Long-range atmospheric transport and transformation of persistent organic pollutants in the Eastern Mediterranean (POPLRTMED)

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- Introduction and motivation

Environmental exposure towards persistent organic pollutants (POPs) is determined by long-range atmospheric transport (LRT). Most POPs are semivolatile organic compounds, i.e. partition between the phases of aerosols and undergo re-volatilisation from the sea and soils (multi-hopping). Their cycling (LRT, local procsesses such as air/sea exchange, air/soil exchange, gas/particle partitioning, and chemical reactivity) is insufficiently understood. We have addressed processes of POPs cycling by measurements in aerosols at polluted and remote sites (e.g., Lammel et al., 2009a, 2010a, 2010b), of fluxes at the ground (terrestrial: Lammel et al., 2011; Škrdlíková et al., 2011; marine: Lammel et al., 2013; Mai et al., 2013) and large-scale modelling and source attribution studies (e.g., Lammel et al., 2009b; Dvorská et al., 2012; Stemmler and Lammel, 2012).

- Scientific objectives

We aim to advance the understanding of POP cycling far from sources by addressing key processes in the marine boundary layer in air masses characterized at a receptor site and influenced by regional and remote sources (concurrently with measurements at other sites in the receptor region, see below, Method and Exp'l setup). Choice of site and time are furthermore motivated by the results of earlier studies carried out by the host institution (University of Crete, Dept. of Chemistry) and in the context of international field campaigns. In particular, it had been shown that semivolatile organics undergo photochemistry (at least to some extent) in the Mediterranean atmospheric environment (Mandalakis et al., 2003; Tsapakis and Stephanou, 2007). Dry deposition and eventually accumulation in (Mandalakis et al., 2005; Guitart et al., 2010) and volatilisation from (e.g. Berrojalbiz et al., 2011; Tsapakis et al., 2006) the sea surface layer are other relevanted processes.

This project addresses:

- Concentrations in air, aerosol mass size distributions and determination of environmental parameters influencing the gas/particle partitioning of POPs,
- concentrations in seawater and determination of environmental parameters influencing the air/sea exchange of POPs,
- concentration changes along transport and determination of environmental parameters influencing the reactivity of POPs (in cooperation with sampling at other stations (see below) and meteorological analysis).

The selected POPs are: polycyclic aromatic hydrocarbons (PAH), nitro- and oxo-PAH, polybrominated diphenyethers (PBDE), organochlorine pesticides (e.g. HCH, DDT), polychlorinated biphenyls (PCB). For some of these substances very few data from remote environments exist so far.

- Reason for choosing station

Finokalia is situated in a receptor region, receiving air influenced by regional (Aegean) and remote (central and eastern Europe) sources (in particular in summer). The Large scale flow in the Aegean is

often carrying pollution from central and eastern Europe, most likely in summer (Mihalopoulos et al., 1997; Lelieveld et al., 2002).

The measurements could be complemented by other simultaneous measurements (with similar methods, partly to be analysed in the same laboratory) in the region (run by university institutes in Thessaloniki, Bursa, Izmir and the NCSR Demokritos institute; Fig. 1). In the direct vicinity of Finokalia the shore could be accessed in order to address air-sea exchange of organics.

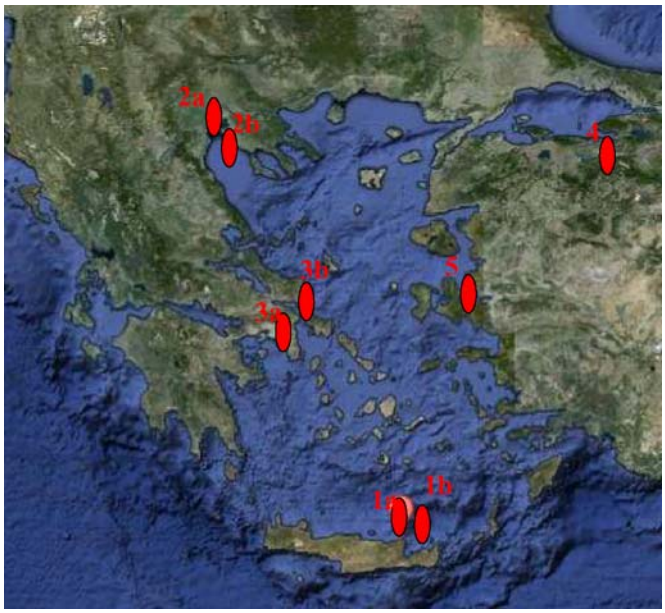

Fig. 1: Sites contributing air (1-5) and water (1, 2) measurements to POPLRTMED, intensive measurement period 2.-13.7.2012

- Method and experimental set-up

Particle-size resolved and (total) filter sampling of the particulate phase and collection of trace gases to sorbents was performed using a 6-stage cascade impactor, 2 high-volume samplers (F = 32-68 m^3/h) and 1 low-volume sampler (F ≈ 2 m^3/h; for off-line analysis in the laboratory) at Finokalia observatory. Day and night sampling (sampling durations between 9 and 72 h). Sampling protocols and methods were harmonized among the locations of simultaneous sampling in the region. Aerosol number concentration, N (cm-3), was determined at Finokalia using an optical particle counter (Grimm; 31 channels between 0.25 and 32 µm of aerodynamic particle diameter).

At a coastal site in ca. 3 km direct distance from Finokalia, Selles (site 1b in Fig. 1), directly at the shore, air-sea exchange (vertical flux) of POPs was addressed by micrometeorological measurements, low-volume sampling for organics and in situ-measurement of ozone, CO_2 and water vapour at 2 heights above ground (vertical gradient; e.g. Lammel et al., 2011). In addition, meteorological parameters were measured using mobile stations and seawater was sampled (for off-line analysis in the laboratory).

Passive air samples (method: Klánová et al., 2006) have been exposed at Finokalia and Selles and passive water samples (method: Booij and Smedes, 2010) 2 sites close to the shore of Selles. In addition, few surface (film) and grab water samples were collected.

- Preliminary results and conclusions

The chemical analysis of 235 air samples (gaseous and particulate fractions) and 6 water samples from Finokalia (including Selles) and ca. 250 samples from sites 2-5 (Fig. 1) will expectedly be completed in 6-9 months.

The routine measurements at Finokalia indicated little anthropogenic influence on atmospheric composition as expected. The POP levels in air data will be analysed and interpreted together with data from simultaneous sampling at other locations run by partner institutions in the region, as well as from own monitoring programmes (in the Czech Rep. and Europe-wide). The large scale flow was favourable with this regard, with advection of air parcels to Finokalia across the Aegean Sea. Many of these had passed Izmir or Bursa 10-24 h before. According to relatively high wind speeds (>5 m/s almost throughout the measurement period) at Selles we expect particular difficulties for detection and quantification of vertical gradients and, hence, fluxes.

- Outcome and future studies

Not much can be said before the samples collected have been analysed. We expect complementary data for a number of substances which had been rarely observed in the marine boundary layer (e.g. nitro- and oxy-PAHs, PBDEs), and insights into the processes determining gas-particle partitioning and sinks of few PAHs and, eventually, PCB congeners in a clean marine boundary layer, i.e. photochemical transformation and air-sea exchange.

Future studies are tentatively planned to focus on air-soil exchange, but planning is subject to outcome of this campaign among other unknowns.

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