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MULTI-COMPONENT DETERMINATION OF ATMOSPHERIC SEMI-VOLATILE ORGANIC COMPOUNDS IN TARRAGONA COUNTY, CATALONIA, SPAIN

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Introduction

Semi-volatile organic compounds (SVOCs) are chemicals characterized by their bio-accumulative potential, environmental persistence and toxic effects in humans and wildlife¹. These properties make SVOCs transboundary chemicals via long-range atmospheric transport (LRAT), capable to reach remote and sensitive regions, away from the emission sources²⁻⁷. SVOCs include a wide variety of compounds, such as brominated flame retardants (BFRs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs)⁸, whose environmental analysis is a crucial step in their global control.

The need for SVOCs monitoring has led to the development of a wide range of sampling devices and analytical methods. However, some of these are time-consuming and/or use large amounts of organic solvents, with potential environmental problems and high economic costs^{8,9}. For this reason, the implementation of alternative sampling and analytical methodologies is an essential step in atmospheric monitoring. Passive sampling can provide a first approximation of SVOCs concentrations in the environment, involving low maintenance and allowing sampling in remote or poorly accessible areas^{5,6,10}. Passive air samplers (PAS), which are based on the theory of physical advection and diffusion¹¹, are commonly used and a suitable complement to vegetation and soils¹²⁻¹⁵. Moreover, it is also important to develop analytical methods covering the detection of a large number of environmental pollutants. Very recently, Silva et al.⁸ developed a multi-component method to simultaneously extract 5 classes of SVOCs (BFRs, PCBs, OCPs, PAHs, and synthetic musk fragrances) from one sample, being validated for the analysis of pine needles.

This study was aimed at estimating the levels SVOCs concentrations in Tarragona County (Catalonia, Spain), where the most important chemical/petrochemical complex in Southern Europe is located. Passive samplers, including polyurethane foam disks (PUFs), as well as vegetation and soil, were employed. Subsequently, the multi-component protocol developed by Silva et al.⁸ was used to quantify the content of SVOCs in each sample. In this abstract, preliminary results on the analysis of PUFs are detailed.

Materials and methods

PAS with PUFs (Newterra, Beamsville, ON, Canada) were used for air monitoring. Prior to their deployment, PUF-disks were pre-cleaned by Soxhlet extraction for 24 hours with dichloromethane (DCM)¹⁶. Then, they were dried in a vacuum desiccator, and stored in DCM-cleaned brown glass jars¹⁶. Eight PAS containing PUF-disks were deployed for a period of 2 months (November 2014-January 2015) at several areas of Tarragona County (Figure 1), each one characterized by the presence of different potential emission sources. The distribution of the sampling sites was as follows: two samples under the potential influence of petrochemical emissions, including a big oil refinery (Puigdelfí=P1 and Constantí=P2); two samples close to chemical industries (La Laboral=C3 and La Canonja=C4); two samples in urban areas (Tarragona=U5 and Vila-seca=U6); and two samples in background sites, at least 30 km away from the area of influence of all the suspected sources of contamination (Cambrils=B7 and

Torredembarra= B8). In parallel, 27 samples of vegetation (*Piptatherum* sp.) and 29 of surface soil were also collected in the 4 areas under study.

Air levels of five classes of SVOCs (BFRs, PCBs, hexachlorobenzene (HCB), PAHs, and synthetic musk fragrances) were simultaneously quantified in each one of the PAS. For that purpose, for the very first time an innovative multi-component protocol⁸ was used for the extraction of PUFs. Air extracts were obtained by ultrasonic solvent extraction (USE) and quantified by gas chromatography/mass spectrometry (GC/MS), with an ion trap mass spectrometer operated in electron ionization mode (70 eV). The vegetation and soil samples are currently being processed.

Results and discussion

The total amounts of SVOCs accumulated in air samples from different areas of Tarragona County (Catalonia, Spain) are depicted in Figure 2. PAHs levels ranged from 2098 to 4333 ng/PUF (Figure 2A), being in agreement with other surveys previously conducted in this area^{10,17}. In 2013, PAHs amounts in PAS deployed for 2 months ranged from 670 to 7530 ng/PUF, while in 2014, minimum and maximum levels were 1363 and 7866 ng/PUF, respectively. The highest concentrations of PAHs were found in the petrochemical area (max: 4333 ng/PUF), more specifically in the point P1, corresponding to the neighborhood of Puigdelfí (village of Perafort). This finding agrees with the results of the 2014 campaign¹⁰, when Puigdelfí also showed the highest incidence of PAHs (7866 ng/PUF). In addition, the present value is relatively close to that reported in the 2013 campaign for the village of Vilallonga del Camp (7530 ng/PUF)¹⁷, a nearby town. This sampling point is located in the vicinity of a big oil refinery, thus under the potential influence of petrochemical emissions. This is confirmed by a general increase of PAHs associated to the presence of chemical industries reported by other international studies¹⁸.

Regarding PCBs, the values detected in Tarragona County ranged from 2.88 to 120 ng/PUF (Figure 2B). In contrast to PAHs, the highest concentrations of PCBs were found in the chemical zone (max: 121 ng/PUF), more specifically in point C3 (La Laboral). These chemicals were extensively used worldwide in electric industries for their chemical stability¹⁹. Although their production was banned in most countries, the current value could be due to the presence of a chlor-alkali plant and various electrical substations in the vicinity, as well as the legacy of their use in the past.

Finally, similar concentrations of synthetic musk fragrances (0.38 to 13.4 ng/PUF), BFRs (1.30 to 2.80 ng/PUF) and HCB (4.65 to 16.4 ng/PUF) were observed irrespective of the sampling area (Figures 2C, D and E). This would be probably due to the fact that these compounds are mainly associated to a wide variety of products and emission sources, not specifically representing fingerprints of the activities in the study area.

In summary, the present results provide a comprehensive approach to the air levels of SVOCs in Tarragona County, taking advantage of multi-component protocols. Future data provided by the current determination of SVOCs in soil and vegetation will unveil potential correlations between environmental monitors and emission sources.

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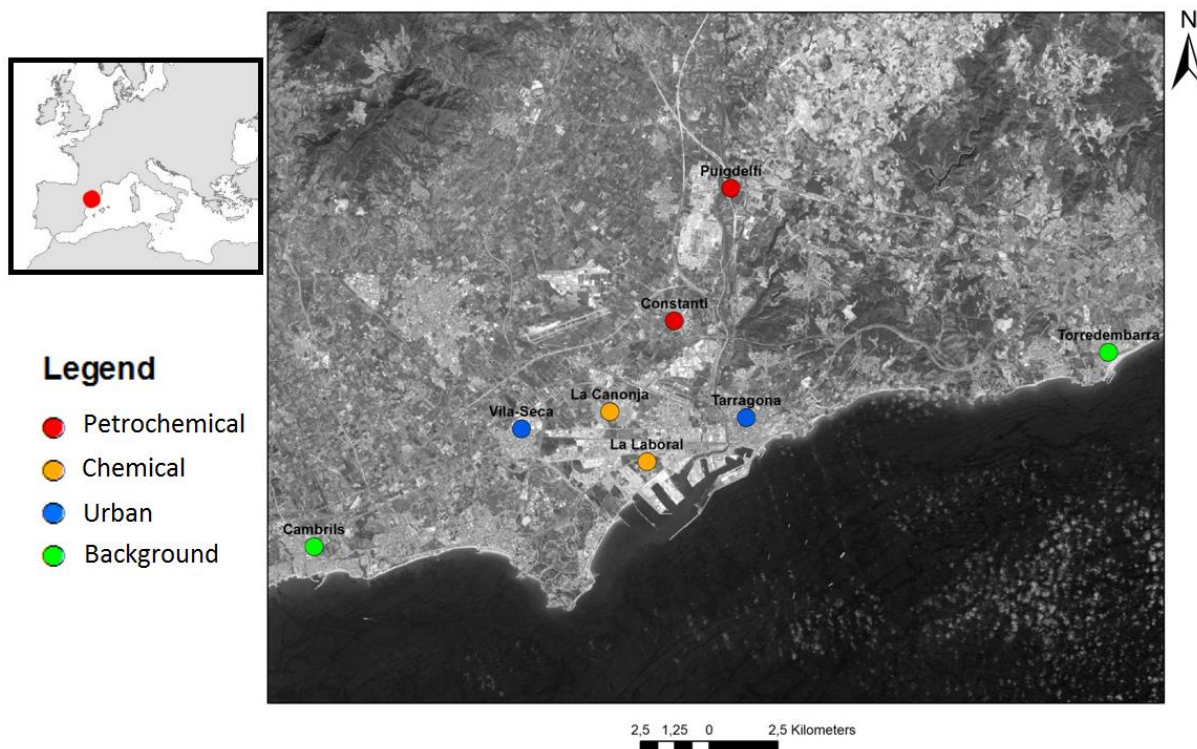


Figure 1. Location of PUF-disks sampling points in Tarragona County (Catalonia, Spain).

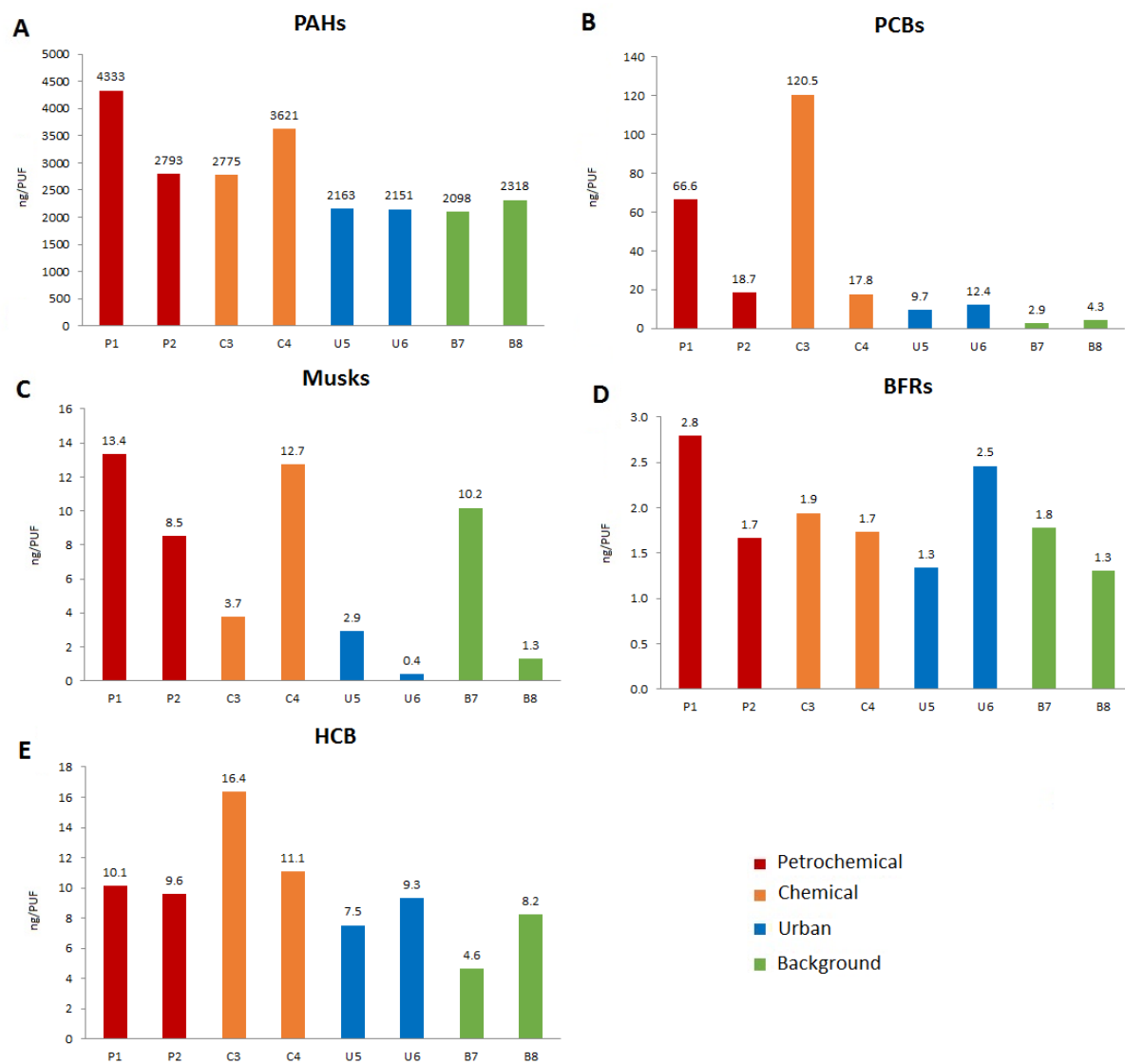


Figure 2. SVOCs levels in air samples according to the sampling area.