Chemosphere 185 (2017) 47–55

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Towards improved comparability of studies addressing atmospheric concentrations of semivolatile organic compounds based on their sequestration in pine needles

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HIGHLIGHTS

- Coniferous needles are suitable passive air sampler of ambient air pollution.
- Various storing, washing and drying methods have no effect on SVOC concentration.
- Separation of foliage leaves from dwarf shoots before extraction step is crucial.
- Distribution of SVOC in needle structure is a function of log K_{ow} and molar weight.

ARTICLE INFO

Article history:
Received 10 May 2017
Received in revised form
27 June 2017
Accepted 28 June 2017
Available online 30 June 2017

Handling Editor: R Ebinghaus

Keywords:
Passive air sampling
Pine needles
Methodology
SVOC
Monitoring

ABSTRACT

Coniferous needles can be used as a passive air sampler of semivolatile organic compounds (SVOC) and an indicator of atmospheric pollution patterns and trends. There is limited information on whether different parts of the plant (e.g., foliage leaves, dwarf shoots, twig, etc.) contain different levels of SVOC. Only few studies have compared levels of SVOC surface layer of wax and to their total content in all needle tissues and what affects an uptake and distribution of SVOC. It is important to have better understanding of the extent to which sampling and sample preparation procedures affect measured levels of SVOC in pine needles and reduce comparability of data from samples processed in different ways. In the present study, we assessed an impact of various sampling and sample preparation techniques on the levels of SVOC in *Pinus sylvestris* needles. While the impact of various storing, washing and drying methods was not significant, presence of dwarf shoots in the sample or structural damage of needles affected the results significantly. Results show that levels of SVOC in dwarf shoots are 2–8 times higher than those in foliage leaves. Therefore, dwarf shoots must be carefully removed before foliage leaves extraction to improve comparability of results. There were different patterns in SVOC on the surface of the foliage leaves compared to the whole leaves. An uptake of these substances by the surface wax as well as their occurrence in the internal structure was of function of the physico-chemical properties of the substances (log K_{ow}, molar weight).

1. Introduction

Semivolatile organic compounds (SVOC) and in particular persistent organic pollutants (POPs) are groups of compounds presenting a risk to living organisms due to their carcinogenic, mutagenic, teratogenic, neurotoxic, and immunosuppressive properties (Migaszewski et al., 2002). Protection of human health from their adverse effects is the main goal of the Stockholm Convention (SC) on POPs (Klánová and Harner, 2013; Munoz-Arnanz et al., 2016). An assessment of their levels, spatial distribution, and long term trends in ambient air, human milk and blood is one of the primary goals of the Global Monitoring Plan (GMP), which was developed as a tool for effectiveness evaluation of the SC measures.

SVOC in the atmosphere have been monitored on a long-term basis by a number of national and international monitoring programs using active air sampling techniques (CIT EMEP (Halse et al.,

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http://dx.doi.org/10.1016/j.chemosphere.2017.06.121

2011; Holoubek et al., 2007a; Pistocchi, 2008), AMAP (Hung et al., 2010), IADN (Hillery et al., 1997; Simcik et al., 1999; Venier and Hites, 2010, 2008)). Passive air samplers have been developed in the last decade as a cheaper alternative to this conventional approach and are now increasingly used in newly established global and regional monitoring networks (CIT GAPS (Pozo et al., 2009, 2006), MONET (Klánová et al., 2009; Přibylová et al., 2012)).

Vegetation has also demonstrated the ability to accumulate organic compounds and it offers another cheap alternative for sampling remote and poorly accessible environments. The spatial distribution of SVOC has been investigated in coniferous needles (Di Guardo et al., 2003; Falandysz et al., 2012; Lehndorff and Schwark, 2004; Piccardo et al., 2005; Ratola et al., 2014; van Drooge et al., 2014), tree bark (Salamova and Hites, 2013; Tarcau et al., 2013), lichens and mosses (Fuga et al., 2008; Guidotti et al., 2003; Kosior et al., 2014; Riget et al., 2000; Schrlau et al., 2011).

When compared to broadleaf species, conifers offer an advantage of longer leaf turnover (and SVOC accumulation) time. *Pinus sylvestris* used in the present study, for instance, retain needles for up to 3 years, while the "life-time" of *Pinus mugo* needles is up to 8 years (Kylin et al., 1994).

1.1. Foliage morphology

The whole needle is divided into two parts – the foliage leaves (needle-like leaves) and the dwarf shoots (brachyblasts) (Fig. 1).

The foliage leaves surface is covered by a cuticle consisting of long-chain polyesters (Dolinová et al., 2004). This epicuticular wax represents an important mechanism in the plant defense against desiccation, ultraviolet radiation, bacterial and fungal pathogens (Kunst and Samuels, 2003). At the same time, it is capable of scavenging atmospheric pollutants with low water solubility, high *n*-octanol-water partition coefficient, and low vapour pressure (Di Guardo et al., 2003). It has been demonstrated that 'wax crystals' at the foliage leaves surfaces (Barthlott et al., 1998) can absorb gas phase-associated (Di Guardo et al., 2003) as well as particle-bound POPs (Yang et al., 2007).

However, establishment of a link between the levels of SVOC found in needles and their atmospheric concentrations is not straightforward. SVOC accumulation rates of needles depend on tree species (differences in the uptake kinetics were demonstrated for spruce (*Picea abies*) and pine needles (*Pinus nigra*) (Di Guardo et al., 2003) or for species within the genus *Pinus* too (Piccardo et al., 2005)), and their foliage leaves structures (differing in number of resin channels or wax crystals structure) (Di Guardo et al., 2003), needle age (negatively affecting the thickness of the wax layer) and wax composition (undergoing seasonal fluctuations) (Kylin and Sjödin, 2003), as well as geographical and meteorological factors (elevation, seasonal temperature or humidity) (Cesar et al., 2004). External stress (dust concentration, chemical pollution, acid rains, mechanical abrasion, presence of moulds) can also negatively affect a quantity and a quality of the epicuticular wax (Cesar et al., 2004) causing in turn losses of previously accumulated compounds (Piccardo et al., 2005).

Comparability of results is further affected by the lack of standardized methods for needle sampling and sample preparation prior to analysis. In some studies foliage leaves (needle-like leaves) are separated from dwarf shoots (Fig. 1) prior to analysis while in

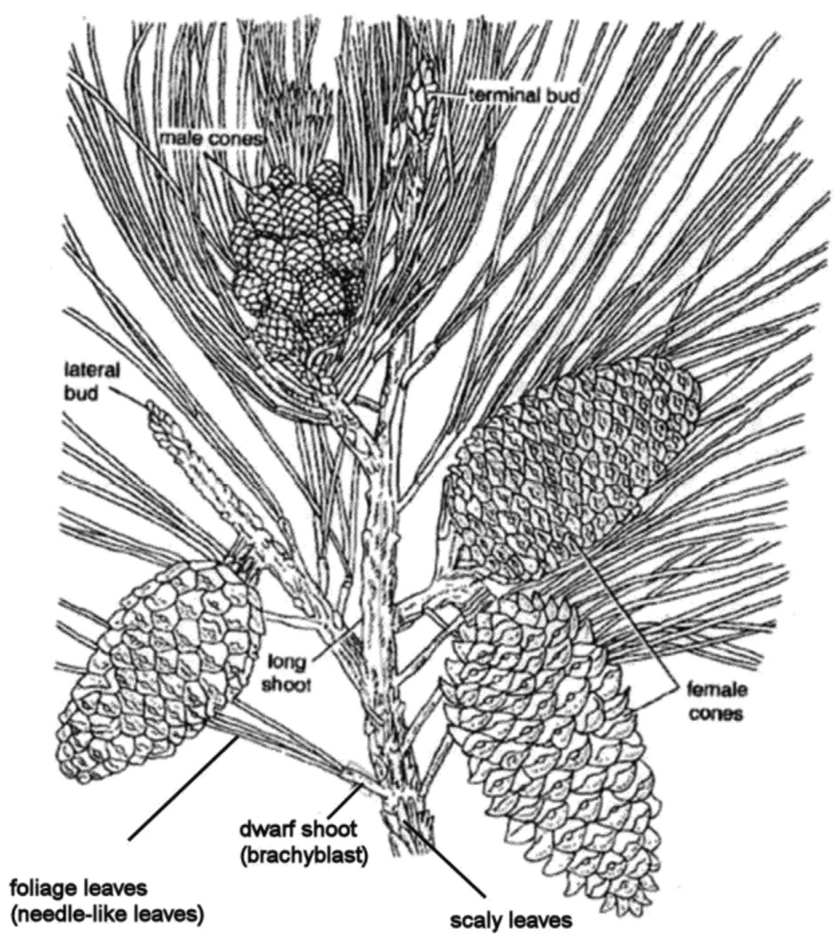

Fig. 1. Structure and description of a pine spur (Singh et al., 2010).