Multi-component determination of atmospheric semi-volatile organic compounds in soils and vegetation from Tarragona County, Catalonia, Spain

Noelia Domínguez-Morueco [a,b], Mariana Carvalho [c], Jordi Sierra [b,d], Marta Schuhmacher [b], José Luis Domingo [a], Nuno Ratola [c,*], Martí Nadal [a]

[a] Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Sant Llorenç 21, 43201 Reus, Catalonia, Spain
[b] Environmental Engineering Laboratory, Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalonia, Spain
[c] LEPABE-Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[d] Laboratory of Soil Science, Faculty of Pharmacy, Universitat de Barcelona, Avda Joan XXIII s/n, 08028, Barcelona, Catalonia, Spain

HIGHLIGHTS

- Five classes of SVOCs were analysed in soil and vegetation of Tarragona County.
- PAHs had in general the highest concentrations, followed by SMs.
- SVOCs levels showed clear differences between the two matrices.
- SVOCs sources are a mix between petrogenic and pyrogenic in the short term.

GRAPHICAL ABSTRACT
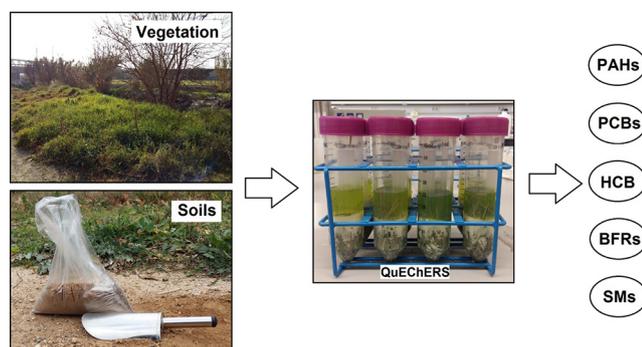
ARTICLE INFO

ABSTRACT

Tarragona County (Spain) is home to the most important chemical/petrochemical industrial complex in Southern Europe, which raises concerns about the presence and effects of the numerous environmental contaminants. In order to assess the levels and patterns of five classes of semi-volatile organic compounds (SVOCs) - polycyclic aromatic hydrocarbons (PAHs), synthetic musks (SMs), polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs) and one organochlorine pesticide, hexachlorobenzene (HCB), 27 samples of soil and vegetation (*Piptatherum* L.) from different areas (petrochemical, chemical, urban/residential, and background) of Tarragona County were analysed. The results show that PAHs levels in soils ranged from 45.12 to 158.00 ng/g and the urban areas presented the highest concentrations, mainly associated with the presence of a nearby highway and several roads with heavy traffic. PAHs levels in vegetation samples ranged from 42.13 to 80.08 ng/g, where the greatest influence came from the urban and petrochemical areas. In the case of SMs, levels in soils and vegetation samples ranged from 5.42 to 10.04 ng/g and from 4.08 to 17.94 ng/g, respectively, and in both cases, background areas (at least 30 km away from the main SVOCs emission sources) showed the highest levels, suggesting an influence of the personal care products derived from beach-related tourism in the coast. PCBs (from 6.62 to 14.07 ng/g in soils; from 0.52 to 4.41 ng/g in vegetation) prevailed in the chemical area in both matrices, probably associated

* Corresponding author.
E-mail address: nrneto@fe.up.pt (N. Ratola).

with the presence of two sub-electrical stations located in the vicinities. In general terms, BFRs and HCB values recorded in soil and vegetation samples were quite similar between matrices and sampling areas.

1. Introduction

It is well-known that chemical and petrochemical industries can potentially release a considerable number of pollutants to the environment, such as semi-volatile organic compounds (SVOCs) (Nadal et al., 2011; Alghamdi et al., 2015). SVOCs include a wide variety of chemicals, known for their volatility, toxic effects in humans and wildlife, and some having bio-accumulative potential and environmental persistence (UNEP, 2008a, 2008b, 2008c). These characteristics make SVOCs transboundary chemicals via long-range atmospheric transport (LRAT), capable to reach remote and sensitive regions, far away from the emission sources (UNEP, 2008a, 2008b, 2008c). In this study, five families of compounds are targeted: polycyclic aromatic hydrocarbons (PAHs), mainly associated with combustion processes (Domínguez-Morueco et al., 2017); polychlorinated biphenyls (PCBs), used in for instance in transformers, capacitors orpaints (Erickson and Kaley, 2011); brominated flame retardants (BFRs), present in electrical appliances and furniture (McGrath et al., 2016); the organochlorine pesticide hexachlorobenzene (HCB), historically used as a fungicide in agriculture, as a wood-preserving agent and in many industrial applications as a porosity-control, peptizing or fluxing agent, among others being also generated as a by-product or waste in chlorination processes (Barber et al., 2005; Roots et al., 2010; Zhu et al., 2014); and synthetic musks (SMs), chemicals of emerging concern widely incorporated in personal care and household products (Silva et al., 2015). Some SVOCs such as PCBs, BFRs, and OCPs were already classified as "persistent organic pollutants" (POPs) by the Stockholm Convention (www.pops.int), while others like PAHs are usually characterized as "potential POPs" (Cai et al., 2008; Silva et al., 2015). All these compounds are emitted by anthropogenic sources only (industrial activities, agriculture, vehicle transit, etc.), except PAHs, which can also have natural origins (forest fires, volcanic eruptions, etc.). And despite the restrictions or bans of, for instance, PCBs and OCPs in most developed countries (UNEP, 2008a), they remain in the environment due to their persistence and past extensive use.

The atmosphere is the main recipient of SVOCs in the environment through direct emissions, although other pathways have been identified, like spraying onto soils and vegetation (He and Balasubramanian, 2010). Once applied or released into the atmosphere, SVOCs are transported and deposited (through dry or wet deposition) over different environmental matrices such as water, soil, biota, or even in ice-cores of remote areas (Herbert et al., 2004; Schuhmacher et al., 2004; Nam et al., 2008; He and Balasubramanian, 2010; Nadal et al., 2011; Yogui et al., 2011; Ratola et al., 2014; Liu et al., 2016). Experimental observations and modeling results (Diamond et al., 2001; Kwamena et al., 2007; Cai et al., 2008; Bao et al., 2015, 2016; Domínguez-Morueco et al., 2016a) demonstrate that soils are one of the main reservoirs of SVOCs, given their high affinity for hydrophobic organic pollutants. In this sense, soil sampling can provide current SVOCs levels, as well as long-term information on the so-called "legacy SVOCs", already banned. This fact, coupled with the natural re-volatilization processes associated with changes in climate, make soils a secondary source of SVOCs (Ma et al., 2011; Komprda et al., 2013; Bao et al., 2016), reaching other environmental matrices such as water bodies and vegetation. However, plants can absorb SVOCs not only by root uptake from the soil, but mainly via deposition from the surrounding atmosphere into their aerial parts, especially leaves (Barber et al., 2004; Yogui et al., 2011). Once captured, the rapid kinetic of exchange between vegetation and air causes some SVOCs to return to the atmosphere (Barber et al., 2003). This re-volatilization process is higher than in the case of soils, so vegetation plays an important role as short-term source and sink of SVOCs (Bao et al., 2016).

Passive sampling devices often have a high initial cost and require electricity and maintenance, which is a disadvantage in many areas, in particular more remote ones (Mari et al., 2008; Zhu et al., 2015; Domínguez-Morueco et al., 2017). Thus, biomonitoring based on collecting environmental samples such as soil and vegetation can provide a first approximation of the concentrations of SVOCs in the environment and assess short and long-term trends, avoiding most of the mentioned constraints. However, it is important to develop expedite analytical methods that allow the quantification of a large number of environmental pollutants in these complex matrices, while reducing the use of potentially harmful inputs like organic solvents (Domínguez-Morueco et al., 2016b). In order to comply with these guidelines, a protocol for the simultaneous analysis of the 5 target classes of SVOCs, based on the "green" alternative QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe), and GC/MS quantification was used (work submitted for publication).

The objective of this study is then to determine the levels and patterns of PAHs, SMs, PCBs, BFRs, and HCB in soil and vegetation samples from different areas of Tarragona County (Spain), where the most important chemical/petrochemical industrial complex in Southern Europe is hosted. Moreover, source apportionment and human health risk factors derived from the exposure to those contaminants were also evaluated and here presented, in order to determine the effects of this potential pollution "hot spot" area.

2. Materials and methods

2.1. Sampling

By the end of January 2016, a total of 27 soil samples and 27 vegetation samples were collected in different zones of Tarragona County, with the following distribution: 7 in a zone under the potential influence of petrochemical complex, which includes a big oil refinery; 9 in the vicinity of the chemical area and 6 in residential and urban zones of Tarragona County. These sampling sites were located <2 km from the considered pollution sources. In addition, 5 sampling points were selected in background areas, about 30 km away from the potentially primary sources of contamination. The geographic location of each sampling point is shown in Fig. 1.

Approximately 100 g of soil were collected from the soil horizon A (0–5 cm depth) in each sampling point and kept in polyethylene bags. In the lab they were dried at room temperature and sieved through a 2-mm mesh screen (Nadal et al., 2004a, 2009, 2011). The sampled soils are basically of urban and industrial origin which can be classified as Regosol soils according to FAO Word Reference Base - developed on calcareous sedimentary materials, with loamy texture, poor in organic matter (1–2% of organic carbon) and with moderately alkaline pH. Likewise, a total of 50 g of vegetation in each site (from the ground species *Piptatherum* L.) were obtained by cutting the plants 5 cm above ground, which were then dried at room temperature (Nadal et al., 2009, 2011). All samples were properly stored until the analysis.

2.2. Reagents and materials

Acetone, dichloromethane (DCM) and n-hexane (Hex), used as extraction solvents, were supplied by VWR BDH Prolabo (Leuven, Belgium). For the preparation of QuEChERS, anhydrous magnesium sulphate ($MgSO_4$) and sodium acetate ($NaCH_3COO$) were from Sigma-