MODELLING THE BEHAVIOUR OF LEGACY AND EMERGING POLLUTANTS IN THE ATMOSPHERE OF THE IBERIAN LEVANTINE COAST

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Introduction

The amount of legacy and emerging compounds being object of concern raises some barriers when trying to obtain a comprehensive assessment. Being the atmosphere a key route of transport, it is important to measure the levels of the target contaminants in the air. And even if some effects are already reported in literature, there are still numerous regions where the most basic information does not exist. In this sense, the southeast Iberian Peninsula is one of those areas. With specific climatic fingerprints, it can be an excellent location to assess the atmospheric distribution of contaminants and the influence of the meteorological parameters associated.

Given the low maintenance costs and easy set-up, several types of passive air samplers (PAS) have been recently used at regional, continental and global scales and their feasibility was demonstrated in deployments across large areas[1,2]. Passive air samples were collected in 13 sites, deploying polyurethane foam (PUF) disks sequentially for three months in the period of one year, comprising four sampling campaigns, one per season.

The establishment of strategies for sampling and modelling of SVOCs in the atmosphere aiming the definition and validation of their spatial, temporal and chemical transport patterns can be achieved by an integrated system of third-generation models that represent the current state of knowledge in air quality modelling and field data collected in sampling campaigns.[3,4] This has implications in the fields of meteorology, atmospheric chemistry and even climate change. The modelling methods currently applied for SVOCs use very simple mass balance techniques or have deterministic approaches, reflecting the complexity to characterise adequately the chemical transport processes. These limitations urge for more experimentally-based information and hence the need to combine both experimental campaigns and modelling in order to address the problem properly[5], including multi-matrix approaches whenever possible. Moreover, measurements of pollutants such as PAHs are labour-intensive compared to those of criteria air contaminants such as ozone and particulate matter, and the processes governing their atmospheric fate and representation within chemistry transport models (CTMs) are not yet well understood[6]. A number of atmospheric modelling studies have tried to characterise the levels and spatial-temporal patterns of PAHs (most of them focusing specifically on BaP) using CTMs both on global[7,8] and regional scales[9,10]. These authors identify a lack of measurement data in Europe to evaluate the behaviour of the CTMs against observations.

Five different chemical classes were analysed: brominated flame retardants (BFRs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and synthetic fragrances (musks). The first four have been studied for some time, but musks only recently have raised concern, due to their high consumption and release into the environment, important bioaccumulation and endocrine disrupting potential[11].

The main objective of this work was to assess the levels and the spatial and temporal patterns of these pollutants in the Levantine coast (south-east Iberian Peninsula). Atmospheric transport features were also investigated, in correlation with the meteorological data, showing a decisive influence of these parameters. Field data and CTMs were combined to produce a comprehensive overview of a region with a severe lack of information on these pollutants of concern.

Materials and methods

Field sampling sites

The deployment of the polyurethane foam (PUF) disks for the passive air sampling of the target compounds was done in 13 sites, as shown in Figure 1. The disks were collected and replaced by new ones every 3 months, comprising 4 campaigns (one per season, covering a whole year).

Figure 1. Sampling map (SE Iberian Peninsula).

Analytical methodology

To proceed to the quantification of the PUFs, a new multi-compound analytical procedure based on Soxhlet extraction and two clean-up methods - solid phase extraction (SPE) and gel permeation chromatography (GPC) - was employed before quantification by GC/MS to help on the understanding of the atmospheric behaviour of semi-volatile organic contaminants (SVOCs) in the southern Iberian Peninsula.

PUF disks were extracted with 200 mL of Hex/DCM (1:1) in a J.P. Selecta (Barcelona, Spain) tandem Soxhlet ultrasonic bath for 16 hours. After solvent cool-down, extracts were transferred into pear-shaped flasks and evaporated to approximately 1 mL in a Büchi R-210 rotary evaporator (Flawil, Switzerland). Solid phase extraction (SPE) clean-up was performed using glass columns packed with 5 g alumina topped with sodium sulphate. Gel permeation chromatography (GPC) was used as an additional clean-up step. For this, glass columns equipped with PTFE stopcocks and glass caps were prepared using 6 g of Bio-Beads® S-X3. Samples were eluted with 40 mL of Hex/DCM (1:1) of which the first 15 mL were discarded. Subsequently, solvent was evaporated to near dryness by rotary evaporation and nitrogen blow-down and reconstituted in 100 μL.

Instrumental analysis of the samples was performed using two different methods. For BFRs, PCBs and OCPs, a Varian GC-MS system (Palo Alto, CA, USA), equipped with a Varian 450-GC gas chromatograph, a CP-1177 split/splitless injector, a CP 8410 autosampler and a Varian 240-MS ion trap mass spectrometer operated in

electron ionization mode (70 eV) with a filament emission current of 50 mA was used. Chromatographic separation was carried out using an Agilent (Santa Clara, CA, USA) CP-Sil 8 CB capillary column (50 m x 0.25 mm I.D., 0.2 µm film thickness) equipped with a fused silica deactivated retention gap (5 m × 0.25 mm I.D.). Temperatures of the transfer line, manifold and ion trap were 250 °C, 50 °C and 250 °C, respectively.
For PAHs and musks, a Varian 4000 GC/MS (Palo Alto, CA, USA) ion trap mass spectrometer also operated in in electron ionization (70 eV) mode with a filament emission current of 50 mA equipped with the same kind of injector and autosampler was used. Capillary column was an Agilent J&W DB-5 (30 m x 0.25 mm, 0.25 µm film thickness). Transfer line, manifold and ion trap temperatures were 250 °C, 50 °C and 200 °C.
In both methods, acquisition was done using time-scheduled selected ion storage (SIS) using retention time windows. Identification of the target compounds was based on the GC retention times relative to the internal standard and relative abundance of the monitored ions.

Modelling

In this study, the Weather Research and Forecasting (WRF)+CHIMERE modelling system, with a resolution of 9 km for the Iberian Peninsula and 3 km for southeastern Iberian Peninsula has been run and evaluated against the available observation from the monitoring campaign, from December 2012 to November 2013. A summary of the set of parameterisations employed can be seen in Table 1.

Table 2. Set of parameterisations used in the WRF+CHIMERE modelling system.

WRF	**CHIMERE**
Microphysics → **WSM3** PBL → **Yonsei University** Radiation → **CAM** Soil → **Noah LSM** Cumulus → **Kain-Fritsch**	Chemical mechanisms → **MELCHIOR2** Aerosol chemistry → Inorganic (thermodynamic equilibrium with **ISORROPIA**) and organic (**MEGAN SOA** scheme) aerosol chemistry Natural aerosols → **dust, re-suspension and inert sea-salt** Boundary conditions → **LMDz-INCA+GOCART**

As a complement, back trajectories of the air masses in each sampling point were assessed using the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model from the NOAA (National Oceanic and Atmospheric Administration).

Results and discussion

As seen in Figure 2, for the total PAHs levels ranged between 58.5 and 5674.7 ng/PUF and for total SMCs between 0.1 and 1343.2 ng/PUF. For PCBs levels were 0.1 – 25.2 ng/PUF, for BFRs 0.2 – 9.5 ng/PUF and for OCPs, 1.6 – 6.2 ng/PUF.
Higher levels for PAHs and SMCs were detected in the colder months (autumn/winter) while lower levels were found in the warmer ones (spring/summer). The same was observed for OCPs. In the case of PCBs and BFRs, the predominance was usually found in the spring/summer seasons.
Briefly considering the individual locations, the highest concentrations of PAHs and SMCs were detected in Caravaca and San Javier. The PUF in the latter site was placed close to an airport, which can account as a point source. For BFRs, PCBs and OCPs the prevalence was seen in the largest urban settings, such as Cartagena.

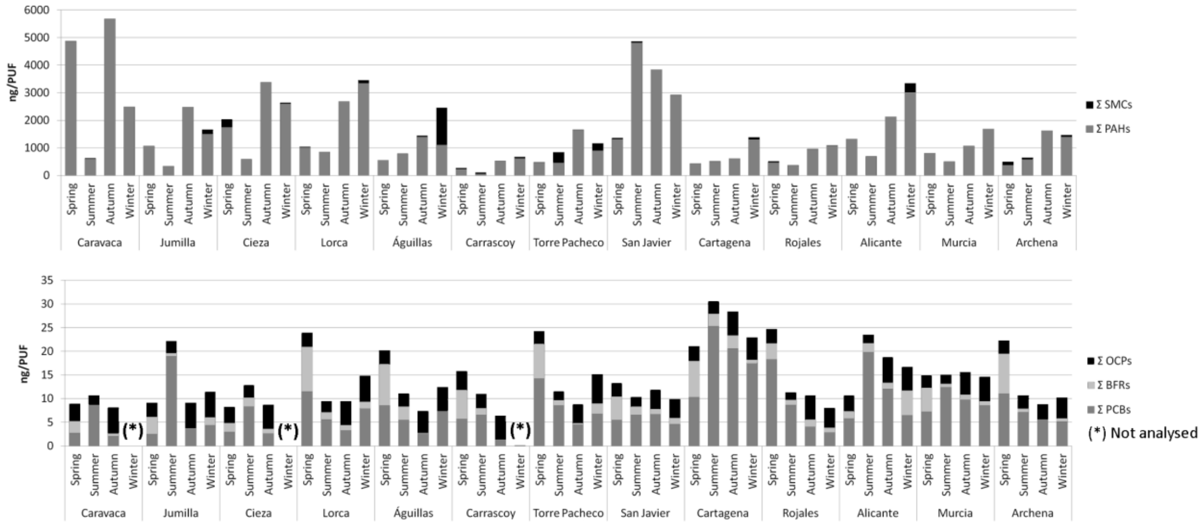

Figure 2. Levels for total SMCs, PAHs, OCPs, BFRs and PCBs for the four seasons in the 13 sampling sites.

Overall, PAHs and SMCs showed the main levels in the atmosphere. Different patterns of occurrence were found for the different chemical classes. In this first approach, the geographical and land use patterns found preclude very important findings, and the coupling of these field data and chemistry transport models (CTMs) to assess comprehensively the behaviour of all these compounds produced valuable information in such regard.

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