

Modelling of transport and degradation of selected organic pollutants in the atmospheric environment of the Mediterranean

Persistent organic pollutants (POPs) are organic chemicals that resist abiotic and biotic degradation in the environment (lifetimes of many days in air, many weeks to years in seawater and soil), 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. Several pollutants (hundreds of individual substances and isomers) are covered by international conventions, like the Stockholm Convention (UNEP, 2001) and UNECE Convention on Long-range Transboundary Air Pollution (CRLTAP) (UNECE, 1998).

Due to the cycling characteristics (volatilisation from ground surfaces, phase partitioning in air) 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. The aim of this study is the development and application of data analysis and numerical modelling tools suitable for the investigation of POPs cycling in the atmospheric environment. Gas-particle partitioning models are tested in order to advance the understanding of phase partitioning of POPs in air and, hence, better assess their long-range transport potential. Pathways of long-range atmospheric transport are analysed in order to identify and assess sources on the regional scale.

The most common route of export of pollutants out of Europe leads through the central and eastern Mediterranean, resulting in elevated concentrations in there. Two field data sets from this region were used to apply existing and develop new data evaluation tools. The first, contains air and seawater concentrations of selected POPs (PAH, PCBs, DDXs, PBDEs, penta- and hexachlorobenzene) that were measured during a ship-borne campaign in 2010. The second includes concentrations of PAHs and a few of their degradation products in air, sampled at two coastal locations in the Aegean in 2012.

The first was used to test gas-particle partitioning models, apply an air-sea exchange model and a Lagrangian particle dispersion model (FLEXPART). The gas-particle partitioning models tested for selected PAHs and PCBs, underpredict the particulate mass fraction in most of the samples. The application of FLEXPART to track air mass origin was further developed towards a quantification of various sources on the regional scale (100-1000 km) contributing to individual samples.

The diffusive air-seawater gas exchange flux, simulated with a non-steady state two box model, showed that the PAHs fluoranthene and pyrene were mostly 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. To identify sources contributing to the pollution of the marine atmospheric environment by POPs, air masses were categorized according to pathways taken, besides other.

For selected transport paths between two locations in the Aegean, the chemical and physical degradation processes are simulated by a Lagrangian travelling box model. This model is developed, to study the gas-particle partitioning, wet and dry deposition and reaction with oxidants for selected POPs (PAHs, PCBs, PBDEs) during transport. The meteorological parameters and oxidant levels along the pathways are obtained from FLEXPART-WRF and the Multiscale Atmospheric Transport and Chemistry (MATCH) model.