres.

Please also correct the grammar error, "which are advected from sources on land, primary and secondary, such as volatilization from contaminated soils". I suggest revising to, "which are advected from primary sources on land and secondary sources, such as volatilization from contaminated soils."
To be corrected by shortening. The new text will read: "The marine atmospheric environment is a receptor for persistent organic pollutants (POPs) which are advected from primary and secondary sources on land."

Lines 42-43: What are the sources of POPs to surface waters that can lead to a buildup of concentrations? Does deposition alone lead to elevated POP concentrations in surface water?
Will be specified. The new text will read: "…fed by riverine or atmospheric deposition input."

Lines 80-81: Please explain why these two heights were chosen for determining the vertical gradient. How does height selection potentially affect the vertical concentration and flux gradients?
Will be explained. The new text will read: “According to the Monin-Obukhov similarity theory of turbulent transport in the surface layer (Monin and Obukhov, 1954; s. supplement, sect. S1.3), vertical concentration profiles are expected to be logarithmic, while – due to the vertically non-linear behaviour of the eddy diffusivity – the resulting vertical flux is *per definitionem* constant. For a given surface source (sink) of gases or particles corresponding negative (positive) vertical concentration gradients ($\partial c/\partial z$) will be maximal close to the source (sink). Therefore, over aerodynamically smooth surfaces, the lower inlet height should be preferably in the order of a few tenths of a meter, while the distance to the upper inlet height, should be maximized to yield large (and consequently statistically significant) vertical concentration differences. However, the choice for the upper inlet height is limited by the horizontal extension of the so-called "fetch", i.e. the up-wind surface homogeneity (in terms of orography, structure, and vegetation), which should be at least $100 \times z_2$ (e.g. Foken, 2008). In the case of our study, the choice of the lower inlet height (z_1=1.05 m) is just due to the design of the aerosol sampler which does not allow sampling below 1.05 m above ground, while the upper inlet height (z_2=2.80 m) accounts for the limited surface homogeneity (200 m) of the Selles Beach site."

Line 146: All equations should be labeled with numbers as well as in the text chronologically.
Will be done

Line 223: I suggest replacing with “universal gas constant R (Pa m3 mol-1 K-1), and both sea surface temperature (SST or Tw) and salinity corrected: : :”
Will be done

Lines 277-283: Only gas-phase pollutants are volatilize from the sea surface. Please mention if the ratios are based on gas-phase concentrations or gas+particulate concentrations and include the range of these ratios over the sampling period in addition to the average.
Will be specified. The new text will read: “For PAHs the mean ratio of day/night concentrations (gaseous only), c_{day}/c_{night}, 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 c_{day}/c_{night} = 1.41-1.53.”

Lines 283-284: What could be the reasons for the lower Cday/Cnight ratio for chlorinated compounds specifically?
Thanks for pointing this out. The individual data indicate that there is no significant trend hidden. More in depth analysis for a sub-set of samples is presented later in the text (section 3.5). The new text will read: “For chlorinated substances, we find mean $c_{day}/c_{night} < 1$, namely 0.56-0.66 for HCH isomers, and 0.68-0.94 for PCBs and DDE, while the individual values range widely, 0.04-4.8.”

Lines 302-304 and lines 329-336: Volatilization tends to occur during daytime. Please explain how this process contributes to the elevated nighttime concentrations. Could wind speed be another factor controlling volatilization of gases other than temperature?
Volatilization tends to occur during daytime driven by surface heating during the day and surface cooling during the night – which was not the case during the measurements reported here (SST_{day} - SST_{night} = 0.1-0.9 K, see Table S4). Other processes overcompensated for this small difference in SST, the most prominent being variation of mixing depth (low during the night, high during the day). This hypothesis is tested with the non-steady state 2-box model (presented in section 2.6).

Lines 336-341: The temperature difference between daytime and nighttime (0.5-1.5K) is too small to explain the differences in daytime and nighttime concentrations and fluxes. What would be the corresponding difference on sea surface temperatures?
SST_{day} - SST_{night} = 0.1-0.9 K (see Table S4 and previous reply, above)

Lines 363-365: What are the implications of frequent changes in the direction of air-sea exchange in terms of estimating the deposition budget of POPs? If the fluctuations are so frequent, it would be difficult to obtain an accurate deposition budget.
True. The statement "Implicitly, dry deposition is difficult to budget." will be added to the revised text. The same is/was expressed in the text (section 4, conclusions): "Both flux directions were observed (fluctuation) (…), 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. (…) 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 (…) or seasonally (…)."
This text will be slightly extended in the revised text. "… In general, longer observations and across seasons of the flux is needed to assess dry deposition fluxes and the state of air-sea exchange …"

Fig. 2: Label which series is the predicted and observed data.
Will be done

Lines 382-384: The vertical flux gradient of gases is based on a height difference of 1.8 m. How representative is this flux estimate of the overall deposition flux?
According to the Monin-Obukhov similarity theory of turbulent transport in the surface layer (Monin and Obukhov, 1954; see section S1.3), vertical concentration profiles are expected to be logarithmic, while – due to the vertically non-linear behaviour of the eddy diffusivity – the resulting vertical flux is *per definitionem* constant. New text to be added (in section 2.2, after line 1149): "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 $c(z_2) - c(z_1) > 0$)."

Line 388: It is not clear which height the concentration corresponds to in this equation for determining the deposition velocity. Is it the average concentration of the two heights or just the ground-level concentration?
Thanks. Will be clarified in the revised text: "based on measurement at z_1 = 1.05 m"

Line 422: New sentence is needed after "reason"
Will be done

Line 432: It is not clear which height the concentration corresponds to in this equation for determining the particle deposition flux.
Will be specified. Modified text will read: "$F_{p\,dep} = -v_{dep}\, c_p$ (equ. 4) with v_{dep} being determined by particle size and wind speed and c_p determined close to the sea surface."

Lines 446-450: The lack of particle size distribution data is a major source of uncertainty in the dry deposition flux calculations, since lower molecular weight PAHs are likely to partition

onto particles of various sizes. See the variation of aerosol dry deposition velocities with particle sizes in Petroff and Zhang (2010, Geoscientific Model Development).
We agree; 3-4 ring PAHs are expected to re-distribute in the aerosol mass size distribution. However, as the difference between gaseous and particulate deposition fluxes was anyway huge (≈3 orders of magnitude), the estimate made still leads to the same qualitative statement. This discussion will be correspondingly extended in the revised version. (see above, reply to Reviewer #2)

Lines 470-473: Could the upward flux of particulate-phase POPs be related to sea-salt emissions from waves?
Thanks for pointing this out. The particle source sea spray will contain POPs, whenever these were accumulated in surface waters. Therefore, upward flux could be related to waves (sea spray). Explanation will be given in the new text: "Marine aerosol contains organic matter (OM), mostly in the accumulation mode, in particular over biological productive surface waters and under low wind speeds (Gantt et al., 2011; Albert et al., 2012). A considerable part of OM is water insoluble (O'Dowd et al., 2004; Facchini et al., 2008). Hence, the marine aerosol contains traces of POPs, which previously were in either dissolved form or associated with suspended OM. The upward flux of particulate-phase POPs could be caused by sea spray."

Albert, M.F.M.A., Schaap, M., Manders, A.M.M., Scannell, C., O'Dowd, C.D., and de Leeuw, G.: Uncertainties in the determination of global sub-micron marine organic matter emissions. Atmos. Environ., 57, 289-300, 2012.
Facchini, M.C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E.D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17814, 2008.
Gantt, B., Meskhidze, N., Facchini, M.C., Rinaldi, M., Ceburnis, D., and O'Dowd, C.D., 2011. Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol. Atmospheric Chemistry and Physics, 11, 8777-8790, 2011.
O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y.J., and Putaud, J.P.: Biogenically driven organic contribution to marine aerosol. Nature, 431, 676-680, 2004.

Lines 492-493: The meaning of the sentence, "Fluctuation of more substances might have been hidden by the method's uncertainties." is unclear. Did you mean insufficient number of POPs analyzed or not enough samples collected?
Will be clarified in the new text by indicating for both PAHs and chlorinated species (Fig. 1a and 1b) and by rephrasing: "Fluctuation of more substances addressed might have been hidden by gaps in the time series of fluxes (limited by the uncertainties of sampling and analysis) or the time resolution (limited by the sensitivity of the analytical method)."

Title: The paper is lacking some discussion specifically on the accumulation of POPs in the nocturnal marine boundary layer, as stated in the title. I feel the paper discussed the diel variation (both daytime and nighttime) of POPs.
Findings of night-time maxima and accumulation were presented and discussed (sections 3.1 and 3.2, Fig. 1 and 2), also covered in the conclusions and abstract. But, yes, we agree, should be more emphasized. The revised text will read (in section 3.1, lines 288-289) "This results in night-time accumulation. Diel variation, apart from mixing, is related to …" and (in section 3.2, lines 299-302) "The modelling results support that (during advection of one air mass) the diel variation of contaminant concentrations in air and, particularly, the night-time accumulation was explained by the combination of volatilisation from the sea surface and atmospheric mixing depth." The visualized volatilization fluxes (Fig. S4) had not been referenced in the text. In the revised text this (lines 302-305) will read: "Volatilisation from the sea surface has significantly contributed to the night-time maxima of HCB (upward flux, Fig. 2a) and PCB28 (Fig. 2b), as well as of PYR during 1 night (Fig. S4a; Table S5). This, to

our knowledge, had never been observed before." To this end, the corresponding flux plots (Fig. S4) will be moved to the main text (revised Fig. 2) and complemented by HCB (not shown in Fig. S4, but in revised Fig. 2). In the conclusions all substances for which observations (mentioned in lines 329-331) or modelling (lines 302-305) suggests that volatilization from the sea surface sustained night-time accumulation in the BL i.e., HCB, HCH, PCB28, PCB52 and PYR, will be mentioned (not just 1 of these as now, in line 481).

Supplement: There are two Table S6 in the supplement.
Thanks, will be corrected (Tables S6, S7).

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

Gerhard Lammel[1,2*], Franz X. Meixner[3], Branislav Vrana[1], Christos Efstathiou[1], Jiři Kohoutek[1], Petr Kukučka[1], Marie D. Mulder[1], Petra Přibylová[1], Roman Prokeš[1], Tatsiana P. Rusina[1], Guo-Zheng Song[3], Manolis Tsapakis[4]

[1] Masaryk University, Research Centre for Toxic Compounds in the Environment, Brno, Czech Republic

[2] Max Planck Institute for Chemistry, Multiphase Chemistry Dept., Mainz, Germany

[3] Max Planck Institute for Chemistry, Biogeochemistry Dept., Mainz, Germany

[4] Hellenic Centre for Marine Research, Institute of Oceanography, Gournes, Greece

* lammel@recetox.muni.cz

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

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 primary and secondary 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, fed by riverine or atmospheric deposition input. 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). 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 ~~the~~ 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 ($F \approx 2.3$ m^3 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

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. According to the Monin-Obukhov similarity theory of turbulent transport in the surface layer (see section S1.3), vertical concentration profiles are expected to be logarithmic, while – due to the vertically non-linear behaviour of the eddy diffusivity – the resulting vertical flux is *per definitionem* constant. For a given surface source (sink) of gases or particles corresponding negative (positive) vertical concentration gradients ($\partial c/\partial z$) will be maximal close to the source (sink). Therefore, over aerodynamically smooth surfaces, the lower inlet height should be preferably in the order of a few tenths of a meter, while the distance to the upper inlet height, should be maximized to yield large (and consequently statistically significant) vertical concentration differences. However, the choice for the upper inlet height is limited by the horizontal extension of the so-called "fetch", i.e. the up-wind surface homogeneity (in terms of orography, structure, and vegetation), which should be at least $100 \times z_2$ (e.g. Foken, 2008). In the case of our study, the choice of the lower inlet height (z_1=1.05 m) is just due to the design of the aerosol sampler which does not allow sampling below 1.05 m above ground, while the upper inlet height (z_2=2.80 m) accounts for the limited surface homogeneity (200 m) of the Selles Beach site.

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 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

130 to Vogelezang and Holtslag (1996) using the critical Richardson number. According to wind
131 direction during sampling we allocate BL depths at upwind locations well off shore (70-100
132 km) or inland (≈20 km), respectively, as the relevant BL depth for interpretation of
133 atmospheric concentrations at the coastal site. The mean BL depth during sampling intervals
134 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 ≈200 m distance (2) and ≈100 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
155 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}):

$$F_c = - v_{tr} \Delta c_z = - v_{tr} [c(z_2) - c(z_1)] \quad (1)$$

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. 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 $c(z_2) - c(z_1) > 0$).

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

2.3 Chemical analysis

For organic analysis all samples were extracted with dichloromethane during ≈1 h in an automatic extractor (Büchi B-811). Surrogate extraction standards (D_8-naphthalene, D_{10}-phenanthrene, D_{12}-perylene, PCB30, PCB185, ^{13}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

Scientific fused silica column DB-5MSUI (60 m × 0.25 mm × 0.25 µm) for 2-4-ring PAHs (naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BAA), and chrysene (CHR).Terphenyl was used as injection standard. The temperature program was 80°C, 15°C min^{-1} to 180°C, 5°C min^{-1} to 310°C. The injection volume was 1 µL in splitless mode at 280°C, with He used as a carrier gas at constant flow of 1.5 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 µm) for *α*-HCH, *β*-HCH, *γ*-HCH, *δ*-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^{-1} to 200°C, 5°C min^{-1} to 305°C. The injection volume was 3 µL in splitless mode at 280°C, with He used as a carrier gas at constant flow of 1.5 mL min^{-1}.

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 µm). The resolution was set to > 10000 for BDE 28–183, and > 5000 for BDE 209. ^{13}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^{-1} to 250°C, followed by 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 in splitless mode at 280°C, with He used as a carrier gas at constant flow of 1 mL min^{-1}.

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%.

The mean of 4 field blank values was subtracted from the air sample values. Values below the mean + 3 standard deviations of the field blank values were considered to be <LOQ. Field blank values of most analytes in air samples were below the instrument limit of quantification (ILOQ), which corresponded to 6-34 pg m^{-3} for PAHs, 7-23 pg m^{-3} for PCB and OCPs and 0.003-0.04 pg m^{-3} for PBDEs (SI, Table S2). Higher LOQs were determined for analytes in gaseous air samples, namely 0.18 and 0.50 ng m^{-3} for FLN and PHE, and typically 28 pg m^{-3} for HCB. In the particulate phase a higher LOQ resulted for PHE, i.e. 170 pg m^{-3}. The breakthrough in PUF samples was estimated, and as a consequence, NAP, FLN, HCB and PeCB results are not considered as the sampled air volume (typically ≈25 m^3 for PUFs) expectedly lead to breakthrough under the prevailing temperatures (Melymuk et al., 2016).

Free dissolved water concentrations of analytes in PWS were calculated from amounts accumulated in SRs using the exponential uptake model described in Smedes (2007). The required sampling rates were estimated by fitting performance reference compounds 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 OCPs and 0.0003-0.037 pg L^{-1} for PBDEs (SI, Table S2). Site specific LOQs were 1–10 pg L^{-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 pg L-1 for α-HCH) and 0.01–0.11 pg L^{-1} for PBDEs (but 0.59 pg L^{-1} for BDE209).

2.4 Vertical gradients of trace organics' concentration in air

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

Three standard deviations of field blank concentrations are considered as the absolute uncertainty of concentration measurements, c, and twice that much as the uncertainty of concentration differences, Δc_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).

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:

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

with gas-phase concentration c_a (ng m^{-3}), dissolved aqueous concentration c_w (ng m^{-3}), universal gas constant R (Pa m^3 mol^{-1} K^{-1}), and both sea surface temperature (SST or~~),~~ T_w~~,~~(K)) and ~~both T_w and~~ salinity corrected Henry's law constant $H_{Tw,salt}$ (Pa m^3 mol^{-1}; see S1.1 for details), and air temperature T_a (K). T_a was adopted from the on-site measurement (see above). c_w is derived as the average of the results at two localities, 2 replicas each (see above, 2.1). SST data, measured on the sampling day and in the area, were downloaded from respective database (see S1.4 for details). Air and water sampling was not totally in phase: sampling in air was over 12 days (2-13 July), while SR exposure was during 28 days (3-30 July) i.e., collection was done 10 days after air sample collection. Consequently, for those substances which are quickly equilibrated (within a few days) in PWS i.e., HCH and 3-ring PAHs, no simultaneous measurement in air and water was done (see section 2.1). Although the seawater concentrations of HCH and 3-ring PAHs might have been stable over 28 days, no such 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 uncertainty of the Henry's law constant, $H_{Tw,salt}$, and measured concentrations and

temperature changes during sampling (e.g., Bruhn et al., 2003; Castro-Jiménez et al., 2012). Substance property data are taken from the literature (SI, Table S1). This conservative uncertainty margin is also adopted here, while $f_a/f_w > 3.0$ indicates net deposition and f_a/f_w <0.3 net volatilisation.

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 state zero-dimensional model of intercompartmental mass exchange (Lammel, 2004; Mulder et al., 2014) in order to test the hypothesis that the diurnal variation of contaminant concentrations in air during a period of on-shore advection of one air mass is explained by the combination of volatilisation from the sea surface and atmospheric mixing depth, while 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 ordinary differential equations that solve the mass balances for the two compartments, namely the atmospheric marine BL and seawater surface mixed layer. Processes considered in air are dry (particle) deposition, removal from air by reaction with the hydroxyl radical, and air-sea mass exchange flux (dry gaseous deposition), while in seawater export (settling) velocity, deposition flux from air, air-sea mass exchange flux (volatilisation), and degradation (as first order process) are considered. Input parameters are listed in the SM, Table S3.

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 (gaseous only), c_{day}/c_{night}, was 0.67 (0.54-0.85) for ACE, while c_{day}/c_{night} it ranged wider, 0.25-3.35, was c_{day}/c_{night} = 1.4-1.55 for PHE, FLT and PYR, with mean values of c_{day}/c_{night} = 1.41-1.53. 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 driven volatilisation from surfaces overcompensating for photochemistry (Lee et al., 1998; Tsapakis and Stephanou, 2007). For chlorinated substances, we find mean $c_{day}/c_{night} < 1$, namely 0.56-0.66 for HCH isomers, and 0.68-0.945 for PCBs and DDE, while the individual values range 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) 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 results in night-time accumulation. Diel variation~~This~~, apart from mixing, is related to advection and air-sea mass exchange and studied in more detail in Section 3.2~~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, Fig. 2; PYR: mostly downward~~,~~; Fig. S4a~~5~~). 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 di~~e~~urnal variation of contaminant concentrations in air and, particularly, the night-time accumulation 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 (upward flux, Fig. 2) and PCB28 (Fig. 2), as well as of PYR during 1 night (~~night-time upward fluxes~~Fig. S4a; 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 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. Diel variation of PCB52 air-sea exchange flux direction is well reflected by the model (Fig. S4b). This trend is most significant for the HCH isomers for which a stronger volatilisation flux from the 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

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_c, of HCH during night than during
363 day, caused by a slightly lower sea surface temperature, may have caused $c_{day}/c_{night} < 1$ in
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.

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 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 frequency, as found here. Implicitly, dry deposition is difficult to budget. However, fluctuation may also occur in response to seasonal trends: In summer 2010 FLT and PYR were found close to phase equilibrium in the eastern Mediterranean, while retene (RET) was found mostly volatilisational. A model simulation had revealed that seasonal primary emissions and subsequent deposition of RET (from open fires in the region) are triggering seasonal flux reversal, which over many weeks, however, is fluctuating with a high frequency (< 24 h). (Mulder et al., 2014) Obviously, longer observations are needed to assess the prevailing vertical flux direction. Extrapolation of the observations to annual fluxes is not justified, as day/night fluctuations may be part of a more complex temporal pattern. The seawater surface as secondary source of pollution should be assessed based on flux measurements during several seasons and over longer time periods.

3.4 Quantification of vertical fluxes of gaseous contaminants

Vertical fluxes, F_c, can be quantified for periods with transfer velocity, v_{tr}, determined, which 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 parameter was 70%, however, i.e., satisfying time coverage of sampling intervals was achieved during 14 out of 20 sampling intervals, 11 days (by average 5.5 cm s^{-1}) and 3 nights (by average 3.5 cm s^{-1}) (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±7.0 µg m^{-2} d^{-1}), 8 upward (ranging F_c = 0.8±0.6 µg m^{-2} d^{-1}) and insignificant ($|F_c| < (0.7±0.7)$ µg m^{-2} d^{-1}) in 13 cases.

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

$$v_{dep} = -F_c / c_g \quad (3),$$

this corresponded to a mean deposition velocity for gaseous PHE of v_{dep} = 0.0043±0.0031 cm s^{-1}, 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^{-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 (1 standard deviation criterion).

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 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).

3.5 Particulate phase concentrations and total deposition

Only PAHs and PBDEs were found exceeding LOQ in the particulate phase. Their day-night variation was minimal (Table S3a, b), by average c_{day}/c_{night} = 0.90-1.18 for particulate PAHs, 1.03 and 1.07 for the PBDEs. This supports the perception that particulate PAH is not attacked by the hydroxyl radical, but 'shielded' by the particle matrix (e.g. Zhou et al., 2012). 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. While c_{day}/c_{night} = 1.20 and 1.37 for gaseous PBDEs suggests volatilisation from ground during the day, the absence of $c_{day}/c_{night} > 1$ for the particulate phase may indicate that the species are not in gas-particle phase equilibrium. This has been pointed out based on previous PBDE measurements in the region (Cetin and Odabasi, 2008). However, the data set 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, $F_{p\ dep}$, can be estimated based on

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

with v_{dep} being determined by particle size and wind speed and c_p determined close to the sea 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 in the submicrometer range (Lipiatou and Saliot, 1991), also during the measurements reported here (own, unpublished data measured simultaneously). For particles of 0.5 µm aerodynamic size $v_{dep} \approx 0.1$ cm s^{-1} can be expected for the mean wind velocity at Selles Beach, i.e. 5 m s^{-1}~~. Actually, v_{dep} is not very sensitive to wind speed for this particle size range.~~ (Slinn and Slinn, 1980). Adopting $v_{dep} = 0.1$ cm s^{-1} would suggest $F_{p\ dep} \approx$ -0.023, -0.016 and -0.010 µg m^{-2} d^{-1} for PHE, FLT and PYR (c_p = 0.26, 0.19 and 0.11 ng m^{-3}, 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 deposition of PHE was negligible ($F_{cp\ dep} \approx 1000 \times F_{p\ dep}$; F_c = -26 µg m^{-2} d^{-1}) and $F_{p\ dep}$ negligibly compensated for net-volatilization of FLT and PYR in diffusive air-sea exchange (F_c = +0.91 and +0.79 µg m^{-2} d^{-1} for FLT and PYR, respectively). The values of v_{dep} integrated over the entire size spectrum may differ considerably from values of v_{dep} for MMD (Ruijgrok et al., 1995). Furthermore, the mass median diameter of the semivolatile PAHs FLT and PYR might well be larger than 0.5 µm as a consequence of redistribution in the aerosol along transport. However, even then, particle deposition is unlikely to~~could not~~ have significantly compensated for net-volatilization, as even for ~~for 1 µm~~ particles grown to 1.5 µm $F_{p\ dep}$ would be higher by not more than~~approximately~~ a factor of 10~~3~~ (Slinn and Slinn, 1980). For PHE, FLT and PYR $F_{p\ dep}$ = -0.021, -0.018 and -0.009 µg m^{-2} d^{-1}, respectively, were determined experimentally at Finokalia Observatory in 2001 (mean of 25 weeks between March and October; Tsapakis et al., 2006). This means that within measurement uncertainties the particle deposition fluxes found in 2012 are the same 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 $F_{p\ dep}$ = -0.010- -0.015 µg m^{-2} d^{-1} for the same PAHs based on assuming $v_{dep} \approx 0.2$ cm s^{-1} (Castro-Jiménez et al., 2012).

A similar calculation ~~of~~ for the BDEs for one day-time sampling interval (c_p = 0.16 and 0.20 ng m^{-3} for BDE47 and BDE99, respectively, 6 July for which F_c was determined, Table S5b) suggests that the contribution of $F_{p\ dep}$ to dry deposition of BDE47 was negligible, too ($F_{\text{~~cp dep~~}} \approx 100 \times F_{p\ dep}$; F_c = +3.0 µg m^{-2} d^{-1}), while no direct comparison can be made for BDE99 ($|F_c| \lesssim 3.8$ µg 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~~close to 1 µm near the sources~~ 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).

Significant vertical concentration differences in the particulate phase, $\Delta c_p/\Delta z > 0$ and $\Delta c_p/\Delta z < 0$, were found. Notably during one day-time and sequential night-time sampling (6-7 July) and during day-time of 9 July all significant gradients determined for particulate phase contaminants were negative, i.e. higher concentrations at the lower level, z_1 (PHE and FLT each 1, PYR 2 cases; PBDEs each 1 case; Table S3), while the opposite gradient was found in other nights and days. Marine aerosol contains organic matter (OM), mostly in the accumulation mode, in particular over biological productive surface waters and under low wind speeds (Gantt et al., 2011; Albert et al., 2012). A considerable part of OM is water insoluble (O'Dowd et al., 2004; Facchini et al., 2008). Hence, the marine aerosol contains traces of POPs, which previously were in either dissolved form or associated with suspended OM. ~~Apart from particle sources at the ground (not relevant here), v~~Vertical particle gradients may be sustained by turbulent diffusion (Pryor et al., 2008). While average wind speed was highest during day-time of 9 July, it was average during 6-7 July. No fluxes can be derived from the gradients determined in this study, downward or upward.

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~~PCB28~~. 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^{-3} concentration range), 3 OCPs, 3 PCBs and 2 PBDEs (in the lower pg m^{-3} 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.

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 addressed might have been hidden by ~~the~~ gaps in the time series of fluxes (limited by the uncertainties of sampling and analysis) or the time resolution (limited by the sensitivity of the analytical method)~~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 dry deposition fluxes and 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).

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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)

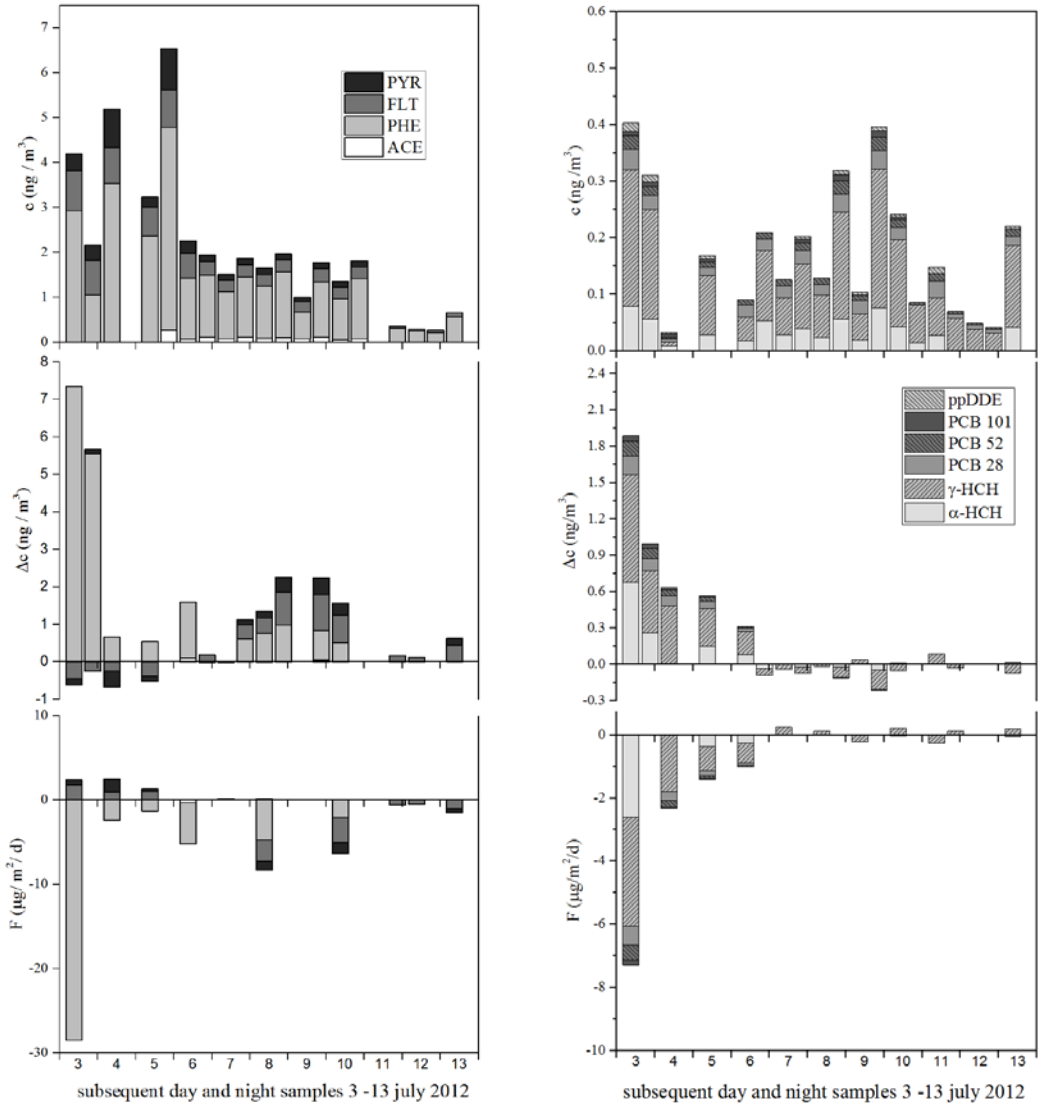
740 Table 2. Concentrations in air (gaseous, ground level, z = 1.05 m, if >LOQ for most samples)
741 (ng m^{-3}, except PBDEs: pg m^{-3}) and surface seawater (pg L^{-1}) and fugacity ratios, f_a/f_w.

	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

742

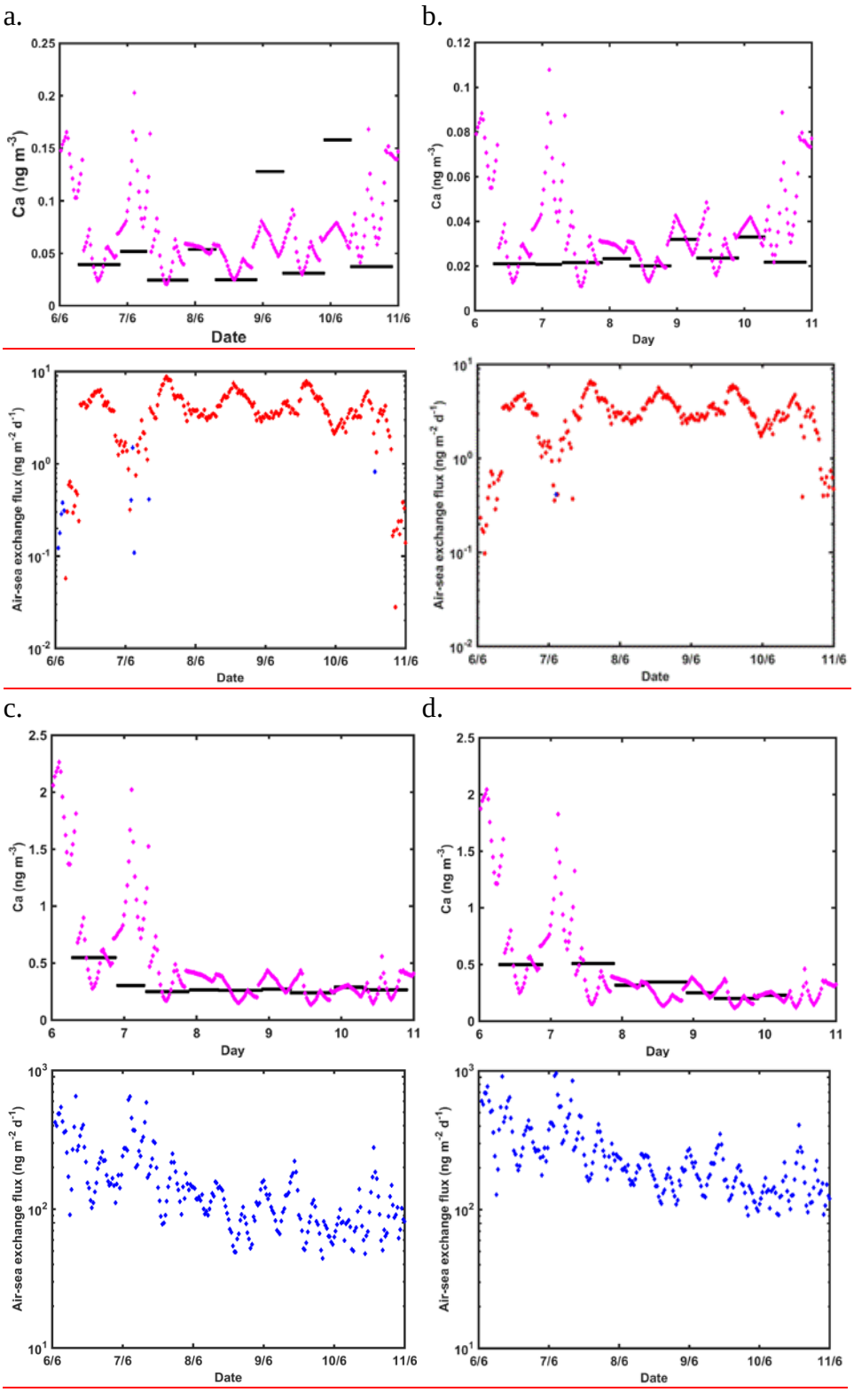
743 Figure captions
744
745 Fig. 1. Gaseous (a) PAH and (b) halogenated substances' concentrations at ground level, z_1 =
746 1.05 m (upper), vertical concentration differences, $\Delta c_z = c_{z2}-c_{z1}$, over Δz = 1.75 m (middle)
747 and vertical fluxes, $F_c = -v_{tr} \Delta c_z$ (positive = upward, negative = downward; lower). Only
748 significant data (exceeding uncertainty thresholds) shown, gaps = no data.
749
750 Fig. 2. Predicted (pink) and observed (black) concentrations (ng m^{-3}) and predicted diffusive
751 air-sea exchange fluxes, F_c, (lower: red upward and blue downward, ng m^{-2} d^{-1}) of selected
752 contaminants, (a) HCB, (b) PCB28, (~~b~~c) FLT and (d~~c~~) BDE47 during 6-10 July 2012.
753

754 Fig. 1
755 a. b.



756
757

Fig. 2.


a.
b.
Ca (ng m-3)
Date
Day
Air-sea exchange flux (ng m-2 d-1)
c.
d.
6/6
7/6
8/6
9/6
10/6
11/6