Semi-volatile organic pollutants in the Mediterranean: long-range atmospheric transport, (photo)chemistry and air-sea exchange

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Abstract

Due to the cycling characteristics (re-volatilisation, phase partitioning) the investigation of persistent organic pollutant (POPs) in the atmosphere requires a methodological approach which goes beyond the one established for the investigation of conventional air pollutants. This thesis presents methods for data analysis and numerical modelling tools suitable for the investigation of POPs transport on regional scales in the lower troposphere and their application to experimental data and model output. Meteorological and chemical data was extracted from data sets of two campaigns, the RV Urania cruise in the central and eastern Mediterranean sea, in summer 2010, and a campaign including five sites around the Aegean Sea in summer 2012.

With data from the first campaign, three gas-particle partitioning models could be tested and were found to underestimate for four selected polycyclic aromatic hydrocarbons (PAHs): benzo(a)anthracene, triphenylene, chrysene, benzo(b)fluoranthene. Fugacity ratios and vertical fluxes were estimated for three different PAHs: fluoranthene (FLT), pyrene (PYR), retene (RET). While FLT and PYR were found close to equilibrium, RET was net-volatilisation in a large sea region. Regional fire activity records in combination with 2-box model simulations quantifying diffusive air–sea mass exchange suggest, that the seasonal depositional input of retene (from biomass burning) into the surface waters during summer is followed by an annual reversal of air–sea exchange. Future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air–sea exchange.

The central and eastern Mediterranean is known as a receptor area for persistent organic pollutants (POPs) emitted in western, central and eastern Europe, particularly during summer. Analyses of long-range transport provided information on the significance of sources, and enabled estimation of photochemical degradation of PCBs between a source and a receptor location. Predictions of photochemistry of PCBs and PBDEs during transport from continental sources to the open sea agreed very well with the observations in some cases, but overpredicted in others. The two gas-particle partitioning models tested for PCBs mostly underpredict partitioning to the particulate phase.

From the second campaign, data of the Lagrangian field experiment was used to test the developed Lagrangian travelling box model i.e., a box model coupled to a Lagrangian particle dispersion model, FLEXPART-WRF. Concentration changes during 7 transport episodes studied were found to be dominated by dilution. Three reactivity schemes were tested for the transformation of the parent PAHs fluoranthene and pyrene (FLT, PYR) into their derivatives 2-nitrofluoranthene and 2-nitropyrene (2NFLT, 2NPYR), respectively. It is found that the chemical kinetic data do capture photochemical degradation of the 4-ring PAHs under ambient conditions on the time scale of hours to one day, while the corresponding NPAH production is by far underestimated. Observed levels can be explained, if kinetic data uncertainties related to the OH-adduct are explored by means of a theoretically based estimate.

The presented data analysis methods and numerical modelling tools enhance the investigation of POPs transport and transformation on regional scales. Underestimations of observations, challenge the applicability of theoretical chemistry in simulated ambient conditions.
Abstrakt

Kvůli specifickým vlastnostem (cyklické vypařování, fázové rozdělování) vyžaduje výzkum persistentních organických polutantů (POPs) využití metodiky, která překračuje tradiční modely atmosférického znečištění životního prostředí. Tato disertační práce prezentuje metody analýzy dat a numerické modely vhodné pro výzkum transportu POPs na regionální úrovni ve spodní vrstvě troposféry včetně jejich použití na experimentálních data. Meteorologické a chemické údaje byly shromážděny ze dvou kampaní, první z plavby RV Urania ve středním a východním Středozemním moři v létě 2010 a druhé z pěti míst v okolí Egejského moře v létě 2012.

Na datech z první kampaně bylo možné testovat tři modely rozdělování plyn-částice a bylo zjištěno, že podhodnocovaly výsledky čtyř polycyklických aromatických uhlovodíků (PAHs): benzo(a)anthracen, triphenylen, chrysen a benzo(b)fluorantén. Poměry fugacity a vertikální tokby byly určeny pro tři PAHs: fluorantén (FLT), pyren (PYR) a reten (RET). Zatímco FLT a PYR se blížily rovnovážnému stavu, RET se znovu vypařoval napříč rozlehlou mořskou oblastí. Zaznamen�� o regionálních požárech spolu se simulací toku difuzní výměny hmoty pomocí krabicového modelu vzduch-moře naznačily, že sezónní ukládání RET (ze spalování biomas) do povrchových vod v l�tě je následov�no ka��doročn�� zp��tnou v��m��nou vzduch-mo��. Budoucí klesající emise nebo sezónní variabilita lokálních zdroj�� h mohly zapo��nit, �e m��b� se stalo sekund��rn��m zdrojem PAH kv��li zp��tn�� difuzn�� v��m��n� vzduch-mo��.

Je zn��mo, �e cen��ln� a v��chodn�� St��domo�� je p��jemcem POPs emitovan��ch, zvl��at v l�t�, ze z��pn��, v��chodn�� a st��dn�� Evropy. Anal��za d��lkov��ho transportu poskytila informace o signifikanci zdroj�� a umo��nila odhad fotochemick�� degradace polychlorovan��ch bifenylov�� (PCBs) mezi zdroji a m��zь pr��jimu. Predikce fotochemick��ch d��j�� pro PCBs a polybromovan��ch dietyl��ter�� b��hem transportu z kontinent��ln��ch zdroj�� na otev��en�� mo�� v n��kter��ch pr��padech velmi dob�� odpov��dala m��r��m hodnotm, ale v jin��ch v��sledky nadhodnocovala. Oba dva modely rozd��len�� plyn-�t��cie testovan�� pro PCBs v��t��nou podhodnocovaly tendenci polutant�� k v��skytu v pevn�� f��zi.

Ve druh�� kampani byla vyu��ta data z lahrangeovsk��ho ter��nn��ho experimentu. Data byla testov��na vyvinut��m lahrangeovským krabicov��m modelem cestov��n� tj., krabicov�� model dopln��ny o lahrangeovsk�� model rozptylu t��tice, FLEXPART-WRF model. Hlavn�� vliv na zm��hy koncentr�� b��hem transportu bylo z��edov��n��. T�� reak��n schmata byla testov��na pro transformac�� PAHs, konkr��tn�� FLT a PYR, na jejich nitro deriv��ty 2-nitrofluoranteni a 2-nitropyren. Uk��halo se, �e chemick� kinetick�� data dob�� zachycuj�� fotochemickou degradaci PAHs se ch��rmi j��dy za standartn��ch podm��nek v �asov��m rozsahu hodin a�� jednoho dne, zat��mco odpov��d��j�� produkce nitro deriv�t��h PAHs je jimi v��znan�� podhodnocen��. Pozorovan�� hladiny mohou b��t vysv��len��, pokud nejistoty kinetick��ch dat souvisej�c�� s OH aduky o��et��me pomoc� teoreticky odvozen��ch odhadu.

Prezentovan�� anal��za dat a numerick�� modelov��ny vylep��ly v��zkum transportu POPs a jej�� transformac�� na region��ln�� �rovni. Podhodnocen�� pozorov��n� vyb��z k p�ezkoum��n�� pou��itelnosti teoretick��ch poznatk�� chemie v simulovan��ch standartn��ch podm��nkách.
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List of acronyms and symbols

2NFLT      2-nitrofluoranthene
2PYR       2-nitropyrene
\( a_{\text{atm-BC}} \) available surface of atmospheric BC
\( a_{\text{soot}} \) available surface of diesel soot
BAA        benzo(a)anthracene
BBF        benzo(b)fluoranthene
BC         black carbon
c\(_a\)     gas-phase air concentration
c\(_{\text{bulk}}\) bulk seawater concentration
c\(_{\text{DOC}}\) dissolved organic carbon concentrations
c\(_g\)     gas-phase air concentration
CHR        chrysene
c\(_j\)     constant in Junge–Pankow model
c\(_{\text{NPAH}}\) NPAH concentration in air
c\(_{\text{PAH}}\) PAH concentration in air
c\(_p\)     gas-phase air concentration
c\(_{\text{POC}}\) particulate organic carbon concentrations
c\(_{\text{TSP}}\) concentration of total suspended matter
c\(_w\)     seawater concentration
DDT        dichlorodiphenyltrichloroethane
D\(_{\text{H2O,air}}\) diffusivity of H\(_2\)O in air
D\(_{\text{air}}\) diffusivity of substance i
ECMWF      European Centre for Medium-Range Weather Forecasts
f\(_z\)      fugacity from air
f\(_{\text{aw}}\) diffusive air–seawater gas exchange flux
F\(_{\text{dep}}\) particulate phase deposition flux
FLEXPART   FLEXible PARTicle dispersion model
FLEXPART-WRF FLEXible PARTicle dispersion model version that reads in data from the Weather Research and Forecasting (WRF) model
FR         fugacity ratio
F\(_{\text{sea_PAH}}\) diffusive gas exchange flux with the sea surface in LBM
f\(_w\)      fugacity from water
GC         gas-chromatography
GFAS       Global Fire Assimilation System
HCB        hexachlorobenzene
HCH        hexachlorocyclohexane
h\(_{\text{f}}\) flux layer height for F\(_{\text{sea_PAH}}\)
h\(_{\text{mix}}\) mixing depth in atmosphere
H\(_{\text{Tw,salt}}\) water-temperature- and salinity-corrected Henry’s law constant
HYSPLIT    HYbrid Single-Particle Lagrangian Integrated Trajectory
j          photolysis rate coefficient of NPAHs in the particulate phase
k\(_N\)     reaction rate coefficient is reaction N
k\(_s\)     mass transfer in air
k\(_{\text{dep_PAH}}\) dry particle deposition rate coefficient
k\(_{\text{all}}\) pseudo reaction rate coefficient for in-parcel dilution
k\(_{\text{DOC}}\) partition coefficient for sorption to dissolved organic carbon
k\(_{\text{NPAH}}\) second order rate coefficient for chemical degradation of NPAHs in the gas-phase
K\(_{\text{OA}}\) octanol air partitioning coefficient
\begin{itemize}
  \item $k_{oc}$ degradation rate in seawater
  \item $k_{al}$ air–water gas exchange mass transfer coefficient
  \item $K_p$ gas-particle partitioning coefficient
  \item $K_{pOC}$ partition coefficient for sorption to particulate organic material
  \item $K_{SA}$ soot air partitioning coefficient
  \item $K_w$ mass transfer in water
  \item LBM Lagrangian box model
  \item LOQ limit of quantification
  \item LRT long-range transport
  \item MATCH Eulerian Multiscale Atmospheric Transport and Chemistry model
  \item MS mass-spectrometry
  \item N number of particles in grid cell
  \item NO$_3$ nitrate
  \item NPAHs nitro polycyclic aromatic hydrocarbons
  \item O$_3$ ozone
  \item OC organic carbon
  \item OCPs organochlorine pesticides
  \item OH hydroxyl radical
  \item OM organic matter
  \item $p^*$ sub-cooled liquid vapour pressure
  \item PAHs polycyclic aromatic hydrocarbons
  \item PBDEs polychlorinated dibenzo- \linebreak[0] phe
thers
  \item PCBs polychlorinated biphenyls
  \item PeCB pentachlorobenzene
  \item PM$_{10}$ particulate matter with diameter of less than 2.5 $\mu$m
  \item PM$_{10}$ particulate matter with diameter of less than 10 $\mu$m
  \item POP persistent organic pollutant
  \item R universal gas constant
  \item RET retene
  \item RV research vessel
  \item $S$ aerosol surface concentration
  \item $S_{CCO_2}$ Schmidt number for CO$_2$
  \item $S_{ci}$ Schmidt number for substance i
  \item $T_a$ air temperature
  \item TPH triphenylene
  \item TSP total suspended particles
  \item $T_w$ sea-water temperature
  \item $U_{10}$ wind speed at 10 m
  \item $\nu_{dep}$ deposition speed
  \item $\nu_{exp}$ export (settling) velocity in seawater
  \item $\gamma_i$ yield of substance i
  \item $\Theta$ particulate mass fraction
  \item $\rho_{oct}$ density of octanol
\end{itemize}
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1. Introduction

The atmosphere plays an important role in the transport, chemical transformation and seawater surface exchange of chemicals. Studying these topics is vital to interpret observations, both episodes (such as campaign-based) and long-term trends (monitoring stations). The transport and dilution can be estimated using, for example, computed trajectories (paths of travelling air parcels). To study chemical transformations along transport concentration fields of relevant oxidants can be extracted from global or regional atmospheric transport and chemistry models. Subsequently, concentrations can be interpolated to parcel positions. The gas exchange between the atmosphere and the water surface is especially relevant when studying seasonal variations.

Among the semi-volatile organic pollutants, the persistent organic pollutants (POPs) are organic chemicals that remain intact for exceptionally long periods of time, they bio-accumulate, are toxic and prone to long-range transport. The atmosphere plays an important role in distribution of POPs over the globe. Many POPs are ubiquitous in the environment, and cycle between air, land surfaces (including biota), seawater (including biota) and ice (UNEP, 2003). Polycyclic aromatic hydrocarbons (PAHs) are often included in this group, although only a sub-group of this substance class is persistent and bio-accumulative. Many pollutants are covered by international conventions, like the Stockholm Convention (UNEP, 2001) and UNECE Convention on Long-range Transboundary Air Pollution (CRLTAP) (UNECE, 1998).

In this thesis, the following substances will be covered: polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenylethers (PBDEs) and PAHs. The main sources of PAHs are incomplete combustion processes, from power plants to traffic (Keyte et al., 2013). The primary sources of the banned PCBs are transformers and capacitors; by now the majority of them are removed and the significant sources are secondary (e.g. polluted soils; Lammel and Stemmler, 2012). The sources of the banned OCPs are also mostly secondary. PBDEs are flame retardants, leaching out of consumer products such as plastics, textiles, electronics, synthetic building materials, waste (water) and waste (water) processing (de Wit, 2002; Besis and Samara, 2012) and, as waste is internationally traded, are subject to technospheric long-range transport, too (Breivik et al., 2016).

Due to the cycling characteristics (re-volatilisation, phase partitioning) the investigation of persistent organic pollutants (POPs) in the atmosphere requires a methodological approach which goes beyond the one established for the investigation of conventional air pollutants. A considerable amount of research has been conducted on the transport of conventional air pollutants in Europe, as well as the spread of emissions, effectiveness of sinks and physical and chemical removal processes. However, there are still many unanswered questions concerning POPs.

Computing the long-range transport (LRT) of air parcels is a valuable method to explain the varying concentrations at sampling sites (Dvorská et al., 2009). It can provide information on the significance of source contributions (Eckhardt et al., 2009), and enables estimation of photochemical degradation between a source and a receptor location. To increase our understanding of POPs prone to LRT and cycling in the marine environment, there is the need to identify air mass origins and potential source areas influencing the samples.

During transport, PAHs and PCBs can be degraded by photo-oxidants like the hydroxyl radical (OH) (Finlayson-Pitts and Pitts, 2000; Keyte et al., 2013; Mandalakis et al., 2003), while PBDEs can be photolyzed directly (Raff and Hites, 2007). To study this in the field, observations are needed at (at least) two locations downwind from each other, preferably with no significant sources in between. Then, at the receptor site, the modelled and observed concentrations can be compared and the
selected degradation methods evaluated. To this end a Lagrangian box model (LBM) is developed that simulates the chemical and physical sinks (and production of PAH derivatives) along transport. Subsequently, it is applied to selected transport episodes from Izmir (West Turkey) to Finokalia (Crete, Greece).

The Eastern Mediterranean is a unique area to study atmospheric chemistry. Adveected air pollutants from Central, Eastern and occasionally Western Europe provide a background air concentration of mixed origin, including degradation products (Lelieveld et al., 2002). In addition, source areas surrounding the Aegean Sea are significant contributors such as the Athens, Istanbul and the Izmir area (Kanakidou et al., 2011). Besides affecting human health and main land environment, significant lipophilic and bioaccumulation contribute to POPs being a hazard to the marine environment (e.g. Lipiatou and Saliot, 1991; Borgà et al., 2001; Borgà et al., 2004).

Air sea exchange of pollutants is relevant in areas where pollutants are delivered downstream or downwind of sources (e.g. Castro-Jiménez et al., 2012 Gigliotti et al., 2002; Lohmann et al., 2011, Nizzeto et al., 2008, Mai et al., 2016). After many years of pollutant levels building up in the sea water or after seasonal depositional input, open water bodies can become a source of pollutants (e.g. Stemmler and Lammel 2009). When both air and water concentrations are known, an estimation of the flux can be made.

For this doctoral study, meteorological and chemical data was extracted from data sets of two campaigns: the RV Urania cruise (summer 2010) and a campaign including five areas around the Aegean Sea (summer 2012). The processes are studied on the so-called regional scale (100-1000 km).

Objectives (research questions)
Overall aim: Development of data analysis and numerical modelling tools suitable for the investigation of transport of semivolatile and long-lived organics on regional scales in the lower troposphere and their application to experimental data and model output.

A. Development and application of a Lagrangian box model
Can we simulate removal (chemical, deposition) and transformation of selected PAHs during (long range) atmospheric transport?

B. Application of air-sea gas exchange (fugacity) modelling tools
Can we explain the suspected volatilisation of open fire markers (PAH: retene) from Mediterranean seawater?

Approach (methods)
A. The development and application of a Lagrangian box model (LBM) is needed to study the physical (wet and dry deposition) and chemical (partitioning, reaction with oxidants) processes of selected PAHs and NPAHSs during transport from a selected source station to a selected receptor station. This requires the adaptation and implementation of substance-specific parameterisations, propagation of input uncertainties and model output interpretation. This model is applied to selected transport paths, over the Aegean Sea.

B. Two methods to assess air-sea gas exchange are applied. The fugacity ratio (FR) provides the direction of the flux. This flux can be quantified as the diffusive air–sea gas exchange mass flux (F_{sea}), simulated using a non-steady state two box model.

Three publications have been prepared as part of this PhD study:


2. Theory and methodology

In order to study the cycling and transport of POPs, knowledge of their characteristics is essential. Here a brief summary will be provided, describing sources, sinks and some physical and chemical properties of the substances studied. Similarly, because this study focuses on transport, transformation and air-sea exchange models, chemical sampling and analyses are not described in detail. Next, a short overview is given of gas-particle portioning models, including the few that are used in this study. These were first tested with observations and later employed in the developed Lagrangian box model (LBM).

Two tools to assess air-sea gas exchange are described. The fugacity ratio (FR) gives the direction of the flux and this flux can be quantified as the diffusive air–seawater gas exchange flux ($F_{sw}$). This flux can be simulated with a non-steady state two box model. The model predicts concentrations by integration of two coupled ordinary differential equations that solve the mass balances for the two compartments.

Two Lagrangian transport models are introduced: HYSPLIT and FLEXPART. Several simulations done for this study are described. Finally, the LBM will be introduced: the selected chemical reaction mechanisms and methods to estimate the gas-particle partitioning, dry deposition and dilution (dispersion). A brief overview will be given of the models providing input variables for the LBM.

2.1 Sources, sinks and physical chemical properties of studied pollutants

Persistent Organic Pollutants (POPs) are organic substances (industrial chemicals, by-products of industrial processes, pesticides), that possess a particular combination of physical and chemical properties such that, they:

- remain intact for exceptionally long periods of time (many years);
- become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air;
- accumulate in the fatty tissue of living organisms including humans, and are found at higher concentrations at higher levels in the food chain;
- and are toxic to both humans and wildlife (UNEP, 2001).

Several international conventions exist to ban and monitor POPs, like the Stockholm Convention (UNEP, 2001) and UNECE Convention on Long-range Transboundary Air Pollution (CRTLAP) (UNECE, 1998). The term POPs can be confusing in the case of poly-cyclic aromatic hydrocarbons, in the sense that many are not very persistent (i.e. could degrade within a few hours after emission). Nevertheless, they are considered POPs, because they meet the other definitions. The Convention on Long-Range Transboundary Air Pollution, the 1998 Aarhus Protocol on Persistent Organic Pollutants and European Parliament and Council Regulation (EC) n°850/2004 of 29 April 2004 are concerned with the following four compounds: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene.

The five groups of pollutant studied in this thesis include:

- Poly-cyclic aromatic hydrocarbons (PAHs)
- Polychlorinated biphenyls (PCBs)
- Organochlorine pesticides (OCPs): Hexachlorobenzene (HCB), pentachlorobenzene (PeCB), dichlorodiphenyltrichloroethane (DDT)
- Polybrominated diphenylethers (PBDEs)
PAHs
Poly-cyclic aromatic hydrocarbons (PAHs) consist of two or more aromatic rings. They are emitted during combustion processes, including power plants, biomass burning and road transport (Finlayson-Pitts and Pitts, 2000); at sea: ship exhaust (Donato et al., 2014; Lamml, 2015). NPAHs are both, emitted primarily by combustion sources and formed in the atmosphere by photo-oxidation processes of parent PAHs with atmospheric oxidants (e.g. O₃, NOₓ, and OH radicals) (Albinet et al., 2007; Keyte et al., 2013; Jariyasopit et al., 2014). PAHs are researched for their toxicity, especially their carcinogenicity (Finlayson-Pitts and Pitts, 2000; Keyte et al., 2013 and references therein). The major transformation products of PAHs are: oxy-PAHs, nitro-PAHs, hydroxyl-PAHs. Nitro- and oxy-PAHs (NPAHs, OPAHs) pose a higher health risk in ambient air than parent PAHs (Yaffe et al., 2001; IARC, 2013). NPAHs have a higher mutagenicity, and hydroxylated PAHs (OHPAHs), a higher cytotoxicity and oxidation potential than PAHs (Hayakawa et al., 2007; Yang et al., 2010).

Most research has been focused on the 16 Environmental Protection Agency (EPA) priority PAHs (i.e. naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), indeno(1,2,3-cd)pyrene (IPY), dibenzo(ah)anthracene (DBA) and benzo(ghi)perylene (BPE)). In the current study, besides these 16, 10 more parent PAHs are included (i.e. benzo(ghi)fluoranthene (BGF), cyclopenta(cd)pyrene (CPP), triphenylen (TPH), benzo(jl)fluoranthene (BJF), benzo(k)fluoranthene (BKF), benzo(e)pyrene (BEP), perylene (PER), dibenz(ac)anthracene (DCA), anthanthrene (ATT) and coronene (COR)) and 1 alkylated PAH, retene (RET). Concerning NPAHs secondarily formed (i.e. during transport), 2NFLT and 2NPyR had been suggested as tracers for air pollution on the timescales of hours to days (Ciccioli et al., 1996; Finlayson-Pitts and Pitts 2000; Keyte et al., 2013).

Vapour pressures are in the range 10⁻⁶–10⁻² Pa, at 298K. Hence, they partition between the gas- and particulate-phase. PAHs are not long-lived in air, with half-lives under ozone and light, of several PAHs range from a few minutes to a few hours (Lammel 2015). However, they can also get absorbed into the bulk of aerosol particles, where they remain shielded from oxidant attack and undergo long-range transport (Zhou et al., 2012; Mu et al., 2018). Like in the air, in water PAHs partition between the aqueous and particulate (colloidal and sinking) phases and may bioaccumulate in marine food chains (D’Adamo et al., 1997; Squadrone et al., 2014). In areas with high concentrations in surface water, after an accumulation period, semivolatile PAHs may re-volatilize from the sea surface (reversal of air–sea exchange; Castro-Jiménez et al., 2012, Lohmann et al., 2011, Gigliotti et al., 2002, Nizzeto et al., 2008).

PCBs
Primary emissions of PCBs, urban emissions from transformers and capacitors, are declining, while the emissions from secondary sources increase: re-volatilization from water, soils, and vegetation (Breivik et al., 2007; Lammel and Stemmmer 2012). Before environmental contamination was discovered in the 60s and 70s, PCBs were produced for about 40 years. Although, production ceased for about 20 years now, PCBs are still detected in many environmental matrices. Studying their gas-particle partitioning is relevant to understanding their cycling in the environment, including long-range transport. Of the 209 possible congeners, in this study only the 7 indicator PCBs are studied: 28, 52, 101, 118, 153, 138, 180. The lifetimes of these vary from 5 to over 700 days (Dvorska, 2008). PCBs can undergo photochemical degradation by the OH radical.

Concerning the production of PCBs in the central and eastern Mediterranean: in Italy, PCBs were produced from 1958 to 1983 with a cumulative production of approximately 31 092 tons (Breivik et al., 2007); in Greece, approximately 400 transformers and 15000 capacitors containing PCBs were still in use in 1993 (Mandalakis et al., 2002). The phasing out process was planned to end in 2005 in Italy, and in 2010 in Greece (CLEEN, 2005).
OCPs
HCB, PeCB and DDT entered the environment mostly as pesticides; there should be almost no primary sources left. Secondary sources are re-volatilisation from land and sea surfaces. This list usually includes Hexachlorocyclohexane (HCH), which is not included here, because it was not quantified in sea water (<LOQ) in the field measurements of the two campaigns. Primary HCB sources included the manufacture of chlorinated solvents, the manufacture and application of HCB-containing pesticides, metal production and the residential sector (Gusev et al., 2007). Because HCB became well distributed in the environment, basically all land use types are secondary sources. PeCB sources include: production and application as pesticide, combustion processes, electrical equipment with PCBs (PeCB reduces PCB viscosity) and as by-product from a variety of industrial processes involving chlorine and carbon (Bailey et al., 2009). In the 1940s, DDT became the most widely used insecticide in the world. In the 1970s, agricultural use was banned in most countries, because of its negative impacts on wildlife. In this study, DDT and its metabolites (o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT) are included.

PBDEs
PBDEs are flame retardants and occur in three technical mixtures: pentaBDE, octaBDE and decaBDE. The penta mix formulation consists of ten isomers dominated by the tetraBDEs BDE47 and BDE99 (> 70 %). The octaBDE contains BDE183 as major congener and the decaBDE consists primarily of the fully brominated BDE209 (la Guardia, 2006). The pentaBDE and octaBDE mixtures were banned by the European Union in 2004, while the use of decaBDE was restricted in 2008 (EU, 2003 and 2008). PBDEs leach out of consumer products (if produced before the ban) such as plastics, textiles, television sets, synthetic building materials, cars and computers (Besis and Samara, 2012); other sources are waste processing and separation, sewage and sludge releases, and landfill leachate (Dannerud et al., 2001). PBDEs can undergo direct photolysis. A wide spectrum of rates is expected, quantified only for few congeners, BDE209 among them (Söderström et al., 2004; Raff and Hites, 2007). The following ten PBDE congeners are covered in this study: 28, 47, 66, 100, 99, 85, 154, 153, 183, 209.

2.2 Gas-particle partitioning

Semi-volatile organics partition between the gas and particulate phases of the atmospheric aerosol, influenced by temperature, particulate phase chemical composition and particle size (Keyte et al., 2013). To obtain the gas-particle partitioning from observations, two parameters can be used. The particulate mass fraction, θ, and partitioning coefficient, Kp, are defined by the concentrations in the two phases:

\[
\theta = \frac{c_p}{(c_p + c_g)} \quad (1)
\]

\[
K_p = \frac{c_p}{c_g} \times c_{TSP} = \theta \times [(1 - \theta) \times c_{TSP}] \quad (2)
\]

with particulate- and gas-phase concentrations, \(c_p\) and \(c_g\), in units of ng m\(^{-3}\); \(c_p\) representing the whole particle size spectrum; and \(c_{TSP}\) representing concentration of total suspended matter.

Most models assume instantaneous establishment of the phase equilibrium (equilibrium models). Depending on the substance class, sorption is considered to be dominated by absorption into organic matter (absorption models), adsorption to the unspecific aerosol surfaces (adsorption model, Junge–Pankow), specifically to soot (for PAHs; Dachs and Eisenreich 2004; Lohmann and Lammel 2004) or both. Their application is, at the same time, a test whether the chosen process is in fact determining the partitioning. Considering more candidate processes on the molecular level, or even all of them
should be superior for prediction of partitioning (Goss and Schwarzenbach 2001). In this study are applied: the adsorption model of Junge–Pankow (Pankow, 1987), the adsorption model of Harner and Bidleman (1998) and the adsorption model of Finizio et al. (1997). Other gas-particle partitioning models, not covered by this study are: the Mackay adsorption model, Pankow absorption model, and a poly-parameter linear free energy relationship (pLFER) model.

The adsorption model of Junge–Pankow uses the vapour pressure of the sub-cooled liquid, \( p_i^0 \); \( \theta = c_i \), \( S/ (p_i^0 + c_i S) \), where \( c_i \) is a constant and \( S \) is the aerosol surface concentration. For the constant \( c_i \), 171 Pa cm was adopted for PAHs (Pankow, 1987), and this same value is used in case of the PCBs. In this study, the \( p_i^0 \), for PAHs is obtained from Lei et al., 2002, and for PCBs from Falconer and Bidleman, 1994. Due to lack of information on the aerosol surface concentration, \( S \), a typical value for maritime aerosols of 4.32 \times 10^{-7} \text{ cm}^{-2} (Jaenicke, 1988) was adopted. Harner and Bidleman (1998) choose for their adsorption model the octanol-air partitioning coefficient, \( \log K_{OA} \), and the fraction of organic matter, \( f_{OM} \), in \( \log K_p = \log K_{OA} + \log f_{OM} \), \(-11.91\). The \( K_{OA} \) used here for PAHs was taken from Ma et al., 2010, and for PCBs from Li et al., 2003. The \( f_{OM} \) was not measured in this study, instead a lower boundary of 16\% (Putaud et al., 2004) and upper (45\%; Spindler et al., 2012) were selected to represent the whole diversity of sites in and around Europe. Finizio et al. (1997) use only the \( K_{OA} \) as the predictor in this relation for PAHs: \( \log K_p = 0.79 \times \log K_{OA} -10.01 \); and this one for PCBs: \( \log K_p = 0.55 \log K_{OA} - 8.23 \).

In the third study, for PAHs, the dual OM absorption and BC adsorption model (Lohmann and Lammel, 2004) is applied. This gas-particle partitioning method is used in the LBM and is described in 2.6.2.

### 2.3 Diffusive air–sea gas exchange calculations

Two parameters that can be used to express air-sea gas exchange. These are the fugacity ratio (FR) and the diffusive air–seawater gas exchange flux \( (F_{aw}, \text{ ng m}^{-2} \text{ day}^{-1}) \). These fugacity calculations are based on the Whitman two-film model (Liss and Slater, 1974; Bidleman and McConnell, 1995). Fugacity is defined as the tendency to escape from a phase (mass diffusion); these tendencies are reflected in the vapour pressures (concentrations).

The FR is defined as

\[
FR = f_a / f_w = C_a R T_a / (C_w H_{Tw, salt})
\]  

with fugacities from air and water \( f_a \) and \( f_w \), 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\(^{-1}\)), water-temperature- and salinity-corrected Henry’s law constant \( H_{Tw, salt} \) (Pa m\(^3\) mol\(^{-1}\)) and air temperature \( T_a \) (K). \( C_w \) can be derived from the bulk seawater concentration, \( C_{bulk} \):

\[
C_w = C_{bulk} / (1 + K_{POC} C_{POC} + K_{DOC} C_{DOC})
\]  

with particulate and dissolved organic carbon concentrations, \( C_{POC} \) and \( C_{DOC} \) and partition coefficient for sorption to particulate organic material, \( K_{POC} \), and partition coefficient for sorption to dissolved organic carbon, \( K_{DOC} \).

When applying the FR, the uncertainty from the Henry’s law constant and measured concentrations need to be considered as follows, values between 0.3 and 3.0 are assumed to not significantly different from the equilibrium condition (e.g. Bruhn et al., 2003; Castro-Jiménez et al., 2012; Zhong et al., 2012). Hence, a \( FR > 3.0 \) indicates net deposition and \( FR < 0.3 \) net volatilisation.
According to the Whitman two-film model (Bidleman and McConnell, 1995; Schwarzenbach et al., 2003), the \( F_{sw} \) can be calculated:

\[
F_{sw} = k_\text{a0}(C_w - C_{a0R}T_w / H_{H2O,salt})
\]

with air–water gas exchange mass transfer coefficient \( k_{a0} \) m h\(^{-1}\), accounting for resistances to mass transfer in both water \( k_w \) m h\(^{-1}\) and air \( k_a \) m h\(^{-1}\), defined as

\[
1/k_a = 1/k_w + RT_a/(k_a H_{H2O,salt})
\]

with \( k_a = (0.2U_{10} + 0.3) \cdot (D_\text{air}/D_{H2O,air})^{0.64} \times 36 \) and \( k_w = (0.45U_{10}^{1.64}) \times (Sc_i/Sc_{CO2}) - 0.5 \times 0.01 \). \( U_{10} \) represents the wind speed at 10 m height above sea level (m s\(^{-1}\)), \( D_\text{air} \) and \( D_{H2O,air} \) are the temperature-dependent diffusivities of substance \( i \) and H\(_2\)O in air, and \( Sc_i \) and \( Sc_{CO2} \) are the Schmidt numbers for substance \( i \) and CO\(_2\) (see Bidleman and Mc-Connell, 1995; Zhong et al., 2012; and references therein). In the current study, the \( U_{10}, T_a, T_w \) and air pressure are taken from the ship-based measurements.

### 2.4 Air–sea mass exchange flux non-steady-state two-box model

The air–sea mass exchange flux can be simulated with a non-steady-state zero-dimensional model of inter-compartmental mass exchange (Lammel, 2004). This two-box model predicts concentrations by the integration of two coupled ordinary differential equations that solve the mass balances for the two compartments, namely the atmospheric marine boundary layer and seawater surface mixing layer.

Several processes are covered by these equations. In this study, processes considered in air include dry (particle) deposition, removal from air by reaction with hydroxyl radicals and air–sea gas exchange flux (net process of dry gaseous deposition and re-volatilisation). Furthermore, in seawater, export (settling) velocity, deposition flux from air, air–sea gas exchange flux and biodegradation (as a first-order process) are considered.

This non-steady state 2-box model was applied to test the hypothesis that seasonal depositional input of RET into the surface waters during the fire season triggers later-on reversal of diffusive air–sea gas exchange. The model simulations were run for the period 2005-2010. The comparison of model output with observations will be discussed for the 12 days the air–sea gas exchange flux could be obtained from observations (from the Urania cruise). The model was fed with the fire-related RET emissions of the whole domain and meteorological parameters of a representative station. The output consists of the gaseous air and seawater concentrations and the diffusive air–sea gas exchange mass flux, \( F_{sw} \).

The atmospheric depositions of the emissions from open fires are assumed to provide the only source of RET in seawater. These are available as daily time series for the eastern Mediterranean domain (28°–45°N, 8°–30°E) obtained from the fire-related PM2.5 emissions as provided by the Global Fire Assimilation System (GFASv1.0; Kaiser et al., 2012) in combination with an emission factor (207 mg RET in PM2.5 (kg fuel burnt)\(^{-1}\); Schmid et al., 2008). These fire emissions are averaged over the whole domain and assumed to disperse within the atmospheric mixing layer only.

Two scenarios are considered, the ‘Initially Estimated Parameter Set’ (IEPS) representing mean values (or estimates) for environmental parameters, and the ‘Upper Estimate Parameter Set’ (UEPS) which
represents realistic environmental conditions that favour seawater pollution. The UEPS contains lower estimates for the atmospheric and seawater mixing layer depths, the degradation rate in seawater ($k_{OC}$), the export (settling) velocity in seawater ($v_{exp}$) and an upper estimate of the of fire-related PM$_{2.5}$ emission flux.

2.5 Trajectory models: HYSPLIT and FLEXPART

Atmospheric trajectory models are widely used to map the air mass flows, by computing the paths that air parcels are predicted to follow (forward simulation) or have followed (backward simulation). For this thesis, two of these models were used.

The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is a complete system for computing simple trajectories to complex dispersion and deposition simulations using either puff or particle (air parcel) approaches (Draxler, 1999). The model uses previously gridded meteorological data; for this study (0.5° x 0.5° resolution, 3-hourly) is used from the Global Forecast System (GFS, NCEP, USA). The HYSPLIT model was applied for only a few samples of the Urania cruise. In order to make the photochemistry estimations, the transport times between locations and boundary layer heights were calculated using trajectories generated by the HYSPLIT model. A backward trajectory was started every 2 h. For boundary layer heights, the average of the 4 hours preceding arrival of the back trajectories was used.

The Lagrangian particle dispersion model, FLEXPART (Stohl et al., 1998, 2005), computes trajectories of a large number of so-called air parcels (or computational particles). In this way, the emission (represented by a large number of particles) from a certain source can be simulated and followed forward or backward in time. The output is the 3D distribution containing positions and meteorological information for all the released particles.

In the case of the first data set, samples from the Urania cruise, the FLEXPART model was used with the meteorological data (0.5° x 0.5° resolution, 3-hourly) from the Global Forecast System (GFS, NCEP, USA). For every sample, particles were released every 6 hours. Each of these releases consisted of 100 000 particles, that were released over a time period of 2 hours (randomly between 0 and 100 m altitude). The particles were followed for 5 days backward in time within a large region (30-60°N/10°W-40°E). As model output, a measure of the time that particles resided in a grid cell (residence time) was chosen.

For the second data set, from the Aegean campaign, three types of atmospheric transport simulations were performed. First, to reveal the large scale air mass histories of the sampled air, the Lagrangian particle dispersion model FLEXPART, with ECMWF meteorological data (0.5°x0.5°, 6-hourly), was run for 5 days backward in time. The output is expressed as 'residence time', a measure of the time the computational particles (fictive air parcels) resided in grid cells. Second, the influence of selected urban sources (Athens, Istanbul, Izmir), on Finokalia (Greece) samples was quantified and presented in Lammel et al., 2017. Third, FLEXPART-WRF (Brioude et al., 2013) was run to select transport episodes and provide input for the LBM.

2.6 Lagrangian box model

The next model that is applied is a Lagrangian box model (LBM). Lagrangian means that the equations are not solved for all the grid cells in a domain (as with Eulerian), but only for the cells a parcel travels through. This results in the avoidance of spatial discretization errors like numerical diffusion and saving of computation time.
The LBM (hourly and 0.2\(^*\times\)0.2\(^*\) resolutions, using the MATLAB software) was written to simulate the chemical and physical degradation processes during the atmospheric transport from a selected source station to a selected receptor station. FLEXPART-WRF was run (with a gas tracer) to select transport episodes between a source and a receptor: events with a sufficiently large number of particles crossing the receptor box.

The LBM contains per selected transport episode between 650 – 1000 selected parcels. These parcels are individual travelling boxes of 1 m\(^3\), only the ones that reach the receptor box are considered i.e., 1.4–2.7% of released FLEXPART-WRF particles. For these parcels the following processes are simulated: chemical degradation of PAHs, formation and photolysis of NPAHs, gas-particle partitioning, stochastic dilution, revolatilisation from the sea surface and gas and particulate dry deposition. Each parcel gets assigned the coordinates and meteorological parameters (T (K), mixed layer depth (M, m)) of a selected particle.

From the FLEXPART-WRF output (the particle dump files) of these selected episodes, the computational particle positions and their meteorological parameters (e.g. humidity, temperature, mixed layer depth) were obtained using the MATLAB software. WRF data (3x3 km\(^2\), 30 minutes) were input and FLEXPART-WRF output was generated hourly. In all simulations, the number of particles released was equal to the number of seconds of release time. This varied from 32400 to 49500 (=9-14 h). Fields of relevant radicals, i.e. oxidants (OH, O\(_3\), NO\(_2\) and NO\(_3\)), and fine particulate matter (PM\(_{2.5}\)) concentrations (\(\mu g/m^3\)) are taken from a simulation with the Eulerian Multiscale Atmospheric Transport and Chemistry model (MATCH; Robertson et al., 1999; Andersson et al., 2015) at hourly and 0.2\(^*\times\)0.2\(^*\) resolutions and theoretical levels 250, 500, 750, 1000, 1250, 1500, 2000, and 3000 m. The simulation covered 31 days (from 1-31 July 2012), for a domain of 29.2\(^\circ\) - 70.8\(^\circ\) N and -25.8\(^\circ\) - 45.8\(^\circ\) E, with the TNO-MACC-II emission data.

The LBM (written in MATLAB, see whole code in Annex IV) consists of 7 modules i.e., (1) Read and pre-process FLEXPART-WRF output; (2) Read MATCH output; (3) Create stochastic dilution fields, (4) Assign oxidant concentrations to particle positions; (5) Generate ODE input parameters; (6) Run the ODE’s; and (7) Post-process output.

The PAH degradation and NPAH formation are calculated by integration of ordinary differential equations (ODEs; Euler forward) as follows:

\[
\frac{dc_{\text{NPAH}}}{dt} = k_{\text{NPAH}} \times c_{\text{OA}} \times (1- \theta_{\text{PAH}}) \times c_{\text{PAH}} - j_s \times \theta_{\text{NPAH}} \times c_{\text{NPAH}} - k_{\text{GL}} \times c_{\text{NPAH}} \tag{7}
\]

\[
\frac{dc_{\text{PAH}}}{dt} = F_{\text{sea,PAH}} / h_s - c_{\text{PAH}} \times (k_{\text{PAH}} \times c_{\text{OA}} \times (1- \theta_{\text{PAH}}) - k_{\text{PAH}} \times c_{\text{PAH}} \times \theta_{\text{PAH}} - k_{\text{dep,PAH}} \times \theta_{\text{PAH}} - k_{\text{GL}}) \tag{8}
\]

Where \(c_{\text{PAH}}\) (molec \(cm^{-3}\)) is the PAH concentration, initialised by the one observed at the source station, the \(k_{\text{NPAH}}\) (\(cm^{-3}\) molec\(^{-1}\) s\(^{-1}\)) is the second order rate coefficient for chemical degradation of NPAHs in the gas-phase, \(j\) (s\(^{-1}\)) is the photolysis rate coefficient of NPAHs in the particulate phase, \(\theta_{\text{PAH}}\) and \(\theta_{\text{NPAH}}\) are the particulate mass fractions of the PAHs and NPAHs, respectively, \(k_{\text{GL}}\) (s\(^{-1}\)) is the stochastic dilution rate, \(F_{\text{sea,PAH}}\) (molec \(cm^{-2}\) s\(^{-1}\)) is the diffusive gas exchange flux with the sea surface (net of re-volatilisation and gaseous dry deposition), \(h_s\) is the corresponding layer height, \(k_{\text{PAH}}\) and \(k_{\text{PAH}}\) (cm\(^3\) molec\(^{-1}\) s\(^{-1}\)) are the first order rate coefficients for PAH degradation in the gas and particulate phases, respectively, and \(k_{\text{dep,PAH}}\) (s\(^{-1}\)) is the dry particle deposition rate coefficient. The choice of \(h_s\) was 30 m (same as reference height for deposition in FLEXPART, see Stohl et al., 2005). Wet deposition is not considered, because no precipitation was recorded during the whole campaign.
2.6.1 Atmospheric chemistry

The photochemical formation of NPAHs is described by the following reactions:

(R1-1) \( \text{PAH}_g + \text{OH} \rightleftharpoons \text{PAOH}_g \)

(R2a) \( \text{PAOH}_g + \text{NO}_2 \rightarrow \text{NPAH} \)

(R2b) \( \text{PAOH}_g + \text{O}_2 \rightarrow \text{products} \)

(R3-3) \( \text{PAH}_g + \text{NO}_3 \rightleftharpoons \text{NPAH} \)

(R4) \( \text{PAH}_g + \text{O}_2 \rightarrow \text{products} \)

(R5) \( \text{NPAH}_g \rightarrow \text{hv} \rightarrow \text{products} \)

with PAH standing for either FLT or PYR and indices g and p denoting gas and particulate phase species, respectively. Subsequent to rapid and reversible addition of OH, the main NPAH-forming reaction (R2a comprises all isomers) is a minor pathway in the parallel reactions of the unstable OH- adduct, PAOH, where \( \text{NO}_2 \) (R2a) and \( \text{O}_2 \) (R2b) and the unimolecular decay of the OH-adduct back to the reactants (R-1) compete with each other (Atkinson and Arey, 2007) and where the \( \text{NO}_2 \)-adduct, formed as an intermediate in reaction (R3), is stabilised by a consecutive reaction with \( \text{NO}_2 \) (Atkinson and Arey, 2007). However, this chemistry, sustaining 2NFLT and 2NPYR is incompletely understood: insufficient experimental kinetic data for the NPAH gas-phase formation and photolysis rates are rather limited: For PAHs, except for several monocyclic aromatics, data on reaction R2a and R2b for the PAHs are available for nitronaphthalenes and methylnitronaphthalenes in the gas phase alone (Phousongsphouang and Arey, 2003; Nishino et al., 2008, 2012) and 1NPYR in solution (García-Berriós and Arce, 2012, see below). In laboratory experiments under high \( \text{NO}_x \) ((48-480)×10^{12} \text{ molec/cm}^3; Atkinson et al., 1990) high NPAH/PAH yields were found i.e., \( \approx 0.5\% \) for 2NPYR, and 3% during the day (OH initiated) and 24% during the night (\( \text{NO}_3 \) initiated) for 2NFLT. These should be lower under ambient \( \text{NO}_x \) conditions. Indeed, values for these yields in the lower % range have been observed: at the remote receptor site studied here, the mean NPAH/PAH yields were 4.1 and 1.6% for PYR and FLT, respectively (Lammel et al., 2017). \( \text{NO}_2 \) between the source and receptor site over the Aegean Sea was in the range 0.2-2.0 ppbv (MATCH model). In very clean air over the South Atlantic we found 1.9% for 2NFLT/FLT (unpublished). In polluted atmospheres in summer, 1.2 and 1.7%, were found on average for PYR and FLT, respectively (Athens, residential site; Marino et al., 2000) and \( \approx 0.1 \) and 1.1%, respectively (Grenoble, urban site; Tomaz et al., 2016).

The chemistry is studied as represented by the current state of knowledge (default scheme). This implies that in lack of kinetic data, data of 1-2 ring PAHs are used, taken as representative for the 4-ring PAHs FLT and PYR. In addition and in order to account for the uncertainties related to sufficient kinetic data, we test two more reactivity schemes, which represent findings from FLT and PYR in laboratory studies under unrealistically high \( \text{NO}_x \) conditions (Atkinson and Arey, 1994, 2007; empirical scheme), and an upper estimate for reactivity with regard to NPAH abundance (upper reactivity scheme). In this latter scheme, theoretical chemistry estimates are used (R2).

Default reactivity scheme:

The \( \text{OH} \)-adduct formed in reaction (R1), reacts under NPAH formation in a second reaction (R2a) with rate limiting \( \text{NO}_2 \) addition (Lin et al., 2015). (R2a) is in competition with degradation by \( \text{O}_2 \) in an irreversible reaction pathway (R2b). Assuming steady state for the adduct concentration, \( C_{\text{PAOH}} \), it holds for the NPAH formation rate \( \frac{dc_{\text{NPAH}}}{dt} \):
\[ k_1 (1 - \theta_{PAH}) \times c_{PAH} \times c_{OH} = (k_{2a} c_{NO2} + k_{2b} c_{D2}) \times c_{PAHOH} \]  
(9)

\[ dc_{NPAH}/dt = k_{2a} c_{NO2} \times c_{PAHOH} \times k_3 c_{NO3} (1 - \theta_{PAH}) \times c_{PAH} - j_5 \times \theta_{NPAH} \times c_{NPAH} \]  
(10)

and with \( c_{PAHOH} \) from (a) replaced in (b), we get for the NPAH chemical source and sink terms:

\[ dc_{NPAH}/dt = k_{NPAH} \times c_{PAH} - j_5 \times \theta_{NPAH} \times c_{NPAH} = [k_1 k_{2a} c_{NO2} c_{OH} \times (k_{2a} c_{NO2} + k_{2b} c_{D2}) + k_3 c_{NO3}] \]  
(11)

\[ \times (1 - \theta_{PAH}) \times c_{PAH} - j_5 \times \theta_{NPAH} \times c_{NPAH} \]

For the formation reaction (R2), in lack of kinetic data for FLT and PYR, data for 1-2 ring aromatics are used. The branching ratio R2a/R2b supporting NPAH formation, however, is rather low, expressed as the NO\(_2\) level, \( c_{1/2NO2} \), where 50% of the PAH consumed by OH are scavenged by NO\(_2\) to form NPAHs, it corresponds to \( c_{1/2NO2} = 1.1-13 \) ppmv for monocyclic aromatics (Johnson et al., 2002; Raoult et al., 2004; Koch et al., 2007; Nishino et al., 2008). The selected rate coefficients are \( k_{2a} = 0.36 \times 10^{-12} \) cm\(^3\) molec\(^{-1}\) s\(^{-1}\) and \( k_{2b} = 1.0 \times 10^{-12} \) cm\(^3\) molec\(^{-1}\) s\(^{-1}\) for both FLT and PYR (Table 1, below). For the NPAH sink term, a high estimate of \( j_5 \) is used i.e., \( 1.3 \times 10^5 \) s\(^{-1}\). 5.0 \( \times 10^5 \) s\(^{-1}\) was reported from reactivity on wood smoke particles (Fan et al., 1996). The relevant aerosol is certainly less reactive than wood smoke particles. Between 10 and 100% of 5.0 \( \times 10^5 \) s\(^{-1}\) was estimated on other aerosol surfaces (García-Berriozabal and Arce, 2012). Good agreement between predicted and observed 2NFLT lifetime was found when assuming \( j_5 (2NFLT) = j_5 (2NNAP) = 1.3 \times 10^5 \) s\(^{-1}\) (Atkinson and Arey, 1994).

Heterogeneous oxidation of PAHs as source of NPAHs is neglected, as these are considered to be far less significant in ambient air (Atkinson and Arey, 1994; Zimmermann et al., 2013).

PAH loss by ozone is considered in the particulate phase only, as the homogeneous reaction is considered to be negligible (Keyte et al., 2013; Finlayson-Pitts and Pitts, 2002).

For the ODE for \( c_{PAH} \), this scheme contains the following equation:

\[ k_{NPAH} \times c_{PAH} = [k_1 k_{2a} c_{NO2} c_{OH} \times (k_{2a} c_{NO2} + k_{2b} c_{D2}) + k_3 c_{NO3}] \times (1 - \theta_{PAH}) \times c_{PAH} \]  
(12)

Empiric reactivity scheme:

For the NPAH source term, \( k_{NPAH} \times c_{PAH} \), we apply the 2NPAH/PAH yields which were observed in the laboratory under high NO\(_x\) conditions and light. These were found to not extrapolate to zero for low NO\(_x\) conditions, which raises some confidence that they might be applicable under ambient conditions (Atkinson and Arey, 1994).

\[ k_{NPAH} \times c_{PAH} = \left( k_1 Y_{OH} c_{OH} + k_3 Y_{NO3} c_{NO3} \right) \times c_{PAH} \]  
(13)

with \( Y_{OH} \) and \( Y_{NO3} \) being the respective yields, 0.5% for 2NPYR, and 3% during the day (OH initiated) and 24% during the night (NO\(_3\) initiated) for 2NFLT (Atkinson et al., 1990). The corresponding sink term for the parent PAHs is \( k_{SPAH} \times c_{PAH} = (k_1 c_{OH} + k_3 c_{NO3}) \times c_{PAH} \).

Note, that these yields reported are not consistent with the above mechanism: the yields according to this mechanism would be given by \( k_{2a} c_{NO2}/(k_{2a} c_{NO2} + k_{2b} c_{D2}) \), which corresponds to 0.003-0.3% for the ambient relevant range of 0.5-50 ppbv NO\(_2\). In contrast, Atkinson and Arey, 1994, found independence of the NPAH yields of c\(_{NO2}\). Consistent with the laboratory data, the photolysis sink term is not explicitly included in this empiric reactivity scheme. At least the yield for the oxidation by OH was observed in the presence of UV light (<400 nm; Arey et al., 1986), hence, at least a significant fraction of \( j_5 \) was included and sustained the yield observed.
Upper estimate reactivity scheme:
An upper estimate of chemically sustained NPAH is explored by replacing some of the kinetic parameters of the default scheme by upper (NPAH sources) estimates. Deviating from the default reactivity scheme, where the values \( k_{2a} \) and \( k_{2b} \) were adopted from experimental data for 1-2 ring aromatics, a higher value for rate coefficient ratio \( k_{2a}/k_{2b} \) is chosen. It is derived from theoretical chemistry: \( k_{2a}/k_{2b} = 3.6 \times 10^6 \), and is in agreement with theoretical prediction (8 \times 10^4 for the benzene adduct; Ghigo et al., 2006). Because of delocalisation over larger aromatic systems favouring the stability of the adduct and preferential interaction with a radical, \( k_{2a}/k_{2b} \) should be considerably higher for the OH adduct of PAHs with more rings. In this chemical reactivity scheme of high reactivity towards NPAH formation, we enhance \( k_{2a} \) and reduce \( k_{2b} \) such as the ratio \( k_{2a}/k_{2b} \) equals the theoretically predicted value for PYR i.e., 5 \times 10^9 (Ghigo et al., 2006). This is applied for both PYR and FLT as no such theoretical estimate is available for FLT.

Table 1 FLT and PYR chemistry kinetic data for 298 K including yield expressions, \( Y_{OH} \times k_3 \) and \( Y_{NO_3} \times k_3 \), for 2NFLT and 2NPYR formation differing in various reactivity schemes.

<table>
<thead>
<tr>
<th>Scheme</th>
<th>FLT and 2NFLT</th>
<th>PYR and 2NPYR</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_{OH} \times k_3 ) ([10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}])</td>
<td>Default 1\times 11^a</td>
<td>1\times 50^a</td>
</tr>
<tr>
<td>Empiric</td>
<td>0.03\times 11^a</td>
<td>0.005\times 50^a</td>
</tr>
<tr>
<td>Upper</td>
<td>1\times 11^a</td>
<td>1\times 50^a</td>
</tr>
<tr>
<td>( k_{2a} ) ([10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}])</td>
<td>Default 0.36^b</td>
<td>0.36^b</td>
</tr>
<tr>
<td>Empiric</td>
<td>Not applied</td>
<td>Not applied</td>
</tr>
<tr>
<td>Upper</td>
<td>373\times 0.36^b,c</td>
<td>373\times 0.36^b,c</td>
</tr>
<tr>
<td>( k_{2b} ) ([10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}])</td>
<td>Default 1.0^d</td>
<td>1.0^d</td>
</tr>
<tr>
<td>Empiric</td>
<td>Not applied</td>
<td>Not applied</td>
</tr>
<tr>
<td>Upper</td>
<td>1.9 / 373^c,d</td>
<td>1.9 / 373^c,d</td>
</tr>
<tr>
<td>( Y_{NO_3} \times k_3 ) ([10^{-27} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}]) (\times c_{NO_2}))</td>
<td>Default 1\times 0.51^e</td>
<td>1\times 1.6^e</td>
</tr>
<tr>
<td>Empiric</td>
<td>0.24\times 0.51^e</td>
<td>0\times 0.51^e</td>
</tr>
<tr>
<td>Upper</td>
<td>1\times 0.51^e</td>
<td>1\times 1.6^e</td>
</tr>
<tr>
<td>( k_4 ) ([\text{ s}^{-1}])</td>
<td>All 0^a</td>
<td>(7 \times 10^4 c_{O_3}/(3 \times 10^{15} + c_{O_3})^f)</td>
</tr>
<tr>
<td>( j_5 ) ([10^3 \text{ s}^{-1}])</td>
<td>Default 0.13^g</td>
<td>0.13^gh</td>
</tr>
<tr>
<td>Empiric</td>
<td>Not applied</td>
<td>Not applied</td>
</tr>
<tr>
<td>Upper</td>
<td>0.13^g</td>
<td>0.13^gh</td>
</tr>
</tbody>
</table>

^a Keyte et al., 2013
^b adopted from the reaction of the naphthalene-OH adduct with NO\(_2\) (Feilig et al., 1999a)
^c enhancement factor 373 corresponds to the rate coefficient ratio \( k_{2a}/k_{2b} = 5 \times 10^9 \), predicted for PYR (Ghigo et al., 2006)
2.6.2 LBM method for gas-particle partitioning

The particulate fraction can be estimated as:

\[ \theta = \frac{K_p \times \text{TSP}}{(K_p \times \text{TSP} + 1)} \]  

(14)

with particle-gas partition coefficient, \(K_p\) (m\(^3\) \(\mu\)g\(^{-1}\)), and total suspended particulates’ concentration (m\(^3\) \(\mu\)g\(^{-1}\)). For the latter, the PM\(_{2.5}\) (\(\mu\)g m\(^{-3}\)) levels provided by the MATCH model ‘extrapolated’ to PM\(_{10}\) (subsequently used as TSP) by using the observed ratio of PM\(_{10}\)/PM\(_{2.5}\) at Finokalia, as follows:

\[ \text{TSP}_{\text{parcel}} = \text{PM}_{10\text{parcel}} = \text{PM}_{2.5\text{MATCH}} \times \frac{\text{PM}_{10}}{\text{PM}_{2.5}} \]  

(15)

For PAHs the dual OM absorption and BC adsorption model (Lohmann and Lammel, 2004) is applied:

\[ K_p = 10^{12} \left( f_{\text{OM}} / \rho_{\text{oct}} \times K_{\text{OA}} + f_{\text{BC}} / \rho_{\text{BC}} \times K_{\text{soot-air}} \times a_{\text{atm-B/BC}} / a_{\text{soot}} \right) \]  

(16)

with the fraction of organic matter \(f_{\text{OM}}\) derived from the observed fraction of organic carbon \(f_{\text{OC}}\) at Urla (ranging: 0.57 – 0.8, see Annex III, SM table S1), \(f_{\text{OM}} = f_{\text{OC}}/0.6\), the density of octanol, \(\rho_{\text{oct}}\), is 0.820 kg L\(^{-1}\) (Keyte et al., 2013), black carbon (BC) properties are approximated by diesel soot i.e., a density of 1 kg L\(^{-1}\) (e.g. Finizio et al., 1997), \(f_{\text{BC}}\) was observed in Urla (ranging: 0.01 – 0.09, see Annex III, SM table S1), \(a_{\text{atm-B/BC}} / a_{\text{soot}}\) is assumed to be 1. \(K_{\text{OA}}(T)\) are given as log \(K_{\text{OA}} = -4.56 + 3985 / T\) and log \(K_{\text{OA}} = -4.34 + 3904 / T\) for PYR and FLT, respectively (Odabasi et al., 2006). \(K_{\text{OA}}(P)\) are given as

\[ \log K_{\text{OA}} [\text{m}^3 \text{\(\mu\)g}^{-1}] = -0.85 \times \log P_i(\text{Pa}) -3.06 - \log(998/a_{\text{soot}}) \]  

(17)

following van Noort (2003), with \(\log P_i(\text{Pa}) = 11.70 – 4164/T\) and \(\log P_i(\text{Pa}) = 12.47 – 4382/T\) for PYR and FLT, respectively (Odabasi et al., 2006; Lei et al., 2002).

For nitro-PAHs (NPAHs), the particulate fraction, \(\phi_{\text{NPAH}}\), is calculated from the observed concentrations in both phases at the selected receptor station (Lammel et al., 2017) and used for all time steps during the transport from the selected source station to the selected receptor station. The inherent uncertainties are expected to not be larger than when predicting \(\phi_{\text{NPAH}}\) based on a gas-particle partitioning model (see Tomaz et al., 2016), because the model input parameters would be uncertain (estimates) and the temperature change during transport was small (ranged 282-306 K, 5-95% ranged 292-303 K).
2.6.3 LBM method deriving a stochastic dilution rate

The dispersion in the FLEXPART model dilutes the cloud of released particles. According to the definition of a Lagrangian model, inside a particle no dispersion or dilution occurs. However, when simulating concentration changes (of $c_{PAH}$, $c_{NPAH}$) in travelling volumes dilution needs to be applied within these parcels. Similar to budgeting in a puff model (e.g., Scire et al., 2000; Tartakovsky et al., 2013), where mass is conserved, while the volume expands, we simulate the loss of mass and keep the volume constant (1 m$^3$). Dilution is approximated as a first order pseudo chemical reaction, recalculated for each time step:

$$-dN/dt = k_{dil} \times N$$

(18)

$$k_{dil} = -\ln(N_t/N_{t-1}) / 3600$$

(19)

with $k_{dil}$ the pseudo reaction rate coefficient in-parcel dilution, $N_t$ the number of particles per grid cell is taken from a pre-generated gridded field (0.1°×0.1°; 45 vertical levels between the surface and 4500 m). $k_{dil}$ is generated per release group of particles, FLEXPART-WRF was set to release particles every 180 seconds. In order to exclude extremes and represent the mean dilution during passage of grid cells, the median over the $k_{dil}$ of parcels within a release group, is assigned to all parcels in that release group. The terms -$k_{dil} \times c_{PAH}$ and - $k_{dil} \times c_{NPAH}$ are, accordingly, included in the ODEs equ. (7) and (8), respectively.

2.6.4 LBM method for air-sea gas exchange flux

The diffusive gas exchange flux with the sea surface, $F_{sea,PAH}$ (ng m$^{-2}$ h$^{-1}$), was derived from gradient and micrometeorological measurements during the same campaign (Lammel et al., 2016; Table S5). Accordingly, in the model, air-sea gas exchange i.e., volatilisation and gaseous dry deposition, is only accounted for parcels travelling over sea, below a reference height ($h_{ref} = 30$ m) and during day-time. No volatilisation during night time had been observed (Lammel et al., 2016).

2.6.5 LBM method describing particulate phase deposition

The particulate phase deposition flux is defined as follows:

$$F_{dep} = v_{dep} \times h_{mix}$$

(20)

with $v_{dep}$ from Zhang et al., 2001, following Pryor et al., 2008. The mean wind speed (5.4 m s$^{-1}$ based on 30-min averages; see also Lammel et al., 2016) was used to read the $v_{dep}$ from this literature source (Pryor et al., 2008; Figure 2).
3. Results of data analysis and model evaluations

The first two studies were performed with a data set collected in the summer of 2010 during a shipborne survey in the central and eastern Mediterranean, the cruise of the RV Urania. The first study focuses only on PAHs and covers gas-particle partitioning, estimates of air-sea exchange from observations and simulations of air-sea exchange. The second study covers the long-range atmospheric transport of PAHs, PCBs, OCPs and PBDEs and changes of PCB and PBDE congener patterns during transport. As a third study, chemistry and transport during day and night in a cloud-free atmosphere was simulated by a Lagrangian box model i.e., a box model coupled to a Lagrangian particle dispersion model, FLEXPART-WRF, on a regional scale. Based on a Lagrangian field experiment and modelling, was studied the conversion of the semi-volatile PAHs fluoranthene and pyrene into the 2-nitro derivatives.

3.1 Study 1: Air–sea exchange and gas–particle partitioning of polycyclic aromatic hydrocarbons in the Mediterranean

The Mediterranean Sea is a receptor for polycyclic aromatic hydrocarbons (PAHs). These are primarily advected from combustion sources on land: power plants, biomass burning, road transport, domestic heating (Masclet et al., 1988; Tsapakis et al., 2006; Tsapakis and Stephanou, 2005). Marine sources are only significant near transport routes (ship exhaust). A number of PAHs are semi-volatile (vapour pressures at 298K in the range $10^{-6}$–$10^{-2}$ Pa), consequently they partition between the gas and particulate phases of the atmospheric aerosol. When deposited to surface water, PAHs partition between the aqueous and particulate (colloidal and sinking) phases. The aim of this study was to add insight to the cycling of PAHs in the Mediterranean in summer.

During the cruise of RV Urania in the central and eastern Mediterranean (27 August – 11 September 2010), 15 high volume samples (8-36 h) of both the gaseous and particulate phases were collected. The 23 surface water samples were taken using an active sampling device deployed in water at 1.5m depth.

The mean total (i.e. sum of gaseous and particulate) Σ25 PAHs concentration is 1.45 ng m$^{-3}$ (time-weighted), and ranged from 0.30 to 3.25 ng m$^{-3}$, with ≈8% in the particulate phase. The levels reported in this study in the south eastern Mediterranean are for most substances lower than found in earlier studies (Tsapakis and Stephanou, 2005; Tsapakis et al., 2006; Castro-Jiménez et al., 2012). In seawater, only 3 PAHs could be quantified, with the following mean concentrations: RET = 0.1 (<0.1–0.5; n=12) pg L$^{-1}$, FLT = 0.1 (<0.1–0.3; n=10) pg L$^{-1}$, and PYR = 0.2 (<0.2–0.9; n=7) pg L$^{-1}$. These are comparable to levels found previously in this region (Tsapakis et al., 2003; Tsapakis et al., 2006). All samples were extracted with dichloromethane, then volume was reduced under a gentle nitrogen stream at ambient temperature, and fractionation achieved on a silica gel column (Holoubek et al., 2007; Lammel et al., 2009). Gas-chromatography/mass-spectrometric (GC-MS) analysis was performed on a 6890N GC equipped with a 60m×0.25mm×0.25 μm DB5-MS column (Agilent J&W, USA) coupled to 5973N MS (Agilent, USA). The MS was operated in electron impact positive ion mode with selected ion recording (SIR).

Air mass analyses showed that sampled air had been transported primarily across central Europe, partly across Western Europe. Indeed, maxima of PAH concentrations corresponded with air masses having resided over large urban areas.
For four PAHs, i.e. BAA, TPH, CHR and BBF, three gas-particle partitioning models could be tested. All three models under-predicted $\theta$; with the exception of the Finizio et al. (1997) model for one substance, TPH. The $\theta$ predicted by the JP model provided the best approach to the observed values. Neglect of adsorption to soot, which is not covered by the gas–particle partitioning models tested, certainly contributed to underestimation of $\theta$ (Lohmann and Lammel, 2004).

For a few substances, air-sea exchange could be quantified. The fugacity ratios and vertical fluxes are estimated for FLT, PYR and RET. While FLT and PYR were found close to equilibrium, RET was net-volatilised in most samples. Among the highest fluxes of RET (> 50 ng m$^{-2}$ d$^{-1}$) are some samples with very low FR, < 0.03.

RET is commonly considered as biomarker for coniferous wood combustion; RET volatilisation could be explained by a temporal decrease in wildfires. In the Eastern Mediterranean, the fire season starts in the end of June and ends in early October. Daily time series of the fire-related PM2.5 emissions as provided by the Global Fire Assimilation System (GFASv1.0; Kaiser et al., 2012) were used in combination with an emission factor (207 mg RET in PM2.5 (kg fuel burnt)$^{-1}$; Schmidl et al., 2008). More fire activity was observed during the first half of the Urania cruise; hence, volatilisation could be expected in the second half of the cruise.

The hypothesis that seasonal depositional input of RET into the surface waters during the fire season is followed by reversal of diffusive air–sea exchange is tested by box model runs. Atmospheric deposition of RET in PM$\leq$1.5 was considered to be the only source. Two scenarios are considered, an initially estimated parameter set (IEPS) representing mean values for environmental parameters, and an upper estimate parameter set (UEPS) with realistic environmental conditions favouring seawater pollution.

The simulated diffusive air–sea exchange flux, $F_{\text{ouv}}$, during 2005–2010, initialised by the UEPS is shown in Fig. 1a; and during the observations (cruise of RV Urania, 27 August–9 September 2010) in Fig. 1b. The upward flux is probably an underestimation because non-diffusive emission from the sea surface, such as aerosol suspension from sea spray and bubble bursting, were not included.

![Graph showing simulated diffusive air–sea exchange flux (F_{ouv}) from 2005 to 2010.](image)
Figure 1. Diffusive air–sea exchange flux, $F_{\text{air}}$, of RET (ng m$^{-2}$ d$^{-1}$; downward in blue and upward in red) using the upper estimate parameter set (UEPS) for the eastern Mediterranean (28°–45°N/8°–30°E) (a) model predicted for 1 January 2005–31 December 2010 and (b) model predicted and observed (black) for 27 August–9 September 2010. Hourly mean data filtered against offshore winds. Error bars reflect $C_w < $ LOQ.

The minor deviations compared to the published figure resulted in a better agreement with the observed volatilisation. The model confirms the hypothesis that seasonal depositional input flux of RET into the surface waters during the fire season is reversed. The volatilisation flux is predicted to be smaller in magnitude than the net-deposition flux during the fire season, but correspondingly higher after intense fire seasons. Future negative emission trends or inter-annual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air–sea exchange.
3.2 Study 2: Long-range atmospheric transport of PAHs, PCBs and PBDEs to the central and eastern Mediterranean and changes of PCB and PBDE congener patterns in summer 2010

Most of the legacy POPs enter the marine atmospheric environment by long-range atmospheric transport. Ship emissions and volatilisation near river discharges could be significant solely at a local scale. Besides this, volatilisation could occur in areas after considerable atmospheric deposition causes flux reversal.

The testing of gas-particle partitioning models and the analysis of long-range transport (air mass origins) are helpful to understand the cycling of semivolatile organics including POPs in the marine environment. Analyses of long-range transport provide information on the significance of sources, and enable estimation of photochemical degradation between a source and a receptor location. The objective of this study was to identify pathways and types of emissions (urban, fire) contributing to the pollution of the marine atmospheric environment by semivolatile long-lived organics including POPs and PAHs, and to track the change of congener patterns during LRT. To this end, observations from the ship-borne survey in the central and eastern Mediterranean Sea were combined with results of simulations with a Lagrangian particle dispersion model.

During the RV Urania cruise, 27 August – 12 September 2010, 15 (8-36 h) high volume gas- and particulate-phase air samples of selected POPs and meteorological parameters were collected. Analysis was by GC-MS. The pollutants significantly correlated with each other ($r = 0.57-0.95$, t-test, $p > 0.05$), except for the pair HCB and PBDEs ($r = 0.41$). On average, the decabrominated ether (BDE 209) accounted for 37% and congeners related to pentaBDE for 62% of the PBDEs.

The levels of total (gaseous plus particulate) concentrations were similar throughout the cruise (see Fig. 2). Only the pollutant concentration of the samples #8, #13 and #15 exceeded one standard deviation from the mean concentration of the cruise. These samples were taken at night, when pollutants accumulated in the atmospheric surface layer, due to low wind speed and a shallow atmospheric boundary layer. Besides this, according to air mass analyses, sample #8 captured air that had previously resided over the Aliaga-Izmir industrial area (western Turkey). This sample contained the cruise maximum concentration for most substances (most PCBs, HCB, PeCB, high concentrations of DDX and the highest 28 PBDEs). Sample #15 contains the highest levels of DDX and the concentration levels of the other pollutant groups rank second compared to sample #8. Sample #15 included pollution from the harbour of Palermo (Sicily, Italy).

Most concentrations in this study are lower compared to findings in other studies in the region. Nevertheless, due to different sampling protocols, seasonality of emissions and the variation in air mass origins, a decreasing long-term trend cannot be concluded, although emission reductions might have contributed.

The two gas-particle partitioning models tested for PCBs mostly underpredict partitioning to the particulate phase. However, the lack of composition (e.g. fraction of organic matter) and humidity data, and a possible sampling artefact (underestimated $\theta$; Mandalakis and Stephanou, 2002) limit any conclusions. The particulate mass fraction, $\Theta$, of BDEs with $> 4$ Br atoms, should be lower in air masses recently influenced by emissions. Indeed, in our data set, for BDE209 this was the case for samples influenced by urban air (samples #7-9), compared to the average over all samples.

Long-range transport analysis showed that the large scale advection of the air masses that influenced the samples was mostly across central Europe, partly across Western Europe. According to their pathways, the air masses could be categorized in 5 groups (Fig. 2).
Figure 2. Time series of samples during the RV Urania cruise. Top: temperature (°C), wind speed (m s⁻¹), PM10 (µg m⁻³) and air mass origins (green colour coding); bottom: total concentration (gaseous + particulate) of 25 PAHs (ng m⁻³), 7 PCBs, 8 PBDEs, DDX and HCB (µg m⁻³), with possible urban influence (Urban, grey).

Three sample attributes are considered: night-time sampling, PM₂.₅ and PM₁₀ concentrations and possible urban influence. The effect of night-time sampling (low mixing, eventually leading to high concentrations; samples #8, #13, and #15), was most pronounced for PBDEs. Consequently, local sources were assumed to be more important than LRT, as low wind speeds and a relatively low atmospheric mixing layer prevailed. PM levels were not significantly correlated with most pollutants, except for DDX. The low PM₁₀ level of sample #12 reflects a pathway of the air mass without recent influence from land based emissions. The possible urban influence (air mass passage over a metropolitan area e.g., Athens; samples #7-9 and #15) is reflected in high PCB levels.

Predictions of photochemistry of PCBs and PBDEs during transport from continental sources to the open sea agreed very well with the observations in some cases, but overpredicted in all others. The gas-phase reaction with the hydroxyl radical and the direct photolysis in the particulate phase may provide sinks to PCBs and PBDEs, respectively (Mandalakis et al., 2003; Söderström et al., 2004). This is estimated by comparing observed and predicted PCB and PBDE congener concentration ratios, at the ship’s position. Observed PCB data were adopted for the source areas: Athens, Greece (sample #7), Aliaga-Izmir, Turkey (samples #7-8), and for central Europe (samples #4-6 and #15) from Košetice, Czech Republic. Changes of PCB congener patterns along transport routes are in agreement with the perception that the reaction with the OH radical is dominating PCB atmospheric lifetime.

By combining fire distributions and air mass histories, the significance of the source open fires for RET levels could be confirmed for individual samples. The volatilisation from the sea surface may explain RET enrichment in sample #12. For this sample, the time the air travelled over sea is among the longest, and the total RET among PAHs is among the highest of the cruise. The RET enrichment in samples #5 and #6 may be explained by the potential influence of fire-related RET emissions (this is the product of fire-related PM2.5 mass flux and residence times of air masses).
4 Conclusion and outlook

The overall aim of this study was to develop data analysis and numerical modelling tools suitable for the investigation of semivolatile log-lived organics including POPs’ ad PAHs’ transport on regional scales in the lower troposphere and their application to experimental data. Several models have been tested for gas-particle partitioning, and air-sea gas exchange, and several reactivity schemes for regional transport. Three gas-particle partitioning models could be tested for four selected PAHs. Three air-sea exchange models were applied for one certain PAH. Lagrangian box model is developed to simulate removal (chemical, deposition) and transformation of selected PAHs during (long range) atmospheric transport. The development and application of this Lagrangian box model is needed to study the physical (wet and dry deposition) and chemical (partitioning, reactions with oxidants i.e., OH, O3 and NO3) processes of selected PAHs during transport. Three models to assess air-sea gas exchange were applied: The fugacity ratio provides the direction of the flux. The quantification is the diffusive air–seawater gas exchange flux (F_{seaw}). The long-term trend of this flux is simulated with a non-steady state two box model.

In the first study, the air mass analyses showed that the sampled air had been transported primarily across central Europe, partly across Western Europe; maxima of POPs concentrations corresponded with air masses having resided over large urban areas. For four PAHs, i.e. BAA, TPH, CHR and BBF, three gas-particle partitioning models could be tested. All three models under-predicted the particulate mass fraction θ, the Junge-Pankow model provided the best approach to the observed values. The fugacity ratios and vertical fluxes were estimated for FLT, PYR and RET. While FLT and PYR were found close to equilibrium, retene (RET) was net-volatilisation in most samples. Simulations of air-sea gas exchange of RET confirms the hypothesis that seasonal depositional input flux of RET into the surface waters during the fire season is reversed afterwards. Future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air–sea gas exchange. By combining fire distributions and air mass histories, the significance of the source open fires for RET levels could be confirmed for individual samples. The volatilisation from the sea surface may explain RET enrichment in at least one of the samples. This procedure, of combining sampling and modelling, could in the future be applied to quantify the contribution of revolatilisation of air pollutants to pollutant levels in marine air.

The second study included the testing of gas-particle partitioning models and the analysis of long-range transport (air mass origins) to understand the cycling of POPs in the marine environment. Analyses of long-range transport (LRT) provide information on the significance of sources, and enabled estimation of photochemical degradation between a source and a receptor location. The objective of this study was to identify pathways and types of emissions (urban, open fire) contributing to the pollution of the marine atmospheric environment as POPs, and to track the change of congener patterns during LRT. The two gas-particle partitioning models tested for PCBs mostly underpredict partitioning to the particulate phase. The understanding of photochemistry of PCBs and PBDEs could be tested by (shipborne) field data. Changes of PCB congener patterns along transport routes are in agreement with the perception that the reaction with the OH radical is dominating PCB atmospheric lifetime.

As a third study, chemistry and transport during day and night in a cloud-free atmosphere was simulated by a Lagrangian box model i.e., a box model coupled to a Lagrangian particle dispersion model, FLEXPART-WRF, on a regional scale and over many hours to one day. Concentration changes during 7 transport episodes are found to be dominated by dilution, chemistry or dry particle deposition rank second, while re-volatilisation is found to contribute negligibly. Three reactivity schemes were tested for the transformation of the parent PAHs fluoranthene and pyrene (FLT, PYR) into their derivatives 2-nitrofluoranthenone and 2-nitropyrene (2NFLT, 2NPyR), respectively. A
Lagrangian box model was initialised with observations of PAHs from a source site and the results compared to observations of PAHs and NPAHs at a receptor site. The 'default' reactivity scheme, representing the currently available kinetic data, underestimated the observations drastically. This discrepancy is dominated by a largely underestimated branching ratio of the OH-adduct towards NPAH (in competition with reaction with O₂), which must be higher for 4-ring PAHs. These data are needed to constrain the chemistry of NPAH formation on-going in the remote, but also in the polluted environment. More reactions would be needed to be kinetically quantified in order to predict NPAH formation in the polluted environment (presence of photocatalysts) and cloudy atmosphere (aqueous phase chemistry).
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ANNEX I – Study 1
Air–sea exchange and gas–particle partitioning of polycyclic aromatic hydrocarbons in the Mediterranean

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Abstract. Polycyclic aromatic hydrocarbon (PAH) concentration in air of the central and eastern Mediterranean in summer 2010 was 1.45 (0.30–3.25) ng m$^{-3}$ (sum of 25 PAHs), with 8 (1–17) % in the particulate phase, almost exclusively associated with particles < 0.25 µm. The total deposition flux of particulate PAHs was 0.3–0.5 µg m$^{-2}$ yr$^{-1}$. The diffusive air–sea exchange fluxes of fluoranthene and pyrene were mostly found net-depositional or close to phase equilibrium, while retene was net-volatilisational in a large sea region. Regional fire activity records in combination with box model simulations suggest that seasonal depositional input of retene from biomass burning into the surface waters during summer is followed by an annual reversal of air–sea exchange, while interannual variability is dominated by the variability of the fire season. One-third of primary retene sources to the sea region in the period 2005–2010 returned to the atmosphere as secondary emissions from surface seawaters. It is concluded that future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary PAH source through reversal of diffusive air–sea exchange.

Capsule: In late summer the seawater surface in the Mediterranean has turned into a temporary secondary source of PAH, obviously related to biomass burning in the region.

1 Introduction

The marine atmospheric environment is a receptor for polycyclic aromatic hydrocarbons (PAHs) which are advected from combustion sources on land (power plants, biomass burning, road transport, domestic heating). Marine sources may be significant near transport routes (ship exhaust). Long-range transport from urban and industrial sources on land are the predominant sources of PAHs in the Mediterranean (Masclet et al., 1988; Tsapakis et al., 2003, 2006; Tsapakis and Stephanou, 2005a). A number of PAHs are semivolatile (vapour pressures at 298 K in the range $10^{-6}$–$10^{-2}$ Pa) and, hence, partition between the gas and particulate phases of the atmospheric aerosol, influenced by temperature, particulate-phase chemical composition and particle size (Keyte et al., 2013). Upon deposition to surface water, PAHs partition between the aqueous and particulate (colloidal and sinking) phases and may bioaccumulate in marine food chains (Liptatou and Saliot, 1991; Dachs et al., 1997; Tsapakis et al., 2003; Berrojalbiz et al., 2011). They were also found enriched in the sea-surface microlayer relative to subsurface water (Lim et al., 2007; Guitart et al., 2010). Semivolatile PAHs may be subject to re-volatilisation from the sea surface (reversal of air–sea exchange), similar to chlorinated semivolatile organics (Bidleman and McConnell, 1995), in case high concentrations in surface water were to build up. This has been predicted by multicompartamental modelling for two–four-ring PAHs for polluted coastal waters and also the open ocean (Greenfield and Davis, 2005; Lammel et al., 2009a) and was
indeed observed in coastal waters off the northeastern United States (Lohmann et al., 2011). Field studies in the open sea found net deposition to prevail whenever determined (e.g. Tsapakis et al., 2006; Balasubramanian and He, 2010; Guitart et al., 2010; Castro-Jiménez et al., 2012; Mai, 2012). However, some three–four-ring parent PAHs – among them fluorene (FLN), fluoranthene (FLT) and pyrene (PYR) – were reported to be close to phase equilibrium in the Mediterranean, Black and North seas (Castro-Jiménez et al., 2012; Mai, 2012), and net volatilisation of FLT and PYR was observed in the open southeastern Mediterranean Sea in spring 2007 (Castro-Jiménez et al., 2012).

The aim of this study was to add insights on the cycling of PAHs in the Mediterranean in summer, with a focus on sources and phase partitioning in the aerosol.

2 Methods

2.1 Sampling

Gas- and particulate-phase air samples were taken during the RV Urania cruise, 27 August–12 September 2010 (Fig. S1 in the Supplement). The high-volume sampler (Digi-Tel) was equipped with one glass fibre filter (GFF, Whatman) and one polyurethane foam (PUF) plug (Gumotex Bréclav, density 0.030 g cm$^{-3}$, 50 mm diameter, cleaned by extraction in acetone and dichloromethane, 8 h each, placed in a glass cartridge) in series. Particle size was classified in the particulate phase using high-volume filter sampling ($F = 68$ m$^2$ h$^{-1}$, model HVS110, Baghirra, Prague) and low-volume impactor sampling ($F = 0.54$ m$^2$ h$^{-1}$; Sioutas five-stage cascade; PM$_{10}$ inlet, cutoffs 2.5, 1.0, 0.5 and 0.25 µm of aerodynamic particle size and back-up filter; impaction on quartz fibre filters (QFFs); SKC Inc., Eighty Four, USA; sampler Baghirra PM$_{10}–35$). In total 15 high-volume filter samples, exposed for 8–36 h (230–1060 m$^3$ of air), and 3 low-volume impactor samples, exposed for 5 days, were collected. Water sampling was performed using the stainless steel ROSETTE active sampling device equipped with 24 Niskin bottles (volume of 10 L) deployed in water at 1.5 m depth for surface water sampling.

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

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

<table>
<thead>
<tr>
<th></th>
<th>$n_{LOQ}$</th>
<th>mean (min–max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACE</td>
<td>4</td>
<td>0.025 (&lt;0.020–0.089)</td>
</tr>
<tr>
<td>FLN</td>
<td>10</td>
<td>0.137 (&lt;0.030–0.396)</td>
</tr>
<tr>
<td>PHE</td>
<td>15</td>
<td>0.581 (0.144–1.41)</td>
</tr>
<tr>
<td>ANT</td>
<td>13</td>
<td>0.043 (0.008–0.22)</td>
</tr>
<tr>
<td>RET</td>
<td>14</td>
<td>0.016 (0.006–0.030)</td>
</tr>
<tr>
<td>FLT</td>
<td>15</td>
<td>0.262 (0.053–0.795)</td>
</tr>
<tr>
<td>PYR</td>
<td>15</td>
<td>0.203 (0.044–0.564)</td>
</tr>
<tr>
<td>BAA</td>
<td>15</td>
<td>0.01 (0.001–0.031)</td>
</tr>
<tr>
<td>CHR</td>
<td>15</td>
<td>0.04 (0.012–0.092)</td>
</tr>
<tr>
<td>TPH</td>
<td>15</td>
<td>0.018 (0.007–0.032)</td>
</tr>
<tr>
<td>BBN</td>
<td>11</td>
<td>0.018 (0.001–&lt;0.085)</td>
</tr>
<tr>
<td>BBF</td>
<td>15</td>
<td>0.021 (0.004–0.102)</td>
</tr>
<tr>
<td>BKF</td>
<td>14</td>
<td>0.012 (0.002–&lt;0.085)</td>
</tr>
<tr>
<td>BAP</td>
<td>12</td>
<td>0.015 (0.001–&lt;0.085)</td>
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<tr>
<td>BGF</td>
<td>15</td>
<td>0.021 (0.005–0.067)</td>
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<tr>
<td>CPP</td>
<td>7</td>
<td>0.012 (0.001–&lt;0.085)</td>
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<tr>
<td>BJF</td>
<td>15</td>
<td>0.016 (0.002–0.079)</td>
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<tr>
<td>BAP</td>
<td>14</td>
<td>0.019 (0.004–0.088)</td>
</tr>
<tr>
<td>PER</td>
<td>7</td>
<td>0.012 (0.001–0.1)</td>
</tr>
<tr>
<td>IPY</td>
<td>7</td>
<td>0.022 (0.008–0.094)</td>
</tr>
<tr>
<td>BPE</td>
<td>6</td>
<td>0.02 (0.009–0.085)</td>
</tr>
<tr>
<td>COR</td>
<td>5</td>
<td>0.016 (0.002–0.1)</td>
</tr>
<tr>
<td>Σ25 PAHs</td>
<td>15</td>
<td>1.539 (0.44–4.694)</td>
</tr>
<tr>
<td>Ozone</td>
<td>42 (33–65)</td>
<td></td>
</tr>
</tbody>
</table>

With the aim to characterise the potential influences of ship-borne emissions on the samples, passive air samplers with PUF disks (150 mm diameter, 15 mm thick, deployed in protective chambers consisting of two stainless steel bowls; Klánová et al., 2008) were exposed at five different locations onboard during 16 days. The PAH levels of these samples indicated that ship-based contamination was negligible.

2.2 PAHs analyses and quality assurance

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

The extract was fractionated on a silica column (5 g of silica 0.063–0.200 mm, activated for 12 h at 150 °C). The first fraction (10 mL n-hexane) containing aliphatic hydrocarbons was discarded. The second fraction (20 mL dichloromethane) containing PAHs was collected and then reduced by stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into an insert in a vial. Terphenyl was used as syringe standard; final volume was 200 µL. Gas-chromatographic–mass-spectrometric (GC-MS) analysis was performed on a 6890N GC equipped with a 0.25 mm × 0.25 µm DB5-MS column (Agilent J&W, USA) coupled to 5973N MS (Agilent, USA). The MS was operated in selected ion detection mode with selected ion recording (SIR).

The targeted compounds are the 16 Environmental Protection Agency (EPA) priority PAHs (i.e. naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), indeno(1,2,3-cd)pyrene (IPY), dibenzo(a)anthracene (DBA) and benzo(gi)perylen (BPE)), 10 more parent PAHs (i.e. benzo[ghi]fluoranthene (BGF), cyclopenta(cd)pyrene (CPP), triphenylene (TPH), benzo(j)fluoranthene (BFF), benzo(k)fluoranthene (BKF), benzo(e)pyrene (BEP), perylene (PER), dibenzo(ac)anthracene (DCA), anthanthrene (ATT) and coronene (COR)) and 1 alkylated PAH, retene (RET). The injection volume was 1 µL. Terphenyl was used as the internal standard.

Field blank values, b, were gained from GFFs and PUFs manipulated in the field, as far as possible identical to the samples, except without switching the high-volume sampler on. No QFF field blank was taken for impactor sampling. As no PAHs were detected in the stages corresponding to 2.5–10 µm (all PAHs < limit of detection in all such samples), instead the mean of the values of the QFF substrates of the two uppermost impactor stages (in total six) was taken. The respective b value was subtracted from sample values. The limit of quantification (LOQ) needs to take the accuracy of the blank level into account. Lacking a measure for the variation of the field blank, the relative standard deviation (SD) of field blanks from earlier field campaigns (√σc/bc) on a high-mountain site (high-volume sampling, summer 2007, n = 5; Lammel et al., 2009b) and in the Mediterranean (impactor sampling, summer 2008, n = 6; Lammel et al., 2010a) was used (σ = (√σc/bc) × b). Identical samplers, sampling and analysis protocols for all analytes had been applied. Values below the sum of the field blank value (from this campaign) and three relative SDs of the field blank values (from the previous campaigns) were considered < LOQ (limit of quantification, LOQ = b + 3σ). NAP and ACY were excluded from the data set because of the lack of blank values. The field blank values of most other analytes were below instrument LOQ in high-volume PUF and GFF samples. However, higher field LOQs, up to (6–25) pg m⁻³ (according to sampled volume of air), resulted for ANT, PYR and RET, and up to (45–180) pg m⁻³ for ACE, FLN, PHE and FLT in PUF. Field LOQs of PAHs in impactor QFF samples were below instrumental LOQ for most substances, but in the range (8–15) pg m⁻³ for ACE, ANT and FLT; ~55 pg m⁻³ for FLN; and 120–140 pg m⁻³ for NAP and PHE.

The instrument LOQ, which is based on the lowest concentration of calibration standards used, was 0.5 ng, corresponding to 0.5–2.5 pg m⁻³ for high-volume samples, ~8 pg m⁻³ for impactor samples, 6–10 pg m⁻³ for semivolatile PAHs determined in passive air samples and up to 200 pg m⁻³ for non-volatile PAHs in passive air samples.

Water samples (2–2.5 L) were extracted immediately after their collection using solid-phase extraction on C₁₈ Empore disks using a vacuum manifold device. Disks were stored closed in glass vials in a freezer and transported to the processing laboratory; PAHs were eluted from disks using 40 mL of dichloromethane. The above-listed PAHs were analysed using GC-MS (Agilent GC 6890N coupled to an Agilent single quadrupole MS 5973N operating in electron impact ionisation mode). LOQ was 0.1 ng L⁻¹.

2.2.1 Other trace constituents and meteorological parameters

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

2.3 Models of gas–particle partitioning

The data set (15 high-volume samples of separate gas- and particulate-phase concentrations) is used to test gas–particle partitioning models for semivolatile organics in terms of the organics’ mass size distribution and size-dependent particulate matter (PM) composition. The models assume different processes to determine gas–particle partitioning, i.e. an adsorption model (Junge–Pankow; Pankow, 1987) and two absorption models (i.e. KOA models; Finizio et al., 1997; Harner and Bidleman, 1998). Absorption is into particulate organic matter (OM). Adsorption to soot is a significant gas–particle partitioning processes for PAHs, but no soot data or PM chemical composition data are available. We, therefore, refrain from testing dual-adsorption and absorption models (e.g. Lohmann and Lammel, 2004). Particulate mass fraction, θ, and partitioning coefficient, Kp, are defined by the
concentrations in the two phases:

$$\theta = c_p/(c_p + c_g),$$

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

with PAH particulate- and gas-phase concentrations, $c_p$ and $c_g$, in units of ng m$^{-3}$, $c_p$ representing the whole particle size spectrum; and $c_{\text{TSP}}$ representing concentration of total suspended matter.

Different models describe different processes to quantify differences in ad- and absorption between compounds. The Junge–Pankow (JP) model uses the vapour pressure of the sub-cooled liquid, $p_0^c$, $\theta = c_j S / (p_0^c + c_j S)$ (data taken from Lei et al., 2002); and $c_j$ should be approximately 171 Pa cm for PAHs (Pankow, 1987). The aerosol particle surface concentration, $S$, was not measured, and a typical value for maritime aerosols is adopted instead (4.32 $\times$ 10$^{-7}$ cm$^{-1}$; Jaenicke, 1988). Harner and Bidleman (1998) use the log $K_{\text{OA}}$ and $f_{\text{OM}}$: log $K_p = \log K_{\text{OA}} + \log f_{\text{OM}} = -1.19$; Finizio et al. (1997) use only the $K_{\text{OA}}$ as the predictor (data taken from Ma et al., 2010): log $K_p = 0.79 \times \log K_{\text{OA}} - 10.01$. The range of the fraction of OM used here is based on Putaud et al. (2004) (16% lower limit) and Spindler et al. (2012) (45% upper limit).

### 2.4 Air–sea diffusive mass exchange calculations

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

$$\text{FR} = f_a / f_w = C_o R T_a / (C_w H_{\text{Tw, salt}}),$$

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

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

with particulate and dissolved organic carbon concentrations, $C_{\text{POC}}$ and $C_{\text{DOC}}$, from Pujo-Pay et al. (2011) and $K_{\text{POC}}$ and $K_{\text{DOC}}$ from Karickhoff (1981), Lüers and ten Hulscher (1996), Rove et al. (2009) and Ma et al. (2010). 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, $H_{\text{Tw, salt}}$, and measured concentrations (e.g. Bruhn et al., 2003; Castro-Jiménez et al., 2012; Zhong et al., 2012). This conservative uncertainty margin is also adopted here, while FR > 3.0 indicates net deposition and FR < 0.3 net volatilisation. The diffusive air–seawater gas exchange flux ($F_{\text{aw}}$, ng m$^{-2}$ day$^{-1}$) is calculated according to the Whitman two-film model (Bidleman and McConnell, 1995; Schwarzenbach et al., 2003):

$$F_{\text{aw}} = k_{\text{af}}(C_w - C_o R T_a / H_{\text{Tw, salt}}),$$

with air–water gas exchange mass transfer coefficient ($k_{\text{af}}$, m h$^{-1}$), accounting for resistances to mass transfer in both water ($k_w$, m h$^{-1}$) and air ($k_a$, m h$^{-1}$), defined as

$$1/k_{\text{af}} = 1/k_w + RT_a/(k_h H_{\text{Tw, salt}}),$$

with $k_a = (0.2U_{10} + 0.3) \times (D_{i,\text{air}}/D_{H_2O,\text{air}})^{0.61} \times 36$ and $k_w = (0.45U_{10}^{0.46} \times (S_{C^1}/S_{CO_2})^{-0.5} \times 0.01$. $U_{10}$ is the wind speed at 10 m height above sea level (m s$^{-1}$), $D_{i,\text{air}}$ and $D_{H_2O,\text{air}}$ are the temperature-dependent diffusivities of substances $i$ and H$_2$O in air, and $S_{C^1}$ and $S_{CO_2}$ are the Schmidt numbers for substance $i$ and CO$_2$ (see Bidleman and McConnell, 1995; Zhong et al., 2012; and references therein). $U_{10}$, $T_a$, $T_w$ and air pressure are taken from the ship-based measurements.

### 2.5 Non-steady-state two-box model

The air–sea mass exchange flux of RET is simulated by a non-steady-state zero-dimensional model of intercompartmental mass exchange (Lammel, 2004). RET is selected because of the prevalence of one dominating source. This two-box model predicts concentrations by integration of two coupled ordinary differential equations that solve the mass balances for the two compartments, namely the atmospheric marine boundary layer (MBL) and seawater surface mixed layer. Processes considered in air are dry (particle) deposition, removal from air by reaction with the hydroxyl radical and air–sea mass exchange flux (dry gaseous deposition); while in seawater export (settling) velocity, deposition flux from air, air–sea mass exchange flux (volatilisation) and degradation (as a first-order process) are considered. All input parameters are listed in Table S2 in the Supplement.

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

### 2.6 Analysis of long-range advection of air

Distributions of potential sources can be identified by inverse modelling using meteorological input data (Stohl et al., 2003; Eckhardt et al., 2007). So-called retroplumes are generated using operational weather prediction model data and a Lagrangian particle dispersion model, FLEXPART (Stohl et al., 1998, 2005). Hereby, 50,000 virtual particles per hour were “released” and followed backwards in time for 5 days. The model output is a 3-D distribution of residence time.

### 3 Results and discussion

#### 3.1 PAH concentrations in air and seawater

The mean total (i.e. sum of gaseous and particulate) $\Sigma 25$ PAHs concentration is 1.45 ng m$^{-3}$ (time-weighted; 1.54 with values $<$ LOQ replaced by LOQ/2; see Table 1a), and ranged from 0.30 to 3.25 ng m$^{-3}$. The spatial variability of PAH levels in the Mediterranean is large, determined by long-range advection (Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006). The levels found in this study in the southeastern Mediterranean (SEM) are for most substances lower than found earlier (Table 2). In the Ionian Sea and Sicily region (ISS) some PAHs are found somewhat higher than previously measured, i.e. FLT and PYR (in the gas phase) and BAP and PER (in the particulate phase). Due to a sampling artefact BAP and other particulate-phase PAHs could be underestimated by up to 25% (aforementioned, Sect. 2.1). The seasonality of emissions and the variability of advection or advection in combination with different cruise routes being influenced differently by coastal or ship emission plumes can have a large influence and may explain these differences. On the other hand, the duration of temporal averaging atmospheric concentrations was similar across the various studies. Diagnostic ratios (BAA / (BAA + CHR), FLT / (FLT + PYR); Dvorská et al., 2011) in some of the samples (nos. 2, 4, 7, 8 and 15) reflect the influence of traffic and industrial sources. We investigated the potential source distribution of individual samples collected during the cruise (Sect. 2.6) and found that indeed maxima of PAH concentrations corresponded with air masses having resided over large urban areas, and, vice versa, low concentrations corresponded with air masses without apparent passage of such areas (illustrated in Fig. S4). This finding is supported by the ozone data, i.e. 53 (47–65) ppbv during influence from urban areas but 37 (33–62) ppbv otherwise.

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

Most PAH concentrations in surface seawater were $<$ LOQ, while FLT, PYR and RET were quantified in at least part of the samples (Table 1b). These observed seawater contamination levels are comparable to levels found in the region 2 and 1 decades ago (Lipiatou et al., 1997; Tsapakis et al., 2003). The concentrations near Crete (samples nos. 7 and 8a) are very similar to those found in fall 2001 and winter–spring 2002 (Tsapakis et al., 2006; FLT = 0.15 (0.11–0.21) ng L$^{-1}$, PYR = 0.12 (0.07–0.17) ng L$^{-1}$).

#### 3.2 Gas–particle partitioning

Only a small mass fraction of the total, $\theta = 0.08$, is found in the particulate phase, confirming earlier findings from remote sites in the region (Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006; Table 3c). The particulate mass fraction, $\theta$, of four semivolatile PAHs varied considerably along the cruise track (see Fig. S2 in the Supplement). $\theta$ is thought to be strongly influenced by temperature, and doubling per 13 K cooling was found in a Mediterranean environment (Lammel et al., 2010b) apart from PM composition. We refrain from an exploration of the vapour pressure ($p^0_L$) dependence of $\theta$ (or $K_{p_L}$): a low time resolution implies lack of representativeness of the temperature measurement for the phase change (Pankow and Bidleman, 1992). Furthermore, non-equilibrium conditions cannot be excluded (but are likely as a consequence of time resolution; Hoff et al., 1998), and supporting physical and chemical aerosol parameters, necessary to relate to, are lacking. For similar temperatures higher $\theta$ values had been observed at sites in the region influenced by urban and industrial sources (Mandalakis et al., 2002; Tsapakis and Stephanou, 2005b; Akyüz and Çabuk, 2010), which is probably related to the influence of higher organic and soot PM mass fractions. Gas–particle partitioning models (Table 3) underpredict $\theta$, except the Finizio et al. (1997) model for one substance, TPH. $\theta$ predicted by the JP model comes closest. A number of semivolatile PAHs could not be included in this test of gas–particle partitioning models as concentrations in either the gas phase (CPP, BBF, BJF) or the particulate phase (FLT, PYR, BBN) did not exceed LOQ or no insufficient input data were available (BBF). The neglect of adsorption to soot, not covered by the gas–particle partitioning models tested, may explain at least part of the underprediction (Lohmann and Lammel, 2004). Due to the lack of organic and elemental carbon data, an extended examination is not possible.

In size-segregated samples particulate PAH mass was almost exclusively found in the size fraction $< 0.25 \mu$m aerodynamic diameter (AD) ($<$ LOQ in the other stages, except 0.002 ng m$^{-3}$ CPP in the size fraction corresponding to 0.5-1.0 $\mu$m; Sect. S2.1 and Table S4 in the Supplement). Most particulate phase PAHs, 40%, have been found associated
Table 2. Gaseous (a) and particulate (b) concentrations in air (time-weighted mean (min-max), ng m\(^{-3}\)) of selected PAHs compared to other studies in the Ionian Sea and Sicily region (ISS) and in the southeastern Mediterranean (SEM). For calculation of means, values < LOQ were replaced by LOQ/2. RV represents research vessel cruise.

(a)

<table>
<thead>
<tr>
<th></th>
<th>ISS</th>
<th>SEM</th>
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<tbody>
<tr>
<td>FLN</td>
<td>0.16 (&lt;0.027–0.34)</td>
<td>2.25 (1.27–5.65)</td>
<td>0.071 (&lt;0.050–0.40)</td>
<td>0.69 (0.36–1.23)</td>
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<tr>
<td>PHE</td>
<td>0.52 (0.14–1.11)</td>
<td>7.00 (3.52–15.45)</td>
<td>3.5 (0.14–1.41)</td>
<td>3.94 (2.50–6.35)</td>
</tr>
<tr>
<td>ANT</td>
<td>0.040 (&lt;0.021–0.10)</td>
<td>0.37 (0.18–0.55)</td>
<td>0.039 (&lt;0.013–0.22)</td>
<td>0.20 (0.16–0.30)</td>
</tr>
<tr>
<td>FLT</td>
<td>0.14 (0.053–0.31)</td>
<td>0.05 (0.02–0.07)</td>
<td>0.10 (0.061–0.37)</td>
<td>0.07 (0.003–0.11)</td>
</tr>
<tr>
<td>PFR</td>
<td>0.14 (0.058–0.56)</td>
<td>0.04 (0.02–0.06)</td>
<td>0.12 (0.044–0.29)</td>
<td>0.06 (0.003–0.09)</td>
</tr>
<tr>
<td>CHR</td>
<td>0.012 (0.0071–0.021)</td>
<td>0.09 (0.03–0.23)</td>
<td>0.014 (0.012–0.037)</td>
<td>0.03 (0.02–0.05)</td>
</tr>
<tr>
<td>Sum of 6 PAHs</td>
<td>1.0</td>
<td>9.8</td>
<td>0.7</td>
<td>4.9</td>
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</table>

(b)

<table>
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<tr>
<th></th>
<th>ISS</th>
<th>SEM</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>FLN</td>
<td>&lt;0.92 (&lt;0.60–&lt;1.1)</td>
<td>0.001 (0.0009–0.002)</td>
<td>&lt;0.66 (&lt;0.33–&lt;1.4)</td>
<td>0.0013 (0.0011–0.0016)</td>
</tr>
<tr>
<td>PHE</td>
<td>&lt;1.9 (&lt;1.2–&lt;2.3)</td>
<td>0.06 (0.01–0.12)</td>
<td>&lt;1.6 (&lt;0.66–&lt;2.7)</td>
<td>0.04 (0.01–0.13)</td>
</tr>
<tr>
<td>AN2</td>
<td>&lt;0.21 (&lt;0.14–&lt;0.26)</td>
<td>0.007 (0.0009–0.012)</td>
<td>&lt;0.16 (&lt;0.07–&lt;0.32)</td>
<td>0.009 (0.0007–0.023)</td>
</tr>
<tr>
<td>FLT</td>
<td>&lt;0.85 (&lt;0.56–&lt;1.0)</td>
<td>0.099 (0.01–0.19)</td>
<td>&lt;0.62 (&lt;0.30–&lt;1.3)</td>
<td>0.049 (0.01–0.12)</td>
</tr>
<tr>
<td>PFR</td>
<td>&lt;0.11 (&lt;0.070–&lt;0.13)</td>
<td>0.109 (0.06–0.216)</td>
<td>&lt;0.08 (&lt;0.044–&lt;0.16)</td>
<td>0.057 (0.012–0.142)</td>
</tr>
<tr>
<td>CHR</td>
<td>0.0054 (&lt;0.0018–0.025)</td>
<td>0.013 (0.006–0.023)</td>
<td>0.0026 (&lt;0.0006–0.0080)</td>
<td>0.018 (0.004–0.046)</td>
</tr>
<tr>
<td>BBA</td>
<td>0.018 (0.0030–0.076)</td>
<td>0.04 (0.01–0.08)</td>
<td>0.0079 (0.0033–0.020)</td>
<td>0.043 (0.012–0.101)</td>
</tr>
<tr>
<td>BBF</td>
<td>0.023 (&lt;0.0018–0.010)</td>
<td>0.029 (0.012–0.045)</td>
<td>0.011 (0.0042–0.033)</td>
<td>0.033 (0.010–0.060)</td>
</tr>
<tr>
<td>BKF</td>
<td>0.012 (&lt;0.0018–0.057)</td>
<td>0.015 (0.005–0.027)</td>
<td>0.0047 (0.0018–0.015)</td>
<td>0.089 (0.05–0.333)</td>
</tr>
<tr>
<td>BAP</td>
<td>0.013 (&lt;0.0009–0.072)</td>
<td>0.009 (0.04–0.16)</td>
<td>0.0046 (&lt;0.0010–0.0080)</td>
<td>0.034 (0.005–0.081)</td>
</tr>
<tr>
<td>BPE</td>
<td>0.018 (&lt;0.0018–0.079)</td>
<td>0.015 (0.014–0.016)</td>
<td>0.0072 (0.0023–0.031)</td>
<td>0.010 (0.006–0.011)</td>
</tr>
<tr>
<td>BFR</td>
<td>0.019 (&lt;0.0018–0.088)</td>
<td>0.03 (0.02–0.05)</td>
<td>0.0082 (0.0035–0.025)</td>
<td>0.046 (0.017–0.093)</td>
</tr>
<tr>
<td>PER</td>
<td>0.002 (&lt;0.0006–0.011)</td>
<td>0.002 (0.005–0.004)</td>
<td>0.00075 (&lt;0.0006–0.0021)</td>
<td>0.026 (0.0001–0.0068)</td>
</tr>
<tr>
<td>IPY</td>
<td>0.015 (&lt;0.00096–0.094)</td>
<td>0.018 (0.006–0.032)</td>
<td>0.0016 (&lt;0.00052–0.019)</td>
<td>0.009 (0.002–0.013)</td>
</tr>
<tr>
<td>BPE</td>
<td>&lt;0.0014 (&lt;0.00096–0.0018)</td>
<td>0.026 (0.017–0.042)</td>
<td>0.0041 (&lt;0.00052–0.020)</td>
<td>0.081 (0.012–0.210)</td>
</tr>
<tr>
<td>Sum of 15 PAHs</td>
<td>0.09</td>
<td>1.06</td>
<td>0.05</td>
<td>0.54</td>
</tr>
</tbody>
</table>

1 months September and October 2001, February, April and May 2002. No particulate data reported.
2 24 h per month between February 2000 and February 2002.
with particles <0.5 µm out of five size ranges in the marine background aerosol of the sea region (coast of Crete, November 1996–June 1997; Kavouras and Stephanou, 2002). At continental sites in central and southern Europe mass median diameters of PAHs were found to be in the accumulation range, mostly 0.5–1.4 µm (Schnelle et al., 1995; Kiss et al., 1998; Lammel et al., 2010b, c), but also a second, coarse mode was found (up to 2.4 µm; Chrysikou et al., 2009).

### 3.3 Fugacity ratio and air–sea exchange flux

Fugacity ratios (Fig. 1a) and vertical fluxes (Fig. 1b) could be quantified for FLT, PYR and RET. The uncertainty window of $FR = f_a/f_w$ (volatilisation > 3, deposition < 0.3, grey area insignificant deviation from phase equilibrium) and $F_{aw}$ (ng m$^{-2}$ d$^{-1}$; volatilisation > 0, deposition < 0) of FLT, PYR and RET during the cruise of RV *Urania*. Error bars indicate seawater concentration $C_w$ < LOQ. The x axis depicts the correspondence of sequential pairs of air samples (a–c) and water samples (a–e).

Figure 1. Air–sea exchange, (a) fugacity ratios $FR = f_a/f_w$ (volatilisation > 3, deposition < 0.3, grey area insignificant deviation from phase equilibrium) and (b) flux $F_{aw}$ (ng m$^{-2}$ d$^{-1}$; volatilisation > 0, deposition < 0) of FLT, PYR and RET during the cruise of RV *Urania*. Error bars indicate seawater concentration $C_w$ < LOQ. The x axis depicts the correspondence of sequential pairs of air samples (a–c).

The hypothesis that seasonal depositional input of RET into the surface waters during the fire season (summer) triggers reversal of diffusive air–sea exchange, at least in the year 2010, is tested by box model (Sect. 2.5 and Sect. S1.3 in the Supplement) runs. Two scenarios are considered, an “initially estimated parameter set” (IEPS) representing mean values for environmental parameters, and an “upper estimate parameter set” (UEPS) which represents realistic environmental conditions favouring seawater pollution (Table S3 in the Supplement). Simulated diffusive air–sea exchange flux, $F_{aw}$, during 2005–2010 initialised by the UEPS is shown in Fig. 3a, initialised by the IEPS in Fig. S3 in the Supplement and initialised by the UEPS during the observations (cruise of RV *Urania*, 27 August–9 September 2010) in Fig. 3b.

The model confirms the hypothesis that seasonal depositional input of RET into the surface waters during the fire season (July–September, typically in the range $F_{aw} = 10^{-2}$–$10^0$ ng m$^{-2}$ d$^{-1}$ under IEPS) is followed by a period of prevailing flux reversal, typically $F_{aw} = 10^{-2}$–$10^0$ ng m$^{-2}$ d$^{-1}$, which in the years 2008–2010 started in October and lasted until the onset of the fire season, but possibly started later in the years 2005–2007 (at least under IEPS). The volatilisation flux is predicted to be smaller in magnitude than the net-deposition flux during the fire season, but correspondingly, i.e. higher after intense fire seasons. The high RET volatilisation flux, indicated by measured $C_a$ and $C_w$, seems to be
Table 3. Gas–particle partitioning of selected PAHs (mean ± SD (median)), observed and predicted by the models Junge–Pankow (1987) (JP), Harner and Bidleman (1998) (HB) and Finizio et al. (1997) (F), expressed as (a) particulate mass fraction, θ, and (b) log Kp of this study.

<table>
<thead>
<tr>
<th></th>
<th>Observed</th>
<th>JP</th>
<th>HB</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.18±0.07 (0.18)</td>
<td>0.08–0.20</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.24±0.10 (0.24)</td>
<td>0.23–0.46</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.31±0.13 (0.32)</td>
<td>0.09–0.21</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.91±0.40 (0.97)</td>
<td>0.49–0.73</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−1.97±1.14 (−1.84)</td>
<td>2.43–1.98</td>
<td>−1.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−1.80±1.07 (−1.63)</td>
<td>−1.91–1.46</td>
<td>−1.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−1.65±1.01 (−1.46)</td>
<td>−2.41–1.96</td>
<td>−1.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−0.52±0.66 (−0.74)</td>
<td>−1.41–0.96</td>
<td>−1.08</td>
</tr>
</tbody>
</table>

Figure 2. Spatial pattern of fire-related PM2.5 emissions (Global Fire Assimilation System, GFASv1.0; Kaiser et al., 2012) for the eastern Mediterranean (28–45° N/8–30° E), (a) time integral of 10–26 August, (b) time integral of 27 August–12 September 2010, given as sum over each period in metres per milligram. Areas with no observed fire activity are displayed in white. Temporal pattern of domain-integrated (c) daily total PM2.5 emissions over 2010 (c) and yearly total PM2.5 emissions over 2003 to 2012. Labelled in red is (c) the period of the Urania cruise (27 August–11 September 2010) and (d) the year 2010.

4 Conclusions

PAH pollution of the atmospheric Mediterranean environment was below previous observations at the beginning of the decade (2001–2002; Tsapakis and Stephanou, 2005a; Tsapakis et al., 2006), also considering possible losses during sampling. This might reflect emission reductions. The particulate-phase PAHs were concentrated in the size fraction <0.25 µm AD. The residence time in the troposphere is longest for particles around 0.2 µm in size, with ≈0.01 cm s⁻¹ being a characteristic corresponding dry deposition velocity (Franklin et al., 2000), which translates into a residence time of ≈120 days in the MBL (depth of 1000 m; see Table S3 in the Supplement) and deposition flux $F_{dep} = c \times v = 0.03–0.06 \frac{\mu g \cdot m^{-2}}{yr^{-1}}$ for the individual PAHs associated with the particulate phase ($c = 0.01–0.02 ng m^{-3}$; Table 2b), such as BAP, and 0.5 and 0.3 µg m⁻² yr⁻¹, respectively, for the total flux of particulate phase PAHs in the ISS and SEM in summer. The flux will be higher in winter because of the seasonality of the emissions.

Three gas–particle partitioning models were tested and found to underpredict the particulate mass fraction in most of the samples (four PAHs, i.e. BAA, TPH, CHR and BBF). Although input parameters were incomplete, these results confirm the earlier insight that additional processes on the molecular level need to be included, beyond adsorption (Junge–Pankow model) and absorption in OM ($K_{oa}$ models), namely both adsorption and absorption (Lohmann and Lammel, 2004) or even a complete description of molecular interactions between sorbate and PM matrix (Goss and Schwarzenbach, 2001).

Simulations with a non-steady-state two-box model confirm the hypothesis that seasonal depositional input of RET from biomass burning into the surface waters during summer is followed by a period of flux reversal. The volatilisation flux is smaller in magnitude than the net-deposition...
Figure 3. Diffusive air–sea exchange flux, $F_{aw}$, of RET (ng m$^{-2}$ d$^{-1}$; downward in blue and upward in red) using the upper estimate parameter set (UEPS) for the eastern Mediterranean (28–43° N/8–30° E) (a) model predicted for 1 January 2005–31 December 2010 and (b) model predicted and observed (black) for 27 Author–9 September 2010. Hourly mean data filtered against offshore winds (see text). Error bars including both signs of $F_{aw}$ reflect $C_w$ < LOQ.

The Supplement related to this article is available online at doi:10.5194/acp-14-8905-2014-supplement.

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www.atmos-chem-phys.net/14/8905/2014/ Atmos. Chem. Phys., 14, 8905–8915, 2014


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Supplement of

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

M. D. Mulder et al.

Correspondence to: G. Lammel (lammel@recetox.muni.cz)
Supplementary Material

Polycyclic aromatic hydrocarbons in atmospheric aerosols and air-sea exchange in the Mediterranean

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12 pages, 3 tables and 5 figures

S1. Methodology

S1.1 Sampling

Table S1. Sampling times of high-volume air samples

<table>
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<tr>
<th>Air sample</th>
<th>Start time (UTC)</th>
<th>Stop time (UTC)</th>
<th>Duration (h)</th>
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<td>1</td>
<td>27.8.10 20:00</td>
<td>29.8.10 08:00</td>
<td>36</td>
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<tr>
<td>2</td>
<td>29.8.10 11:30</td>
<td>30.8.10 16:30</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>30.8.10 16:45</td>
<td>31.8.10 13:45</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>31.8.10 15:00</td>
<td>1.9.10 12:00</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>1.9.10 13:00</td>
<td>2.9.10 13:00</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>2.9.10 13:30</td>
<td>3.9.10 18:30</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>3.9.10 20:15</td>
<td>4.9.10 18:15</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>4.9.10 20:00</td>
<td>5.9.10 04:00</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>5.9.10 06:10</td>
<td>5.9.10 22:10</td>
<td>16</td>
</tr>
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<td>10</td>
<td>6.9.10 01:00</td>
<td>7.9.10 10:00</td>
<td>33</td>
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<tr>
<td>11</td>
<td>7.9.10 12:15</td>
<td>8.9.10 06:15</td>
<td>18</td>
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<td>8.9.10 18:10</td>
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<td>9.9.10 06:00</td>
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<td>10.9.10 09:00</td>
<td>16.3</td>
</tr>
<tr>
<td>15</td>
<td>11.9.10 20:00</td>
<td>12.9.10 06:00</td>
<td>10</td>
</tr>
</tbody>
</table>
**S1.2 Diffusive air-sea exchange flux calculation**

A sensitivity analysis was done to explore the influence of the variabilities of air and seawater temperatures and wind speed (expressed as their standard deviations) during individual sample duration on the air-sea exchange flux (Table S2).

Table S2. Sensitivity, $S_F$, of the diffusive air-sea exchange flux, $F_{aw}$, calculated as $S_F = |100 \times (F_{aw} + \sigma_i) - F_{aw}|/F_{aw}$, with the standard deviations, $\sigma_i$, of $i =$ wind speed (WS) or air or seawater temperature ($T_a$, $T_w$). See main text for PAH acronyms.

<table>
<thead>
<tr>
<th></th>
<th>FLT</th>
<th>PYR</th>
<th>RET</th>
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<tbody>
<tr>
<td>WS</td>
<td>146</td>
<td>148</td>
<td>185</td>
</tr>
<tr>
<td>$T_a$</td>
<td>1.3</td>
<td>0.19</td>
<td>4.1</td>
</tr>
<tr>
<td>$T_w$</td>
<td>13</td>
<td>9.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Figure S1. Spatial coverage of air (blue and green, numbers) and seawater samples (diamonds)
S1.3 Two-box fugacity model

A non-steady state 2-box model was applied to test the hypothesis that seasonal depositional input of RET into the surface waters during the fire season (summer) triggers reversal of diffusive air-sea exchange.

The model simulations for the period 2005-2010 were initialised by fire-related RET emissions into air for the East Mediterranean (28-45°N, 8-30°E). RET was in the region eventually also emitted to air from coal and crop residues combustion (Bi et al., 2008; Shen et al., 2012), and eventually emitted to seawater influenced by pulp or paper mill effluents (Leppänen and Oikari, 1999) or by diagenesis (Alexander et al., 1995) in the region. However, these sources of RET to air and seawater are neglected as expected to contribute insignificantly and to show less inter-annual variability. Moreover, advection of RET into the model domain e.g., from fires in the western Mediterranean is neglected for simplicity.

Temperature and wind speed data were taken from the Iraklion meteorological station (35°20’N / 25°11’E, 39 m above sea level), located close to the centre of the model domain. Wind speed data were extrapolated to 10 m above sea level assuming neutral conditions all the time (Stull, 1988). Input data are listed in Table S3. Only wind speeds of on-shore winds were considered representative, while periods (hourly data) of off-shore winds observed at Iraklion were rejected, leading to gaps in the time series of predicted F_{aw}. No experimental data for RET lifetime in seawater exist. Degradation rate in seawater is uncertain. It was derived from a model estimated halflife against hydrocarbon biodegradability in freshwater (56 days; BioHCwin; USEPA, 2009), which could be much longer for seawater. A factor of 10 is often applied to estimate lifetime in seawater from data in freshwater (EU, 1996). Gaseous air and seawater concentrations and the air-sea exchange flux, F_{aw}, are output.

Two scenarios are considered, an ‘Initially Estimated Parameter Set’ (IEPS) representing mean values for environmental parameters, and an 'Upper Estimate Parameter Set' (UEPS) which represents realistic environmental conditions favouring seawater pollution (Table S3). UEPS considers lower estimates for the atmospheric and seawater mixing layers, the degradation rate in seawater (k_{OC}) and the export (settling) velocity in seawater (v_{exp}) and an upper estimate of the of fire-related PM_{2.5} emission flux.
Table S3. Input parameters for the 2-box model, initially estimated parameter set (IEPS). For the upper estimate parameter set (UEPS) FRPM25 was replaced by FRPM25×5, KOC by KOC/100, VEXP by VEXP/10, HMIX by HMIX/2, and HMIXM by HMIXM/2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value adopted or mean (min-max)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>COH</td>
<td>OH concentration in air</td>
<td>molec cm$^{-3}$ (0.5-2.2)×10$^6$ during day-time, 0 during nighttime</td>
<td>climatological data (Spivakovsky et al., 2000) temporarily interpolated</td>
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<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
<td>µM 61.5</td>
<td>Pujo-Pay et al., 2011</td>
</tr>
<tr>
<td>FRPM25</td>
<td>fire-related PM$_{2.5}$ emission flux</td>
<td>mg m$^{-2}$ h$^{-1}$ 3.02 (0 - 496)×10$^{-7}$</td>
<td>Kaiser et al., 2012</td>
</tr>
<tr>
<td>FACEMP M25</td>
<td>Emission factor for PM$_{2.5}$</td>
<td>mg (kg fuel burnt)$^{-1}$ 207</td>
<td>Schmidl et al., 2008, Andreae 1991</td>
</tr>
<tr>
<td>HENRY</td>
<td>Henry coefficient of RET</td>
<td>Pa m$^{-1}$ mol$^{-1}$ 2.3</td>
<td>USEPA, 2009</td>
</tr>
<tr>
<td>HMIX</td>
<td>Atmospheric mixing height</td>
<td>M 1000</td>
<td>Estimate</td>
</tr>
<tr>
<td>HMIXM</td>
<td>Mixing depth in ocean</td>
<td>M 40</td>
<td>d'Ortenzio et al., 2005</td>
</tr>
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<td>KDOC</td>
<td>Dissolved organic carbon/water partition coefficient</td>
<td>L g$^{-1}$ 158.49</td>
<td>Karickhoff, 1981</td>
</tr>
<tr>
<td>KOC</td>
<td>1$^{st}$ order degradation rate coefficient in seawater</td>
<td>s$^{-1}$ 1.0×10$^{-7}$ (4×10$^{-8}$ - 4×10$^{-7}$)</td>
<td>USEPA, 2009, T dependence: EU, 1996</td>
</tr>
<tr>
<td>KOH</td>
<td>Gas-phase reaction rate coefficient with OH of RET</td>
<td>cm$^{-3}$ molecule$^{-1}$ s$^{-1}$ 4.2×10$^{-11}$</td>
<td>Lammel et al., 2010a</td>
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<td>KOW</td>
<td>Octanol/water partitioning coefficient of RET</td>
<td>2.24×10$^{0}$</td>
<td>USEPA, 2009</td>
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<td>KOHEOR</td>
<td>Factor E/R in van ’t Hoff equation for OH reaction of RET</td>
<td>K -20.33</td>
<td>Calvert et al., 2002</td>
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<td>KPOC</td>
<td>Particulate organic carbon/water partitioning coefficient</td>
<td>L g$^{-1}$ 2240</td>
<td>assumed to be given by K$_{ow}$; Rowe et al., 2009</td>
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<tr>
<td>KS</td>
<td>Setschenow constant of RET</td>
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<tr>
<td>POC</td>
<td>Concentration of particulate organic carbon in surface seawater</td>
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<td>Air temperature</td>
<td>K</td>
<td>292.1 (275.2 - 311.2)</td>
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<tr>
<td>Tₚ</td>
<td>Surface seawater temperature</td>
<td>K</td>
<td>292.1 (27482 - 311.6)</td>
</tr>
<tr>
<td>THETA</td>
<td>Particulate mass fraction of RET in air</td>
<td></td>
<td>0.05 (0.02 - 0.14)</td>
</tr>
<tr>
<td>VEXP</td>
<td>Export (settling) velocity of particle-sorbed molecule in seawater</td>
<td>m s⁻¹</td>
<td>8×10⁻⁶</td>
</tr>
<tr>
<td>VDEPP</td>
<td>Deposition velocity of particle-sorbed molecule in air</td>
<td>m s⁻¹</td>
<td>6.5×10⁻⁵</td>
</tr>
<tr>
<td>WS</td>
<td>Wind speed</td>
<td>m s⁻¹</td>
<td>6.1 (0.6-30.7)</td>
</tr>
</tbody>
</table>
S2. Results

S2.1 Gas-particle partitioning

a.

![Graph a](image1.png)

b.

![Graph b](image2.png)

c.

![Graph c](image3.png)
The concentrations found in the stage corresponding to smallest particles, <0.25 µm, are shown in Table S4. Concentrations in size fractions corresponding to larger particles were <LOQ, except for CPP in one sample, resulting in 0.002 (<0.001-0.006) ng m\(^{-3}\) CPP in the size fraction corresponding to 0.5-1.0 µm. We refrain from reporting results of 2-3 ring PAHs in impactor samples, as due to vapour pressure very small particulate mass fractions are expected and LOQ were partly high. While all other PAHs particulate phase concentrations based on low-volume impactor measurement (Table S4) are consistent with those based on high-volume sampling (Table 1a), this is not the case for RET (higher concentration in particulate phase size fraction corresponding to <0.25 µm than as total atmospheric concentration from high-volume sampling). This is unexplained and may be related to loss of RET from the QFF.
Table S4. Concentrations of 4-6 ring PAHs found in particulate phase size fraction corresponding to <0.25 µm aerodynamic diameter (AD) (ng m\(^{-3}\)) as time-weighted mean (min-max). \(n_{LOQ}\) = number of samples > LOQ (out of 3). PAHs with concentrations <LOQ in all size fractions not listed. LOQ = 0.001 ng m\(^{-3}\) except for FLT (0.011) and PYR (0.020).

<table>
<thead>
<tr>
<th></th>
<th>(n_{LOQ})</th>
<th>mean (min-max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLT</td>
<td>3</td>
<td>0.046 (0.035–0.054)</td>
</tr>
<tr>
<td>PYR</td>
<td>3</td>
<td>0.047 (0.040–0.051)</td>
</tr>
<tr>
<td>RET</td>
<td>3</td>
<td>0.048 (0.046–0.051)</td>
</tr>
<tr>
<td>CPP</td>
<td>1</td>
<td>0.007 (&lt;0.001–0.022)</td>
</tr>
<tr>
<td>CHR</td>
<td>1</td>
<td>0.002 (&lt;0.001–0.005)</td>
</tr>
<tr>
<td>BJF</td>
<td>1</td>
<td>0.002 (&lt;0.001–0.007)</td>
</tr>
<tr>
<td>BEP</td>
<td>1</td>
<td>0.003 (&lt;0.001–0.008)</td>
</tr>
</tbody>
</table>

**S2.2 Air-sea exchange**

**S.2.2.1 FLT and PYR**

FLT, PYR and dimethylphenanthrenes were near equilibrium or net volatilisational in coastal waters of the southeastern Mediterranean and FLT in the Black Sea, and also FLT (FR = \(f_a/f_w\) = 0.1) and PYR (FR = 0.3) in two pairs of samples collected in May 2007 in the open southeastern Mediterranean Sea, in the same regions as our samples No. 8 and 10 (Castro-Jiménez et al., 2012). In this study (June-July 2006 and May 2007), for FLT and PYR mean deposition fluxes \(F_{aw} = -5.87 (-11.42 – -1.11)\) ng m\(^{-2}\) d\(^{-1}\) and \(F_{aw} = -7.29 (-12.18 – -2.46)\) ng m\(^{-2}\) d\(^{-1}\), respectively, were derived in the ISS, while for the SEM for FLT and PYR mean volatilisation fluxes \(F_{aw} = 14.33 (4.54 – 41.04)\) ng m\(^{-2}\) d\(^{-1}\) and \(F_{aw} = 15.90 (-0.56 – +62.58)\) ng m\(^{-2}\) d\(^{-1}\), respectively, were derived. In our study (August-September 2010), in the ISS (paired air and water samples No. 11-13) we obtain \(F_{aw} = 3.14 (-38.79 – +29.16)\) ng m\(^{-2}\) d\(^{-1}\) and \(F_{aw} = 60.95 (-14.21 – +195.0)\) ng m\(^{-2}\) d\(^{-1}\) for FLT and PYR, respectively, and for the SEM (paired air and water samples No. 7-10) \(F_{aw} = -47.36 (-169.23 – +24.45)\) ng m\(^{-2}\) d\(^{-1}\) and \(F_{aw} = -53.64 (-243.67 – +62.74)\) ng m\(^{-2}\) d\(^{-1}\) for FLT and PYR, respectively. This
comparison shows opposite findings. However, spatial variability was very high during the 2010 cruise: In the ISS different signs of flux are indicated for the various sampling sites. In the SEM the mean fluxes derived from the paired air and water samples No. 7 and 9-10 (neglect of samples No. 8), $F_{aw} = 7.48 (-2.62 - 24.45)$ and $F_{aw} = 42.64 (17.73-62.74)$ for FLT and PYR, respectively, is close to the 2006-07 findings. $C_a$ in sample No. 8 was very high, apparently because the air mass had passed over an industrial area in western Turkey (Izmir; see also Fig. S4a). This caused a correspondingly high deposition flux, similar to the mean annual fluxes derived for 2001-02 at Finokalia, Crete, with then lower $C_w$ (i.e., $F_{aw} = -240$ ng m$^{-2}$ d$^{-1}$ and $F_{aw} = -187$ ng m$^{-2}$ d$^{-1}$ for FLT and PYR, respectively; Tsapakis et al., 2006). In conclusion, considering spatial and temporal variabilities and different seasons (spring vs. summer) no trend, in particular no reversal of air-sea exchange is indicated by these two data sets, 3 years apart.

S2.2.2 RET

Under UEPS (Fig. S3), for 6 out of 12 observed (i.e., fugacity ratio-derived) $F_{aw}$ (all > 0) agreement within one order of magnitude is found (underpredicting), the wrong sign ($F_{aw} < 0$) is predicted for 2 such cases (31.8.2010 and 2.9.2010) and no prediction was possible for 4 such cases. Note that because of a high frequency of nocturnal off-shore winds at the coastal station from where wind speed data were adopted (land breeze at Iraklion, Crete), data gaps in the simulated time series of $F_{aw}$ occur more often during night-time than during day time (visible in Fig. S3). Because of the diurnal variation of temperature and wind speed these data gaps are often corresponding with maxima rather than minima of predicted $F_{aw}$. Underprediction could be due to neglected emissions to air and seawater in the region other than fire related (no or little seasonality) or neglect of advection into the model region (similar seasonality as captured emissions). Therefore, also the amplitude of the high frequency (daily) fluctuations could be underestimated. On the other hand, $F_{aw}$ derived from observed concentrations $C_a$ and $C_w$ is uncertain, too. The biggest contribution is expected to be caused by sampling air and water not simultaneously (but combining short seawater sampling intervals with 10-20 h air sampling periods, often starting or ending when seawater samples were collected).
A sensitivity analysis (section S1.2) was performed to quantify the uncertainty of the calculated flux, $F_{aw}$, accounting for the variabilities of wind speed, air and seawater temperatures during sampling periods (Table S2). $F_{aw}$ is found most sensitive to wind speed, changes on average for all the samples about 160% when adding or subtracting one SD of wind speed (hourly data) from the mean. The flux is much less sensitive to variation of the air and seawater temperatures, leading to changes of approximately 2 and 9%, respectively, when adding or subtracting one SD from the mean. While the sensitivity of $F_{aw}$ to wind speed would be even higher when based on higher time-resolved data, hourly data appear appropriate considering mixing times of surface waters. This sensitivity to input uncertainties may explain part of the underestimate, but not up to one order of magnitude.

Fig. S3. Model predicted diffusive air-sea exchange flux, $F_{aw}$, of RET (ng m$^{-2}$ d$^{-1}$; downward in blue and upward in red) using the initially estimated parameter set (IEPS) for the Eastern Mediterranean (28-45$^\circ$N/8-30$^\circ$E) 1.1.2005-31.12.2010, hourly means. Data filtered against off-shore winds (see main text). (Same as Fig. 3, but IEPS)
S2.3 Long-range transport

a)

b)

Fig. S4. Residence time distribution (left: latitude vs. longitude, right: latitude vs. altitude) of particles in backward simulations corresponding to (a) maximum and (b) minimum atmospheric PAH concentrations.
References


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Figure 2 in Sect. 3.3 on p. 8912 did not show a colour bar and the two maps were erroneously swapped. The correct figure is shown here.

Figure 2. Spatial pattern of fire-related PM$_{2.5}$ emissions (Global Fire Assimilation System GFASv1.0; Kaiser et al., 2012) for the East Mediterranean (28–45° N/8–30° E), (a) time integral of 10–26 August, (b) time integral of 27 August–12 September 2010, given as sum over each period in mg m$^{-2}$. Areas with no observed fire activity are displayed in white. Temporal pattern of domain-integrated (c) daily total PM$_{2.5}$ emissions over 2010 and (d) yearly total PM$_{2.5}$ emissions over 2003 to 2012. Labelled in red is (c) the period of the Urania cruise (27 August–11 September 2010) (d) and the year 2010.
ANNEX II – Study 2
Long-range atmospheric transport of PAHs, PCBs and PBDEs to the central and eastern Mediterranean and changes of PCB and PBDE congener patterns in summer 2010

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HIGHLIGHTS

- PCBs, DDXs, PBDEs, penta- and hexachlorobenzene were measured shipborne in summer.
- Transport paths can explain air samples' composition and concentration levels.
- PCB degraded along transport by reaction with the OH radical.

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- Marine environment
- Persistent organic pollutants
- Mediterranean

ABSTRACT

The central and eastern Mediterranean is a receptor area for persistent organic pollutants (POPs) emitted in western, central and eastern Europe, particularly during summer. Atmospheric concentrations of PCBs, DDXs, PBDEs, penta- and hexachlorobenzene were measured during a ship-borne survey in the summer of 2010. The concentration of PCBs (sum of 7 congeners) was 3.61 (2.08–7.72) pg m⁻³, of which 6.7% was associated with the particulate phase. The mean concentration of DDT isomers and their metabolites, DDE and DDD, was 2.60 (0.46–7.60) pg m⁻³ (particulate mass fraction q = 0.097), of penta- and hexachlorobenzene 0.22 (<0.39–2.80) pg m⁻³ and 6.29 (2.48–24.16) pg m⁻³, respectively, and of PBDEs (sum of 8 congeners) 7.31 (2.80–19.89) pg m⁻³. The air masses studied had been transported mostly across central Europe, some crossing western Europe. The observed changes of PCB congener patterns along transport routes are in agreement with the perception that the reaction with the OH radical is dominating PCB atmospheric lifetime, and indicate an overestimation of the second order gas-phase reaction rate coefficient of PCB153 with OH by structure-activity relationship.

1. Introduction

The marine atmospheric environment is a receptor area for most legacy persistent organic pollutants (POPs) as no significant marine sources exist. In some sea regions, however, accumulation in surface waters due to atmospheric deposition has caused flux reversal (Bidleman et al., 1995; Lakaschus et al., 2002; Mulder et al., 2014). Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are mostly emitted in urban areas. While primary sources of PCBs are still important (Gasić et al., 2010; Schuster et al., 2010), the majority of sources are secondary (e.g. polluted soils; Lammel and Stemmler, 2012). In Italy, PCBs were produced from 1958 to 1983 with a cumulative production of approximately 31,092 tons (Breivik et al., 2007). In Greece, approximately 40 transformers and 15,000 capacitors containing PCBs were still in use in 1993 (Mandalakis et al., 2002). The phasing out process was planned to end in 2005 in Italy, and in 2010 in Greece (CLEEN, 2005). PBDEs occur in three technical mixtures: pentaBDE, octaBDE and decaBDE. The penta mix formulation consists of ten isomers dominated by the tetraBDEs BDE47 and BDE99 (>70%). The octaBDE mixture contains BDE183 as major congener and the decaBDE mixture consists primarily of the fully brominated BDE209 (la Guardia et al., 2006).
pentaBDE and octaBDE mixtures were banned by the European Union in 2004, while the use of decaBDE was restricted in 2008 (EU, 2003 and EU, 2008). Current major PBDE sources are waste processing and separation, sewage and sludge releases, and landfill leachate (Darnerud et al., 2001). Similarly, almost no primary sources should exist, solely combustion and re-volatisation should distribute hexachlorobenzene (HCB), pentachlorobenzene (PeCB) and dichlorodiphenyltrichloroethane (DDT) which mainly entered the environment applied as pesticides. Primary sources of polycyclic aromatic hydrocarbons (PAHs) are combustion processes (power plants, biomass burning and road transport; at sea: ship exhaust, see Donato et al., 2014; Lammel, 2015).

Earlier studies of the central and eastern Mediterranean air, reported PCB at Finokalia and Iraklion, Crete (Mandalakis and Stephanou, 2002; Iacovidou et al., 2009), in and near Athens (Mandalakis et al., 2002), and in Bari, southern Italy (Estellano et al., 2014); PBDEs in Finokalia and Iraklion, Crete (Iacovidou et al., 2009); PAHs in the Bursa area, northwestern Turkey (Esen et al., 2008); PAHs (Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Kaya et al., 2012; Aydin et al., 2014), PCBs (Sofouglu et al., 2004; Cetin et al., 2007; Bozlaker et al., 2008a,b; Kaya et al., 2012; Aydin et al., 2014), and PBDEs (Cetin and Odabasi, 2008) in the Aliaga and Izmir area, western Turkey (and other areas not directly relevant for this study).

Most POPs are semi-volatile (vapour pressures at 298 K in the range 10^-6–10^-2 Pa) and, hence, partition between the gas and particulate phases, influenced by temperature, particulate phase chemical composition and particle size. Due to significant lipophilicity (Kow = 10^-6–10^-6) and bioaccumulation, these substances pose a hazard for marine ecosystems. This paper reports concentrations in air of PCBs, DDT including its metabolites DDE and DDD (substance group called DDX), PBDEs, penta- and hexachlorobenzene sampled in the summer of 2010 aboard the RV Urania cruise. To increase our understanding of PCBs and OCPs arriving from the north to north-west is reported to be the most probable transport mode (Lelieveld et al., 2002) and explained in detail in the SM, S1.2. The target compounds include seven PCB congeners (28, 52, 101, 118, 153, 138, 180), ten PBDE congeners (28, 47, 66, 100, 99, 85, 154, 153, 183, 209), PeCB, HCB, and DDT and its metabolites (p,p’-DDE, p,p’-DDE, p,p’-DDD, p,p’-DDT, p,p’-DDT). The limit of quantification (LOQ) is calculated as the mean of field blanks plus three times the standard deviation. For PBDEs in the particulate phase too few field blanks (2) were available. Therefore, field blanks were used from a campaign using the identical sampling and analysis methods conducted 2 years later in the same region (BDE 47, 99, 100, 209). For other BDE congeners, in lack of field blanks LOD/2 was considered as the field blank and the relative standard deviation of BDE 100 was used to derive LOQ.

PM mass fractions were determined from filter gravimetry (Sprovieri, personal communication).

2.2. Analysis of long-range atmospheric transport

The Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998, 2005) is used to identify air mass origins, pathways and map residence times. The meteorological data (0.5° × 0.5° resolution, 3-hourly) is used from the Global Forecast System (GFS, NCEP, USA). For every sample (8–36 h duration), particles were released every simulated 6 h (100,000 particles were released during 2 h, randomly between 0 and 100 m altitude) at the ship’s position. The particles were followed for 5 days backward in time within a large region (30–60 N/10–W–40 E; see Fig. 1b). The model output was a measure of the concentration-weighted time that particles resided in grid cells. To this end, residence times of particles in individual grid cells were added up. For 2D plots particles in grid cells were added up in one direction, vertically (Fig. 1b and Fig. 3a, Fig. S1) or zonally (Fig. 3b). Transport times between locations and boundary layer heights were calculated using trajectories generated by the HYSPLIT model (Draxler and Rolph, 2003). Back trajectories were run every 2 h. For boundary layer heights the average during 4 h preceding arrival of back-trajectories was used. Furthermore, synoptic weather charts were used for transport analysis.

The daily time series fire-related PM2.5 emissions as provided by
the Global Fire Assimilation System (GFASv1.0; Kaiser et al., 2012) were interpolated to hourly values using a Gaussian curve according to Kaiser et al., 2009. These were used to produce the estimated contribution of fires to the sampled PAH levels and profiles by multiplication with the residence times obtained from FLEXPART (Sections 3.3.3, S2.3).

### 2.3. Models of gas-particle partitioning

The PCB data is used to test three gas-particle partitioning models, i.e. an adsorption model and two absorption models. The models are described in the SM, S1.3.

### 3. Results and discussion

#### 3.1. Concentrations and phase partitioning

Concentrations and particulate mass fractions are listed in Table 1, except for BDE 66, which was not detected in any of the samples, and BDE 183, which was excluded because its concentration exceeded LOQ in only 6 out of 15 samples. Concentrations of the PAHs were recently published elsewhere (Kaiser et al., 2012).

The pollutants were found to be significantly correlated with each other ($r = 0.57$–$0.95$, $t$-test, $p > 0.05$), except for the pair HCB and $p,p^\prime$-DDT ($r = 0.01$).

The decabrominated ether (BDE 209) accounted for 37% and congeners related to pentaBDE for 62% of the PBDEs. These percentages are comparable to what was found in bulk atmospheric deposition, namely 25% (15–35) related to pentaBDE and 73% (63–83) to decaBDE at mountain sites in western and central Europe 2004–07 (Arellano et al., 2014), and 35% related to pentaBDE and 48% to decaBDE in rural northern Italy 2005 (Vivens et al., 2007).

The levels of total (gaseous + particulate) concentrations were similar throughout the cruise, for most pollutant classes within one standard deviation of the campaign’s mean concentration. Only the samples #8, #13 and #15 exceeded one standard deviation of the mean (Fig. 2). Sample #8 represents the maximum concentrations of the cruise for most substances (most PCBs, HCB, PeCB, high concentrations of DDX and the highest sum PBDEs). Air mass analyses revealed that this sample captured air that previously had resided over the Aliaga-Izmir industrial area (western Turkey). Sample #15 picked up pollution in the vicinity of the harbour of Palermo (Sicily, Italy; see SM, Fig. S1c). Moreover, these three samples were taken at night, when a low wind speed and shallow planetary boundary layer (on average 550, 370 and 430 m, during sample #8, #13 and #15, respectively) caused accumulation of pollutants (e.g., Salmond and McKendry, 2005; Gasić et al., 2010). In case of sample #13 mixing seems to be the only explanation.

Few of the fifteen samples have been collected in areas, which had been studied before, such that concentrations can be compared with previous measurements. The concentrations of most compounds found in this study are remarkably low. Samples #3–4 were taken near the harbour of Taranto, for which Estellano et al., 2014, reported a factor ten higher PCB concentrations in summer 2009 for the same seven congeners as reported here (38 pg m$^{-3}$ vs.

### Table 1

Concentrations in air, $c_{tot} = c_g + c_p$ (pg m$^{-3}$) and particulate mass fraction, $\theta$, of (a.) PCBs, (b.) OCPs (PeCB, HCB, DDX) and (c.) PBDEs as time-weighted mean (min–max), $n_{LOQ} =$ number of samples with both $c_g >$ LOQ and $c_p >$ LOQ (out of 15). For calculation of the mean, values $< $ LOQ were ignored.

<table>
<thead>
<tr>
<th></th>
<th>$n_{LOQ}$</th>
<th>$c_{tot}$ (mean (min–max))</th>
<th>$\theta$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB 28</td>
<td>15</td>
<td>0.58 (0.17–1.63)</td>
<td>0.06</td>
</tr>
<tr>
<td>PCB 52</td>
<td>15</td>
<td>0.60 (0.40–1.99)</td>
<td>0.03</td>
</tr>
<tr>
<td>PCB 101</td>
<td>15</td>
<td>0.58 (0.33–1.23)</td>
<td>0.02</td>
</tr>
<tr>
<td>PCB 118</td>
<td>15</td>
<td>0.32 (0.13–0.54)</td>
<td>0.10</td>
</tr>
<tr>
<td>PCB 153</td>
<td>15</td>
<td>0.57 (0.29–1.18)</td>
<td>0.05</td>
</tr>
<tr>
<td>PCB 138</td>
<td>15</td>
<td>0.48 (0.22–0.89)</td>
<td>0.07</td>
</tr>
<tr>
<td>PCB 180</td>
<td>15</td>
<td>0.32 (0.15–0.55)</td>
<td>0.14</td>
</tr>
<tr>
<td>$\Sigma$PCBs</td>
<td></td>
<td>3.61 (2.08–7.72)</td>
<td></td>
</tr>
<tr>
<td><strong>b.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PeCB</td>
<td>5</td>
<td>0.22 (0.39–2.80)</td>
<td>0.01</td>
</tr>
<tr>
<td>HCB</td>
<td>15</td>
<td>6.29 (2.48–24.16)</td>
<td>0.07</td>
</tr>
<tr>
<td>$o,p^\prime$-DDE</td>
<td>15</td>
<td>0.12 (0.028–0.32)</td>
<td>0.04</td>
</tr>
<tr>
<td>$p,p^\prime$-DDE</td>
<td>14</td>
<td>1.06 (0.35–3.70)</td>
<td>0.03</td>
</tr>
<tr>
<td>$o,o^\prime$-DDD</td>
<td>15</td>
<td>0.090 (0.043–0.25)</td>
<td>0.17</td>
</tr>
<tr>
<td>$p,p^\prime$-DDD</td>
<td>15</td>
<td>0.18 (0.061–0.53)</td>
<td>0.10</td>
</tr>
<tr>
<td>$p,o^\prime$-DDT</td>
<td>15</td>
<td>0.39 (0.13–1.07)</td>
<td>0.05</td>
</tr>
<tr>
<td>$p,p^\prime$-DDE</td>
<td>15</td>
<td>0.76 (0.19–1.72)</td>
<td>0.13</td>
</tr>
<tr>
<td>$\Sigma$OCPs</td>
<td></td>
<td>9.11 (2.94–31.48)</td>
<td></td>
</tr>
<tr>
<td><strong>c.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE 28</td>
<td>15</td>
<td>0.088 (0.016–0.46)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>BDE 47</td>
<td>15</td>
<td>2.82 (0.57–7.49)</td>
<td>0.04</td>
</tr>
<tr>
<td>BDE 100</td>
<td>15</td>
<td>0.28 (0.081–1.10)</td>
<td>0.12</td>
</tr>
<tr>
<td>BDE 99</td>
<td>15</td>
<td>1.21 (0.36–4.73)</td>
<td>0.19</td>
</tr>
<tr>
<td>BDE 85</td>
<td>11</td>
<td>0.016 (&lt;0.0085–0.065)</td>
<td>0.33</td>
</tr>
<tr>
<td>BDE 154</td>
<td>15</td>
<td>0.050 (0.019–0.21)</td>
<td>0.34</td>
</tr>
<tr>
<td>BDE 153</td>
<td>15</td>
<td>0.047 (0.017–0.14)</td>
<td>0.29</td>
</tr>
<tr>
<td>BDE 209</td>
<td>15</td>
<td>2.79 (0.717–9.11)</td>
<td>0.13</td>
</tr>
<tr>
<td>$\Sigma$PBDEs</td>
<td></td>
<td>7.42 (2.87–20.056)</td>
<td></td>
</tr>
</tbody>
</table>
The time-weighted mean (min–max; n = 15) of the particulate mass fraction, θ, is 0.05 (<0.01–0.16) for Σ7-PCB, 0.01 (<0.01–0.02) for HCB and PeCB, 0.07 (<0.01–0.20) for DIXX compounds and 0.10 (0.04–0.36) for PBDEs. The mean (min–max; n = 15) PM2.5 and PM10 concentrations were 10.9 (1.8–42.5) and 23.2 (9.7–51.4) μg m⁻³, respectively. The correlation of θ with PM10 was not significant (r = −0.47–0.48, p < 0.01). For PCBs gas-particle partitioning models tested mostly underpredict partitioning to the particulate phase (Table S3). Due to lack of composition (e.g. fraction of organic matter) and humidity data, and a possible sampling artefact (underestimated θ; Mandalakis and Stephanou, 2002) these results are not really conclusive (see discussion in S2.3). Higher brominated BDEs are not expected to be in phase equilibrium as relaxation to disturbances from deposition (or, eventual, re-volatilisation) is slow (Li et al., 2015). Therefore, the particulate mass fraction, θ, of BDEs with >4 Br atoms should be lower in air masses recently influenced by emissions. In our data set, BDE209 in samples influenced by urban air (samples #7–9, 15) was indeed less associated with PM (θ = 0.11 ± 0.11) than by average over all samples (θ = 0.16 ± 0.13).

3.2. Long-range atmospheric transport analysis

The large scale advection of the air masses, which influenced the samples was mostly across central Europe, but also partly across western Europe (Fig. 1).

3.2.1. Pathways of air masses and sample attributes

By the pathways they took, the air masses can be categorised in 5 groups (Fig. 2, Table S4). These are detailed and residence time maps for individual samples are given in the SM, Fig. S1.

According to long-range advection and atmospheric features, we investigated the possible influence of (A) night-time (low mixing eventually leading to high concentrations; samples #8, #13, and #15), (B) PM2.5 and PM10 concentrations, and (C) possible urban influence as indicated by air mass passage over a metropolitan area e.g., Athens (samples #7–9 and #15). The samples with attribute A reflect the highest concentration levels (sum of all measured substances), and are most pronounced for PBDEs. Local sources were suspectedly more important than LRT for A samples.
(various air mass categories), as low wind speeds (2.7, 2.8 and 4.8 m s\(^{-1}\) for samples #8, 13 and #15, respectively), and a relatively low atmospheric mixing layer prevailed (Gogou et al., 1996). Sample #8 contains the highest pollutant levels with regard to PAHs, PCPs, PBDE, HCB and PeCB (but not DDX) found on the cruise. Sample #15 contains the highest levels of DDX and the concentration levels of the other pollutant groups rank second compared to sample #8. Air mass analyses revealed that the air sampled by sample #8 resided a significant amount of time above a high emission area, the Aliaga industrial area, north of İzmir, western Turkey, more investigated below. Similarly, sample #15 was influenced by the urban (and industrial) areas of Palermo and Rome. The pollutant concentrations of sample #13 are about 1.5 times higher than of the previous and the following sample, #12 and #14. This seems to reflect the mixing layer depth change from \(=600\) m (sample #12) to \(=400\) m (sample #13) and back to \(=600\) m (sample #14).

PM (B) levels were not significantly correlated with most pollutants (\(r < 0.44\)), except for DDX (\(r = 0.60, t\)-test, \(p > 0.05\)). The low pollutant levels found in sample #10 can be explained by a high wind speed and a large distance to land. The low PM\(_{10}\) level of sample #12 reflects a pathway of the air mass without recent influence from land based emissions (see Fig. S2).

The fact that PCB sources are predominantly located in urban areas (C), including in the Mediterranean (Mandalakis et al., 2002; Gasic et al., 2010), is reflected in our data set as two samples (samples #9 and #15) among the three with highest PCB content (samples #8—9 and #15) had been influenced by urban areas as shown by the back trajectories. Moreover, the pathways of air masses that correspond to samples #8 and #15, passed over central Europe, which has been remaining a region of major secondary PCB sources (Pistocchi, 2008; Dvorská et al., 2009). PCB and PBDE congener patterns in such samples (C) are discussed below (Section 3.3.2).

### 3.3. Pollution sources influencing the samples collected at sea

#### 3.3.1. Turkish west coast

The polluted air collected in sample #8, with the highest concentrations of PAH, PeCB, HCB, PCB, PBDE and among the highest of DDX during the cruise (Fig. 2), and to a lesser extent in samples #7 and #9 that had passed over the Izmir and Aliaga industrial area, western Turkey. This area hosts major industrial pollutant sources including a large petroleum refinery and petrochemical complex, shipbreaking/scarp iron dockyards, scrap processing iron—steel plants, scrap storage and classification sites, steel rolling mills, related dense a harbour, heavy road and rail traffic, and a natural gas—fired power plant. The majority of the emitted PAHs and PCBs is expected to be deposited in the area (Kaya et al., 2012). The transport model indicates residence times in the Aliaga area within the boundary layer of \(=2–3\) h, \(=30\) h and \(=5–6\) h for the samples #7, #8 and #9, respectively. Fig. 3 shows for sample #8, the five day backward simulation and the vertical (zonally summed) north to south cross section. In particular the right panel shows that before arriving at the ship’s location, the air was influenced by emissions in the Aliaga area: The boundary layer depth during these \(=30\) h ranged 280–630 m. The residence time distributions for samples #7 and #9 (see Fig. S2) also show that the air had passed over the Aliaga area, however, mostly at a much higher altitude (2200–4600 m and 3000–4200 m for samples #7 and #9, respectively, i.e., above the boundary layer), such that surface emissions were not picked up. In this study, the residence time analyses proofs to be an indispensable tool, to explain air sample composition and concentration levels. It is concluded that the Izmir–Aliaga area is also a source of PeCB, HCB and PBDE for the region (apart from PAH and PCB, reported earlier; Sofuoglu et al., 2004; Cetin et al., 2007; besides others). Photochemistry during transport influencing sample #8 is studied below, Section 3.3.2.

#### 3.3.2. Photochemistry of PCBs and PBDEs during transport from continental sources to the open sea

The gas-phase reaction with the hydroxyl radical and the direct photolysis in the particulate phase may provide sinks to PCBs and PBDEs, respectively (Mandalakis et al., 2003; Söderström et al., 2004):

\[
\frac{\Delta c_i}{\Delta t} = -\left(\theta_i j_i + (1 - \theta_i) k_{iOH}^{(2)} \cdot c_i \right)
\]

where \(c_i\) and \(c_{OH}^j\) (molec cm\(^{-3}\)) are the PCB or PBDE and OH radical concentrations, \(k_{iOH}^{(2)}\) (cm\(^3\) molec\(^{-1}\) s\(^{-1}\)) is the PCB or PBDE second order gas-phase reaction rate coefficient, \(j_i\) is the PCB heterogeneous photolysis reaction rate coefficient (set to zero for PCBs), \(\theta_i\) is the PCB or PBDE particulate mass fraction. By comparison of observed and predicted PCB and PBDE congener concentration ratios, \((c_i/c_{j,bad})\) and \((c_i/c_{j,obs})\) respectively (i and j denoting different congeners), at the ship’s position, we test the hypotheses that (a) for PCBs the reaction of the gaseous molecule with the hydroxyl radical was the only sink while direct photolysis is negligible (j set to zero; Mandalakis et al., 2003), and (b) for PBDEs heterogeneous photolysis of BDE209 was the dominant sink. Dry gaseous deposition is assumed to be negligible. This can be expected to hold for PCBs, as these were recently found to be close to phase equilibrium, and hence, are being subject to very low absolute vertical fluxes, at least in the eastern Mediterranean (Berrojalbiz et al., 2014). Simultaneous measurements are not available. Therefore, \((c_i/c_{j,obs})\) is based on previous data from the same season, with the assumption that the observed PCB patterns were conserved in the source areas. This assumption is justified, as the concentration ratios in air are dominated by the ratio of the emission fluxes (which are determined by air and soil temperatures and are similar for the same season) and ratio of the soil burdens (changing very slowly; Lammel and Stemmler, 2012). For PBDEs, we consider heterogeneous photolysis of decabDE (Söderström et al., 2004) and reaction of decabDE and pentaPDE with the OH radical (estimated based on the AOPWIN model; Schenker et al., 2008). PentaBDE’s photolysis is neglected, because it is much less efficient as indicated by studies on photolysis in solvents (Eriksson et al., 2004; Wei et al., 2013). To adjust \(\theta\) to its value at travelling altitude we assume a doubling of the PBDE particulate mass fraction per 13 K temperature decrease, similar to what was observed for PAHs (Lammel et al., 2010), as noc such data are available for PBDEs. Predicted congener concentration ratios are calculated as:

\[
\left(\frac{c_i}{c_j}\right)_{\text{pred}} = \left(\frac{c_i}{c_j}\right)_{\text{src}} \exp \left[-(1 - \theta_i) k_{iOH}^{(2)} - (1 - \theta_j) k_{jOH}^{(2)} c_{OH}^{(i)} \right]
\]

where \((c_i/c_{j,src})\) and \((c_i/c_{j,obs})\) are the observed and predicted concentration ratios of PCB and PBDE congeners i and j, respectively in the source region and at the ship’s position, respectively; and \(\Delta t(s)\) is the daylight travelling time between source area and ship’s position. Transport times and altitudes are based on back trajectories (HYSPIT model). Only daylight times are considered for photochemistry. Climatological input data are used for day-time OH concentration (July, 36°N; Spivakovskiy et al., 2000) and temperature at transport altitude (summer 2010 over Athens; Philandras et al., 2014; USA, 1976). Experimental (PCB28; Anderson and Hites, 1996) or estimated (based on structure-activity relationship for all other congeners, AOPWIN model of the EPI suite; USEPA,
2012; Beyer et al., 2003) temperature dependent reaction rate coefficients, $k_{OH}^0 (T)$, are used. Previously observed PCB data were adopted for the source areas Athens (samples #7) and Aliaga-Izmir (samples #7–8). Such data are not or not available or are insufficient for Rome (sample #15) and for the Po Valley (sample #6). Simultaneously observed PCB data for the source region central Europe (samples #4–6 and #15) were adopted from Košetic, Czech Republic (own data, unpublished), a regional background site (Holoubek et al., 2007; Dvorska et al., 2009). Recent PBDE data were available for Izmir (Cetin and Odabasi, 2008), but not for the other urban areas, which may have influenced the samples. The uncertainty of $c_i/c_{OH}$ is dominated by the uncertainty of the transport time, $\Delta t$ (based on the back-trajectory analyses, specified in Table 2), while $\Delta t$, $\Delta c_{OH}$ (both functions of $\Delta h$) and measurement uncertainties $\Delta (c_i/c_{OH})_n (\Delta c_i = \pm 10\%$ and $\pm 15\%$ for $i = $ PCB and PBDE, respectively, based on the results of side by side active air sampling; own unpublished data) contribute to a lesser extent.

After LRT from central Europe and the Athens and Izmir urban areas the observed PCB congener ratios $c_{PCB28}/c_{PCB153}$, $c_{PCB28}/c_{PCB151}$ and $c_{PCB28}/c_{PCB153}$ agree with prediction (Table 2a–c), in some cases very well. This confirms the perception that the reaction with OH is dominating the atmospheric lifetime of these PCBs. The exceptions are slight overpredictions of $c_{PCB28}/c_{PCB151}$ and $c_{PCB28}/c_{PCB153}$ after transports from central Europe (Table 2b) and $c_{PCB28}/c_{PCB153}$ after transport from Izmir, and overprediction of $c_{PCB28}/c_{PCB153}$ after transport from Athens (Table 2c). The latter could be caused by a slight change of $c_{PCB28}/c_{PCB153}$ during the last decade ($c_{PCB28}/c_{PCB153}$ is based on measurements in the year 2000) related to particularly slow depletion of PCB153 in soils of Athens, or an overestimate of $k_{PCB153OH} (c_1 = 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ rather than $k_{PCB151OH} = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ at 298 K; USEPA, 2012) (or a combination of both). As $c_{PCB28}/c_{PCB153}$ is slightly overpredicted for transports from Izmir (samples #7–8, Table 2c), the latter explanation appears more plausible. After LRT from the Izmir urban area ($q_{DE209}/q_{DE100}$) is in agreement with predicted values (Table 2d). This may suggest that $q_{DE100}$ is inefficient in predicting ambient air and that the photolysis rates of BDE209 (when sorbed on sand and sediment) are spanning the reactivity on ambient aerosol surfaces. Degradation of PBDE congeners along transport cannot be constrained any further due to a lack of kinetic data (Soderstrom et al., 2004; Schenker et al., 2008; Wei et al., 2013).

3.3.3. Emissions from fires and the sea surface

RET, which is a marker for soft wood burning (e.g., Ramdahl, 1983), was found to be net-volatilisation along the cruise (Mulder et al., 2014). This could be explained by the combination of emissions in on-going and previous fires in the region using fire observations from satellite (Mulder et al., 2014). Wildfires in eastern Europe had affected the region until shortly before the cruise (Diapouli et al., 2014), but were not relevant for our samples.

The mean time the air travelled over sea before arriving at the ship’s location is longest for samples #13, #14 and #12 (88 h, 87 h, 82 h and 80 h, respectively, while the average is 51 h). The fraction of total RET among PAHs is correlated ($r = -0.46$) and highest for samples #12, #9, #11 and #6 (0.032, 0.028, 0.027 and 0.020, respectively, while it is 0.013 on average). Thus, volatilisation from the sea surface may explain RET enrichment in sample #12. Another potential indicator for RET enrichment, the ratio of total RET over PM$_{10}$, is negatively correlated with travel time over the sea ($r = -0.59, p < 0.05$) and is highest for three samples #15, #5 and #4 (0.0087, 0.0051 and 0.0042, respectively, while it is 0.0021 on average). The negative correlation can be explained by the large contribution sea-salt emissions make to PM$_{10}$ (Mamane et al., 2008). We mapped the potential influence of fire-related RET on the samples as the product of fire-related PM$_{10}$ mass flux ($\text{kg m}^{-2} \text{s}^{-1}$) and residence times of air masses (shown in Fig. 3 for the entire measurement period). This product ranges 11.4 (0.2–5.61) g m$^{-2}$ for individual samples (summed over the region, see Fig. S3, with maximum values found for samples #1 ($5.61 \text{ g m}^{-2}$), #5 (30.1 g m$^{-2}$), #2 (20.1 g m$^{-2}$) and #6 (17.5 g m$^{-2}$). Thus, primary, fire-related emissions may explain RET enrichment in samples #5 and #6. In conclusion, out of 7 samples enriched in RET (among PAHs or in PM$_{10}$), 2 are suggested to be related to primary and 1 to secondary RET emissions (and others, eventually, explained by a combination of primary and secondary emissions).

4. Conclusions

The observations indicate that the Izmir-Aliaga area is a source of PeCB, HCB and PBDE for the region, apart from PAHs and PCBs (reported earlier: Sofuoglu et al., 2004; Cetin et al., 2007; besides others). By combining fire distributions and air mass histories, the significance of the source open fires for RET levels could be confirmed for individual samples. Changes of PCB congener patterns along transport routes are in agreement with the perception that the reaction with the OH radical is dominating PCB atmospheric lifetime (Mandalakis et al., 2003), and possibly indicate an overestimation of the second order gas-phase reaction rate coefficient of PCB153 with the OH radical by structure-activity relationship (AOPWIN model; USEPA, 2012). The data availability is insufficient to test PBDE photochemistry along transport by observational data. For many PCB and all of the PBDE congeners
occuring in the atmospheric environment, gas-phase rate coefficients of the reaction with the hydroxyl radical, $k_{\text{OH}}^{(2)}$, are needed.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/atmosenv.2015.03.044.

References


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polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Lake Maggiore (Italy and Switzerland). J. Environ. Mon. 9, 589–598.


Supplementary Material

Long-range atmospheric transport of PAHs, PCBs and PBDEs to the central and eastern Mediterranean and changes of PCB and PBDE congener patterns in summer 2010

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S1. Methodology

S1.1 Sampling

Table S1. Sampling times of high-volume air samples. Sampling times varied as being subject to ship motion, besides other.

<table>
<thead>
<tr>
<th>Air sample</th>
<th>Start time (UTC)</th>
<th>Stop time (UTC)</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
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<td>29.8.10 08:00</td>
<td>36</td>
</tr>
<tr>
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<td>29</td>
</tr>
<tr>
<td>3</td>
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<td>31.8.10 13:45</td>
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</tr>
<tr>
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<td>31.8.10 15:00</td>
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<td>21</td>
</tr>
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<td>5</td>
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<td>24</td>
</tr>
<tr>
<td>6</td>
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<td>3.9.10 18:30</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>3.9.10 20:15</td>
<td>4.9.10 18:15</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>5.9.10 22:10</td>
<td>16</td>
</tr>
<tr>
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<td>6.9.10 01:00</td>
<td>7.9.10 10:00</td>
<td>33</td>
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<tr>
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<td>7.9.10 12:15</td>
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<tr>
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<td>15</td>
<td>11.9.10 20:00</td>
<td>12.9.10 06:00</td>
<td>10</td>
</tr>
</tbody>
</table>
S1.2 Chemical analysis

For organic analysis all samples were extracted with dichloromethane in an automated Soxhlet extractor (Büchi B-811). Surrogate recovery standards (D8-naphthalene, D10-phenanthrene, D12-perylene; PCB 30 and 185; 13C BDEs 28, 47, 99, 100, 153, 154, 183 and 209) were spiked on each PUF and GFF prior to extraction. The volume was reduced after extraction under a gentle nitrogen stream at ambient temperature. The extract was split into 2 portions, one for PAHs analysis, the second one for PCBs, OCPs and PBDEs analysis. The first portion of the extract was fractionated on a silica column (5 g of silica 0.063–0.200 mm, activated 12 h at 150 °C). The first fraction (10mL n-hexane) containing aliphatic hydrocarbons was discarded. The second fraction (20mL dichloromethane) was collected and then reduced by stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into an insert in a vial. Terphenyl was used as syringe standard, final volume was 200 µL. GC-MS analysis was performed on a 6890N GC equipped with a 60m×0.25mm×0.25 µm DB5-MS column (Agilent J&W, USA) coupled to 5973N MS (Agilent, USA). Injection was 1 µL splitless at 280°C, with He as carrier gas at constant flow of 1.5 mL min⁻¹. The GC programme was 80°C (1 min hold), then 15°C min⁻¹ to 180°C, followed 5°C min⁻¹ to 310°C (20 min hold). The MS was operated in EI+ mode with selected ion recording (SIR). The second portion of the extract was cleaned-up on a H2SO4 modified (44% w/w) silica column, analytes were eluted with 40 mL DCM/n-hexane mixture (1:1). The eluate was concentrated using stream of nitrogen in a TurboVap II concentrator unit and transferred into an insert in a vial. The syringe standards (13C BDEs 77 and 138 and native PCB 121) were added to all samples, the final volume was 50 µL. HRGC/HRMS instrumental analysis (for PBDEs) was performed on 7890A GC (Agilent, USA) equipped with a 15m × 0.25 mm × 0.10 um RTX-1614 column (Restek, USA) coupled to AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at the resolution of >10000. For BDE 209, the MS resolution was set to >5000. Injection was splitless 2 µL at 280°C, with He as carrier gas at 1 mL min⁻¹. The GC temperature programme was 80°C (1 min hold), then +20° min⁻¹ to 250°C, followed by 1.5° min⁻¹ to 260°C (2 min hold) and 25° min⁻¹ to 320°C (4.5 min hold). GC-MS/MS was used for indicator PCBs and OCPs analysis. 6890N GC (Agilent, USA) equipped with a 60 m × 0.25 mm × 0.25 µm DB-5MS column (J&W, Agilent, USA) coupled to Quattro Micro GC MS (Micromass, Waters, UK) operated in EI + MRM was used. Injection was splitless 3 µL at 280°C. He was used as carrier gas at 1.5 mL min⁻¹. The GC temperature programme was as follows: 80°C (1 min hold), then 15° min⁻¹ to 180°C, and finally 5° min⁻¹ to 300°C (5 min hold).
Passive air samplers (PAS) with PUF disks (150 mm diameter, 15 mm thick, deployed in protective chambers consisting of two stainless steel bowls; Klánová et al., 2008) were exposed at 5 different locations on board during 16 days. The variation of contaminants among these PAS samples was insignificant regarding the uncertainties inherent to the method, except for HCB which showed a high variability across PAS samples which is unexplained.

S1.3 Models of gas-particle partitioning
An adsorption model (Junge-Pankow; Pankow, 1987), and two absorption models (i.e. $K_{OA}$ models; Finizio et al., 1997; Harner and Bidleman, 1998) are tested. The Junge-Pankow adsorption model uses the vapour pressure of the subcooled liquid $p_L^0$, $\theta = c_J S / (p_L^0 + c_J S)$, (data taken from Falconer and Bidleman, 1994), $c_J$ should be approximately 171 Pa cm for PCBs (Pankow, 1987). The aerosol particle surface, $S$, was not measured, instead a typical value for maritime aerosols is adopted (4.32$\times$10$^{-7}$ cm$^{-1}$; Jaenicke, 1988). The absorption model of Harner and Bidleman, 1998, uses the log $K_{OA}$ and fraction of organic matter, $f_{OM}$: $\log K_p = \log K_{OA} + \log f_{OM} - 11.91$; and Finizio et al., 1997, uses only the $K_{OA}$ as predictor (data taken from Li et al., 2003): $\log K_p = 0.55 \log K_{OA} - 8.23$. For the fraction of OM we used lower (16%; Putaud et al., 2004) and upper (45%; Spindler et al., 2012) representing the whole diversity of sites in and around Europe. The particulate mass fraction, $\theta$, and partitioning coefficient, $K_p$, are defined by the concentrations in the two phases:

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

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

with $c_p$ and $c_g$ in units of ng m$^{-3}$, $c_p$ representing the whole particle size spectrum. Dual adsorption and absorption models (e.g. Lohmann and Lammel, 2004) are not tested because soot data or PM chemical composition data are not available.
S2. Results

S2.1 Atmospheric levels

Table S2. Concentrations in air, $c_{tot} = c_g + c_p$ (pg m$^{-3}$), of (a.) PCBs, (b.) OCPs (PeCB, HCB, DDX) and (c.) PBDEs. Values are listed as '<LOQ' (with 'LOQ' replaced by its value), if both $c_g < LOQ$ and $c_p < LOQ$, as $c_{tot} = c_g$, if only $c_p < LOQ$.

a.

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Table S2c.

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<td>0.72</td>
<td>1.41</td>
<td>0.92</td>
<td>5.83</td>
<td>6.20</td>
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<td>6.77</td>
<td>5.30</td>
<td>11.83</td>
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S2.2 Gas-particle partitioning

Table S3. Gas-particle partitioning of selected PCBs (mean log K_p ± standard deviation (median)), observed and predicted by the models Junge–Pankow (JP, assuming c_J = 171 Pa cm, S = 4.32×10^-7 cm^-1; Pankow, 1987), Harner and Bidleman (1998) (HB, assuming f_OM: 0.16–0.45), and Finizio et al. (1997) (F).

<table>
<thead>
<tr>
<th>PCB</th>
<th>Observed</th>
<th>JP model</th>
<th>HB model</th>
<th>F model</th>
</tr>
</thead>
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<tr>
<td>52</td>
<td>-1.56 ± 1.75 (-1.31)</td>
<td>-3.63 ± 1.86 (-3.56)</td>
<td>-4.66 – -4.21</td>
<td>-3.71</td>
</tr>
<tr>
<td>101</td>
<td>-1.56 ± 1.92 (0.00)</td>
<td>-2.95 ± 1.57 (-2.84)</td>
<td>-3.63 – -3.18</td>
<td>-3.43</td>
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<tr>
<td>153</td>
<td>-2.03 ± 1.44 (-2.16)</td>
<td>-2.25 ± 1.27 (-2.10)</td>
<td>-2.96 – -2.52</td>
<td>-3.04</td>
</tr>
<tr>
<td>138</td>
<td>-1.43 ± 1.62 (-0.82)</td>
<td>-2.13 ± 1.21 (-1.97)</td>
<td>-2.89 – -2.44</td>
<td>-2.92</td>
</tr>
<tr>
<td>180</td>
<td>-2.22 ± 1.28 (-2.26)</td>
<td>-1.76 ± 1.16 (-2.45)</td>
<td>-2.18 – -1.73</td>
<td>-2.64</td>
</tr>
</tbody>
</table>

The three gas-particle partitioning models tested (Table S3) underpredict K_p, except for PCB180 by the Junge–Pankow (JP) and Harner and Bidleman (HB) models. Even overestimation by the JP model had been reported for the heavier PCB congeners including PCB180 before (Landlová et al., 2014). Under- as well as overestimation has been reported for absorption models (Lohmann et al., 2000; Landlová et al., 2014). The JP model performs best for samples #6 and #15 (mean difference of K_p with observed: 0.02 and 0.06). These air masses were transported from central Europe and presumably received dust and sea salt.
influences along transport. An extensive evaluation of the gas-particle partitioning is not possible, due to absence of composition (e.g. fraction of organic matter) and humidity data. For the PCBs in most of the samples, the $K_{oa}$ model underestimates $K_p$, even more so considering a possible sampling artifact (underestimated $\theta$; Mandalakis and Stephanou, 2002) (Table 3). Similar (e.g., van Drooge et al., 2002) but also opposite (Mandalakis et al., 2002; Jurado et al., 2004) findings have been reported from remote marine sites, suggesting a strong influence of adsorption (Mandalakis et al., 2002). In conclusion, absorption models are not better predictors than the adsorption model.

### S2.3 Long-range transport

By the pathways they took, the air masses can be categorised in 5 groups (from west to east; Table S4), i.e. (a) south of the Pyrenees (sample #14), (b) west of the Alps (samples #1, partly #2-3, #11-13), (c) east of the Alps (partly samples #2-3, #4-6, partly #7-9, and #15), (d) Ionian Sea (sample #10), and (e) east of the Alps and western Turkey (partly samples 7-9).

#### Table S4. Specifications per advection pathway

<table>
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<tr>
<th>Pathways</th>
<th>Sample #</th>
<th>Direction of advection</th>
<th>Area of major residence time (C = central, S = southern, W = western)</th>
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<tr>
<td>a. South of Pyrenees</td>
<td>14</td>
<td>north-northwest west</td>
<td>Path 1: Ionian Sea, W Balkans 2: Ionian Sea, Italy 3: Balearic Sea, S France, Spain</td>
</tr>
<tr>
<td>b. West of Alps</td>
<td>1-3 11-13</td>
<td>west to northwest north to northwest</td>
<td>Tyrrenhian and Balearic Sea, south of France Ionian Sea, Italy, Adriatic Sea +surrounding countries</td>
</tr>
<tr>
<td>c. East of Alps</td>
<td>2-3 4-6 7-9 15</td>
<td>north to northwest north-northeast west-northeast northwest</td>
<td>Adriatic Sea, W Europe Adriatic Sea, C Europe W Balkans, C Europe Tyrrenhian Sea, Italy, C Europe, W Europe</td>
</tr>
<tr>
<td>d. Ionian Sea</td>
<td>10</td>
<td>North</td>
<td>Libyan, Ionian and Aegean Seas</td>
</tr>
<tr>
<td>e. East of Alps and west coast of Turkey</td>
<td>7-9</td>
<td>north-northwest</td>
<td>Aegean Sea, C Europe</td>
</tr>
</tbody>
</table>

At the start of the cruise air arrived from the west (pathways b), possibly influenced by Rome and Marseille (sample #1). When the ship moved towards west, air was advected from north-northwest, i.e. east of the Alps (pathways c) passing over the Adriatic Sea (samples #2-6). During most of the eastern part of the cruise (samples #7-9), air coming from central Europe underwent subsidence above the Aegean Sea and resided at the west coast of Turkey (pathways e), before arriving at the ship’s position. Back in the Ionian Sea (samples #10-14), air was sampled that circulated in a high pressure system above the Ionian Sea (no suspected influence from land based emissions within the last 24-60 hours before sampling, although
sample #13 might have been influenced by emissions from a nearby harbour). Sample #14 collected air that was transported from the northwest via the high pressure system to the ship’s position, as well as air from the west that had passed over Spain (pathways a). Finally, during sample #15, air again was advected from northwest (pathways c), passing over Vienna and Rome before arriving over Palermo, Sicily.

Figure S1. Concentration-weighted residence times of air masses during the last 5 days before arrival at the ship location grouped per pathways
a) South of the Pyrenees: sample #14
Fig. S1b) West of the Alps: 1, partly samples #2-3 and 11-13
S1c) East of the Alps: partly samples #2-3 (see Fig. 2b), samples #4-6, partly samples #7-9 (see Fig. 2e), sample #15

d) Ionian Sea: sample #10
Fig. S1e) East of the Alps and west coast of Turkey: partly samples #7-9.

Fig. S2. Distribution of the product of fire-related PM$_{2.5}$ mass flux (kg m$^{-2}$ s$^{-1}$) and residence times of air masses during the last 5 days before arrival at the ship location (s) for the entire measurement period, 27.8.-12.9.2010.
References


