

RECENT OBSERVATIONS OF RE-VOLATILISATION OF SEMIVOLATILE ORGANIC COMPOUNDS INCLUDING POPS FROM MEDITERRANEAN SEAWATER

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Introduction

The central and eastern Mediterranean sea is a receptor area of emissions from mainly land based sources, tough 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 air pollution in the Mediterranean. Persistent Organic Pollutants (POPs) are a group of pollutants to be monitored under the auspices of the Stockholm Convention. Due to their long life times they cycle between the different environmental matrices and to bio-accumulate in marine life. Air-sea exchange of POPs and PAHs was reported, showing re-volatilisation to occur, even from open and remote seawater¹⁻⁷. This had been predicted by multicompartamental modelling for 2-4 ring PAHs and DDT⁸⁻¹⁰. This study aims to investigate levels of organic pollutants in air and water in summer in the central and eastern Mediterranean, assess air mass origin and air-sea exchange.

Materials and methods

Samples were collected along a cruise of RV Urania in the central and eastern Mediterranean, 27 August – 11 September 2010 and at 3 coastal sites in the Aegean in July 2012 (Finokalia, Crete, Michaniona and Loudias in the Thermaikos Gulf). During the cruise, 15 high volume samples (8-36 h) of both the gaseous (polyurethane foam plugs, PUF) and particulate phases (glass fibre filters) were collected. The levels of 27 polycyclic aromatic hydrocarbons (PAHs) were analysed, field LOQs corresponded to <0.01-0.33 ng m⁻³ for individual PAHs. Water samples (2–2.5 L) were taken using the stainless steel Rosette sampler equipped with 24 Niskin bottles deployed in water at 1.5 m depth for surface water sampling. LOQ was 0.1 ng L⁻¹. At the coastal sites, passive air samplers (PAS, PUF disk in protective chamber consisting of two stainless steel bowls¹¹) were deployed. All PAS data are corrected for field blanks from the very site. They are expressed as concentrations using effective sampling volumes based on side-by-side high volume active air sampling and PAS at one of the sites (Finokalia) silicone rubber (SR) sheets from Altesil (Altec, Great Britain,) were used (28 days, 1 m depth) as passive samplers of free dissolved contaminants in water^{12,13}. Concentrations were calculated using the exponential uptake model described in Smedes (2007)¹⁴, sampling rates were estimated by fitting performance reference compound dissipation data from sampler to the model described by Booij and Smedes, 2010¹⁵. The contaminants polychlorinated biphenyls (7 PCB congeners), polybrominated diphenylethers (9 PBDEs), penta- and hexachlorobenzene (PeCB, HCB), hexachlorocyclohexane (5 HCH isomers) and DDT (and metabolites, 6) were identified and quantified using GC-MS¹⁶.

State of phase equilibrium and vertical flux at the surface are determined based on the Whitman two-film model^{1, 17, 18}. The fugacity ratio (*FR*) is calculated as: $FR = f_a/f_w = C_a * R * T_a / (C_w * H_{T_w, salt})$, with gas-phase concentration C_a (ng m⁻³), dissolved aqueous concentration C_w (ng m⁻³), universal gas constant R (Pa m³ mol⁻¹ K⁻¹), water temperature and salinity corrected Henry's law constant $H_{T_w, salt}$ (Pa m³ mol⁻¹), and air temperature T_a (K). Uncertainties dominated by the accuracy of the Henry's law constant, $H_{T_w, salt}$, result in an equilibrium window of $0.3 < FR < 3.0$ ^{6,19,20}, subsequently, $FR > 3.0$ indicates net deposition and $FR < 0.3$ net volatilisation. The diffusive air-seawater gas exchange flux (F_{aw} , ng m⁻² day⁻¹) is calculated as $F_{aw} = k_{ol}(C_w - C_a RT_a / H_{T_w, salt})$, with air-water gas exchange mass transfer coefficient k_{ol} (m h⁻¹)^{1,20}.

Assuming wood burning to be the only source of retene (RET) to the East Mediterranean (28–45°N, 8–30°E), F_{aw} in this domain is simulated for the for 2005-2010 by a non-steady state zero-dimensional model of intercompartmental mass exchange²¹. This 2-box model predicts concentrations by integration of two coupled ordinary differential equations that solve the mass balances for the atmospheric marine boundary layer and the

seawater surface mixed layer. The source term is derived from daily fire-related PM_{2.5} emissions as provided by the Global Fire Assimilation System (GFASv1.0²²) in combination with an emission factor²³.

Results and discussion

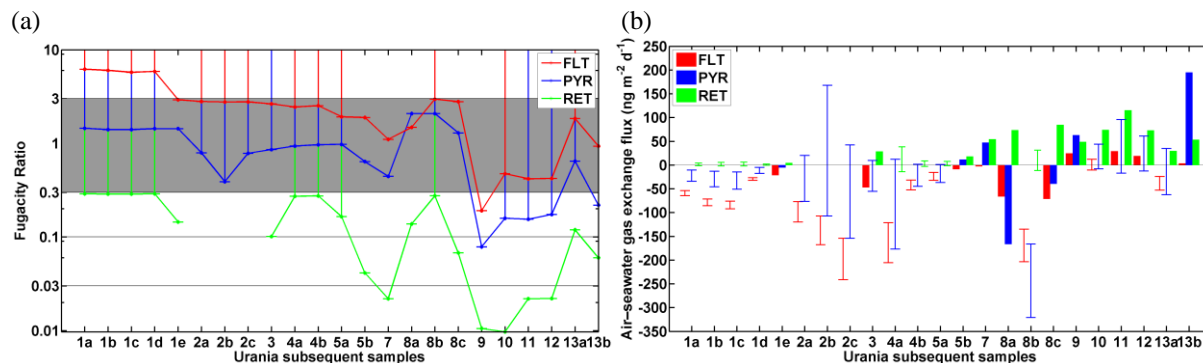
August–September 2010 the mean total (i.e., sum of gaseous and particulate) PAHs concentration found in air, was 1.45 ng m⁻³ (time-weighted mean, 0.30–3.25 ng m⁻³). In seawater, only 3 PAHs could be quantified, RET = 0.1 (<0.1–0.5; n=12) pg L⁻¹, fluoranthene (FLT) = 0.1 (<0.1–0.3; n=10) pg L⁻¹, and pyrene (PYR) = 0.2 (<0.2–0.9; n=7) pg L⁻¹.

The concentrations in air at the Aegean coastal sites, July 2012, ranged: PAHs 0.07–1.0 ng m⁻³, PCBs 8.8–639 pg m⁻³, PeCB ≈ 1 pg m⁻³ (Crete only), HCB 8–100 pg m⁻³, HCH 3.5–310 pg m⁻³, DDTs 3.0–460 pg m⁻³, BDEs 0.22–2.8 pg m⁻³. The concentrations in seawater range: PAHs 0.74–1497 (4.44–871 for the PAHs measured in air) pg L⁻¹, PCBs 0.15–10.1 pg L⁻¹, PeCB 1.11–5.85 pg L⁻¹, HCB 6.44–19.08 pg L⁻¹, HCH 2.07–62.93 pg L⁻¹, DDTs 0.84–159.30 pg L⁻¹, BDEs 3.11–6.24 pg L⁻¹.

During both August–September 2010 and July 2012 the predominant origin of the air masses was central and eastern Europe. During the measurements in July 2012 advection from north which earlier had passed the western Mediterranean occurred during 7 days and from the Caucasus during 7 days.

Fig. 1 presents the fugacity ratios derived for the RV Urania cruise and the Aegean coastal sites samples, and the air-sea exchange fluxes along the RV Urania cruise. Concerning the RV Urania cruise samples, FLT and PYR are indicated to be close to phase equilibrium, with most of the FR values within the uncertainty range, one sample (No. 1) indicating deposition of FLT and two (No. 9 and 13) indicating volatilisation of FLT and PYR, respectively. In comparison with earlier observations of FLT and PYR air–sea exchange in the eastern Mediterranean in 2001/02 and 2007^{3,6} and considering spatial and temporal variabilities no trend, in particular no reversal of air–sea exchange is evident.

At the Aegean coastal stations (July 2012) the FRs of the PAHs and HCHs were in or close to phase equilibrium. At the remote site Finokalia (low atmospheric contamination levels), the FR of some PCBs (5-6 chlorinated) and *p,p'*-DDE indicates net volatilisation. The same holds for PeCB and HCB at all 3 locations. Net deposition of PBDEs (not in Fig. 1c) is obvious with FRs ranging 5.5–1.6 × 10⁵, except for BDE 28 at Finokalia (FR = 0.98).



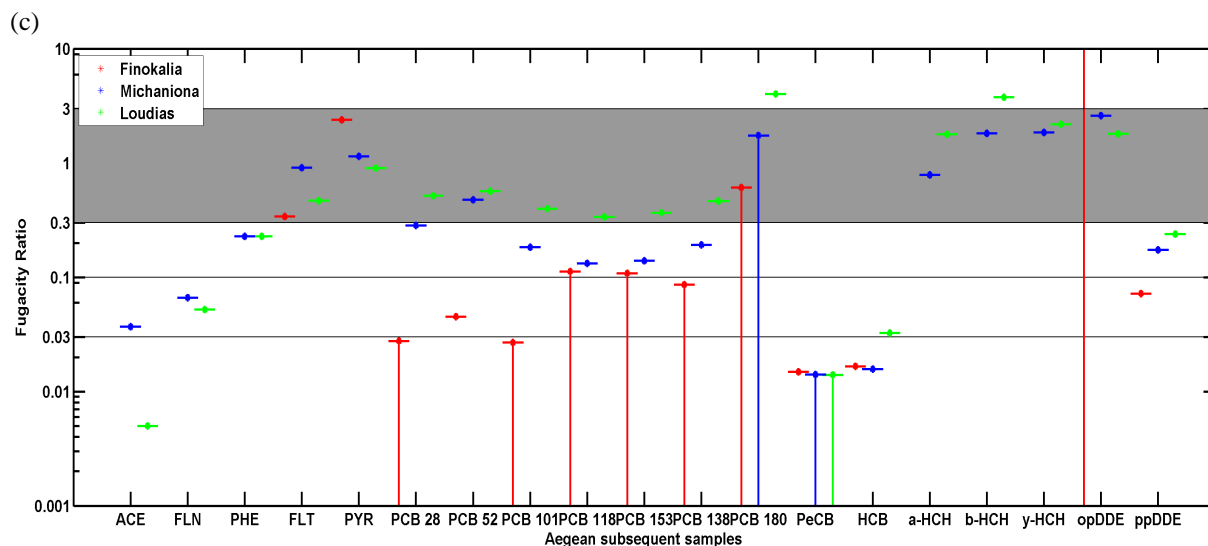


Fig. 1. Air-sea exchange, (a) fugacity ratios $FR = f_a/f_w$ (volatilisation < 0.3 , deposition > 3 , grey area close to phase equilibrium) along the cruise of RV Urania, September-October 2010, (b) flux F_{aw} ($\text{ng m}^{-2} \text{d}^{-2}$; volatilisation > 0 , deposition < 0) of FLT, PYR and RET. Error bars indicate sea water concentration $C_w < \text{LOQ}$ along the cruise, and (c) as (a) but at Aegean coastal sites during July 2012 (*o,p'*-DDE ranges till 151). The x-axis depicts the correspondence of sequential pairs of air samples (1–13) and water samples (a–e).

RET is found net-volatilisation throughout most of the cruise (Fig. 1a,b). Among the highest fluxes ($> 50 \text{ ng m}^3 \text{ d}^{-1}$) are some samples with very low FR, < 0.03 . RET is commonly considered as biomarker for coniferous wood combustion²⁴, hence a decrease in wildfires could explain the suspected RET volatilisation. 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. Fig. 2a shows that volatilisation flux is predicted smaller in magnitude than the net-deposition flux during the fire season, but correspondingly, i.e. higher after intense fire seasons. F_{aw} is predicted highly fluctuating, also during the observational period (Fig. 2b). Even under UEPS the model is underpredicting F_{aw} (Fig. 2b).

POPs and PAH pollution of the atmospheric Mediterranean environment was below previous observations^{3,25,26}. This might reflect emission reductions. It is concluded that future negative emission trends or interannual variability of regional sources may trigger the sea to become a secondary source of POPs and PAHs through reversal of diffusive air–sea exchange.

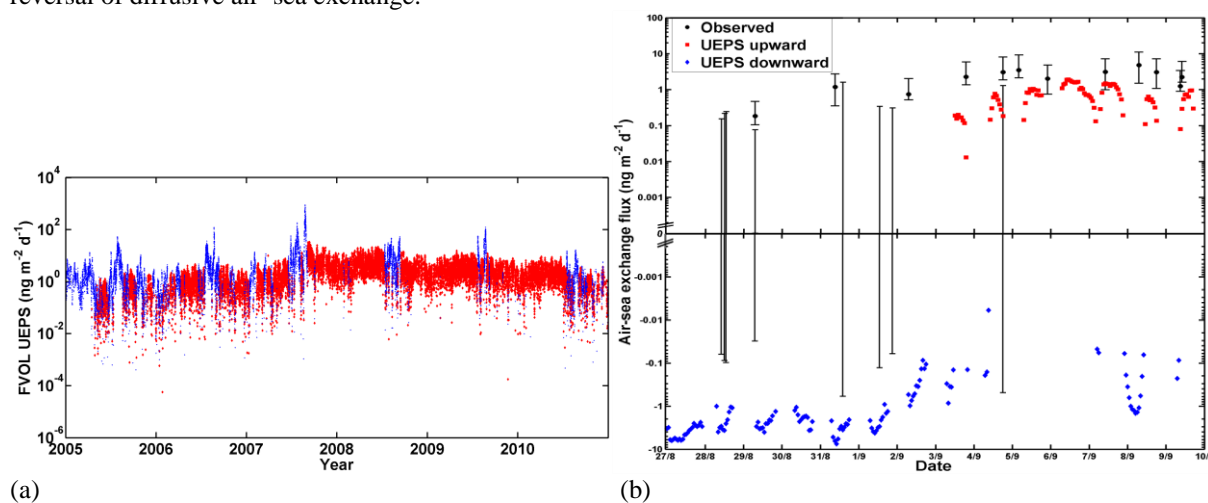


Fig. 2. Diffusive air–sea exchange flux, F_{aw} , of RET ($\text{ng m}^{-2} \text{d}^{-1}$; downward in blue and upward in red) using the upper estimate parameter set (UEPS) for the Eastern Mediterranean (28–45°N/8–30°E) (a) model predicted for 1.1.2005–31.12.2010 and (b) model predicted and observed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

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