



## An analytical multi-residue approach for the determination of semi-volatile organic pollutants in pine needles



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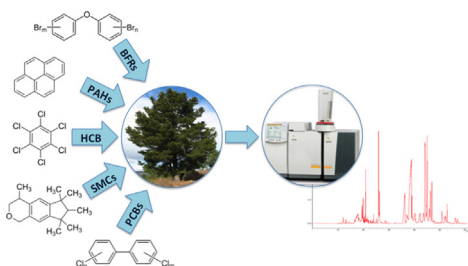
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### HIGHLIGHTS

- Pine needles were used as biomonitors of BFRs, PCBs, HCB, PAHs and SMCs.
- Average recoveries between 75 and 94%, and low LODs were found.
- Synthetic musk fragrances were detected for the first time using vegetation.
- SMCs occur at the same levels as PAHs, higher than for HCB, PCBs and BDEs.
- Field data suggest different behavior patterns for these classes of pollutants.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Vegetation (and pine needles in particular) has been widely used as an alternative to other conventional sampling devices to assess the atmospheric presence of semi-volatile organic contaminants (SVOCs). While most analytical procedures developed focus only on one or two chemical classes, this work intends to establish a multi-component protocol to quantify brominated flame-retardants (BFRs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polynuclear aromatic hydrocarbons (PAHs) and one class of contaminant of emerging concern, the synthetic musks fragrances (SMCs). Pine needles extracts were obtained by ultrasonic solvents extraction (USE), and different cleanup approaches using solid-phase extraction (SPE) employing combinations of sorbents and solvents as well as gel permeation chromatography (GPC) were tested. SPE with alumina followed by GPC yielded the best results, with average recoveries over 80%.

The application of the method under field conditions was proven by the analysis of naturally contaminated samples from 3 sites of different potential exposure (remote, rural and urban). The total detected concentrations ranged from 0.45 to 0.87 ng g<sup>-1</sup> dry weight (dw) for BFRs, 0.35 to 1.01 ng g<sup>-1</sup> (dw) for PCBs, 0.36 to 12.2 ng g<sup>-1</sup> (dw) for HCB, 245.7 to 967.8 ng g<sup>-1</sup> (dw) for PAHs and 20.7 to 277.5 ng g<sup>-1</sup> (dw) for SMCs.

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This methodology is a viable approach for the simultaneous analysis of five different classes of atmospheric pollutants employing less analytical efforts. Moreover, to the author's best knowledge, this is also the first time vegetation is employed in the detection of SMCs.

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## 1. Introduction

The continuous release of hazardous chemicals into the atmosphere urges the development of comprehensive and expedite methodologies for their detection and subsequent study. Current emissions may not only comprise new contaminants, with scarce information about occurrence and impact on environmental health available, but also the so-called legacy persistent organic pollutants (POPs). These compounds belong to a variety of chemical classes that were widely used in the past, but have since been, restricted, banned or discontinued, yet they still remain in the environment due to their persistence [1]. Furthermore, their volatility, toxicity, bioaccumulation capacity and resistance to natural breakdown, either by biological, chemical or photochemical reactions, make them prone to long-range atmospheric transport (LRAT) [2] causing an environmental impact on areas far away from their points of emission. In 2004, the Stockholm Convention on Persistent Organic Pollutants (SCPOP) became effective, aiming to ban or restrict the use of POPs [2]. Examples include polychlorinated biphenyls (PCBs), brominated flame-retardants (BFRs), some organochlorine pesticides (OCPs) and, although not a part of the list but with similar properties, polycyclic aromatic hydrocarbons (PAHs). PCBs were used as cooling and dielectric fluids in transformers and capacitors and banned in 1979 in the USA [3] and 1985 in the EU [4]. BFRs, namely polybrominated diphenyl ethers (PBDEs) were widely incorporated as flame retardants in electrical appliances and furniture, but have now been restricted in several states of the USA [5] and in the EU [6]. Some organochlorine pesticides (OCPs) employed in crop protection and pest control, such as hexachlorobenzene (HCB), have also been banned globally under the SCPOP [2]. While BFRs, PCBs and OCPs are synthetic compounds and therefore exclusively of anthropogenic sources, PAHs derive not only from human activities (combustion in traffic, industries and home heating) but also from natural processes associated with fossil fuels (forest fires, volcanic eruptions, etc.) [7]. The list of POPs is periodically reviewed and new contaminants can be added, once their effect on organisms, persistence and LRAT capacity is evaluated. Synthetic musk compounds (SMCs), widely incorporated in personal care and household products, are one of the “emerging” candidates. Used in rather high quantities on a daily basis, their bioaccumulative potential [8,9] and endocrine disrupting action [10,11] allied to their LRAT [12] make them a current issue of concern.

The implementation of atmospheric monitoring plans is essential to assess the properties and behavior of such contaminants. As opposed to other more onerous approaches, monitoring using vegetation avoids previous sampling site set-up and is arguably the best tool for the estimation of the atmospheric contamination levels at remote or poorly accessible locations [13]. Pine trees proved to be especially suitable, due to their widespread occurrence and the ability to retain lipophilic compounds on their needles, which can remain in the tree for several years [13].

Extraction is an essential step in analytical procedures involving plant matrices and should be able to recover the analytes completely, avoiding the co-extraction of unintended compounds at the same time. The most used extraction technique reported in literature is Soxhlet or Soxtec [14–16] extraction, which offers generally good recoveries, but requires rather large amounts of solvents and is time demanding. Ultrasonic solvent extraction

(USE) [14,17,18] and ultrasonic assisted enzymatic digestion (USAED) [19] have been employed as an alternative, using smaller amounts of solvent much shorter extraction times. Pressurized liquid extraction (PLE) [14,20,21] and supercritical fluid extraction (SFE) [22,23] are other alternatives, but require expensive equipment. A subsequent cleanup of the vegetation extracts for multicomponent analysis is often needed and is always challenging step, given the balance between cleanup efficiency and recovery. Solid-phase extraction (SPE) using cartridges or glass columns are broadly employed for pine needle extracts, with silica [24,25], Florisil<sup>®</sup> [21,26] and alumina [24,26] as the main sorbents. Gel permeation chromatography (GPC), a separation technique based on molecular size [27], is also used, individually [28] or combined with SPE [29].

Our workgroup has previous experience in the development and validation of analytical methodologies to evaluate the levels of PAHs, OCPs and PBDEs in pine needles [13,26,30]. The current study intends to establish an innovative multi-component protocol to extract simultaneously four classes of more “traditional” compounds (BFRs, PCBs, PAHs and OCPs) and, for the first time, SMCs from pine needles. This approach will reduce the workload needed to obtain a comprehensive view of the atmospheric contamination and its deposition in vegetation matrices. To the authors' best knowledge, this is the first time SMCs can be included on a biomonitoring framework using vegetation.

## 2. Experimental

### 2.1. Reagents and materials

High-purity dichloromethane (DCM), *n*-hexane (Hex) and acetone were supplied by VWR BDH Prolabo (Leuven, Belgium). Florisil<sup>®</sup> (magnesium silicate, particle size 0.150–0.250 mm), alumina (neutral aluminum oxide 90, particle size 0.063–0.200 mm), silica (silica gel 60, particle size 0.062–0.200 mm) and sodium sulphate were acquired from Merck (Darmstadt, Germany) and activated overnight at 450 °C. Deactivated alumina was prepared by adding 10% (m/m) of ultrapure water (Fluka Chromasolv, Steinheim, Germany) to the previously activated alumina and stabilized overnight. S-X3 Bio-Beads<sup>®</sup> were acquired from Bio-Rad (Amadora, Portugal).

Individual PBDE standards (congeners 28, 47, 85, 99, 100, 153, 154, 183) were bought as individual 50 µg mL<sup>-1</sup> solutions in isoctane from Sigma–Aldrich (St. Louis, MI, USA). A mix of sixteen PAHs containing naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz(a) anthracene (BaA), chrysene (Chry), benzo(b) fluoranthene and benzo(k) fluoranthene (BbF + BkF), benzo(a) pyrene (BaP), indeno(1,2,3-cd) pyrene (IcdP), dibenzo(a,h) anthracene (DahA), and benzo(g,h,i) perylene (BghiP) at 2000 µg/mL in DCM/benzene (1:1), a PCB mix (congeners 28, 52, 101, 138, 153, 180, 209 as 10 µg mL<sup>-1</sup> in isoctane) and PCB 30 (10 µg mL<sup>-1</sup> in heptane) as well as musk xylene (MX, 100 µg mL<sup>-1</sup> in acetonitrile) were also obtained from Sigma–Aldrich. Dr. Ehrenstorfer standards (Augsburg, Germany) supplied a mix of PCBs (congeners 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189, 10 µg mL<sup>-1</sup> in isoctane), a mix of deuterium labeled PAHs (d-PAHs), containing naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub> and

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