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# Can pine needles indicate trends in the air pollution levels at remote sites?

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*Pine needle monitoring is a feasible tool for an assessment of temporal trends in the atmospheric contamination.*

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ABSTRACT

Data from ten years of integrated monitoring were used here to evaluate whether pine needles are a feasible tool for an assessment of long-term trends of the atmospheric contamination. Pine needles collected once a year were compared to high volume air samples collected for 24 h, every 7 days, and passive air samples integrated over 28-day periods. Results showed the same concentration patterns of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) captured in needles and high volume samples. Passive air samplers were less efficient in sampling the particle-bound compounds. Theoretical air volume equivalent to each needle sample ($V_{EQ}$) was calculated as a ratio of the needle concentration over the mean air concentration. Results indicated different equivalent volumes for PAHs and organochlorines, possibly due to the faster degradation rates of PAHs in needles. The most important finding is that in the long term a needle monitoring gives very similar information on temporal trends of the atmospheric pollution as does a high volume air monitoring.



## 1. Introduction

Persistent organic pollutants (POPs) in the atmosphere are conventionally monitored by an active air sampling technique (Holoubek et al., 2007a). Various passive air sampling devices based on semipermeable membranes or polyurethane foam have been developed in the last years and utilized for spatial and time integrated monitoring of POPs (Bartkow et al., 2004; Farrar et al., 2005; Harner et al., 2006; Klánová et al., 2006). A monitoring of vegetation, however, remains a cheapest and best available tool for estimation of the atmospheric contamination levels at remote and poorly accessible locations like the high mountains. POPs as a group of compounds with a very low water solubility, high *n*-octanol–water partition coefficient, and low vapor pressure tend to accumulate in lipidic tissues. That includes a wax layer on the surface of plants, which can efficiently scavenge and accumulate POPs from the atmosphere over the long time periods (Viskari et al., 2000; Wyrzykowska et al., 2007) and in doing so, serve as an integrative passive air sampler.

Plants selected for such monitoring have to show a high affinity towards compounds of interest while tolerating high concentrations of these substances accumulated in their tissues (Guidotti et al., 2003). Most common matrices used as indicators of the atmospheric contamination (Holoubek et al., 2000; Di Guardo et al., 2003; Lehndorff and Schwark, 2004; Piccardo et al., 2005) are coniferous needles, along with lichens and mosses (Riget et al., 2000; Guidotti et al., 2003; Fuga et al., 2008). A surface of needles is covered by a 1–5 μm thick cuticle consisting of cutin (a polyester of di- and trihydroxy fatty acids) and cuticular wax (lipids, free fatty acids, *n*-alkanes, *n*-alkenes, primary alcohols, α,ω-diols, ketones, and ω-hydroxyacids) (Dolinova et al., 2004). The epicuticular wax layer is a barrier between the plant and its environment: it acts as a protective layer against desiccation and ultraviolet radiation and it is believed to play an important role in the plant defense against the bacterial and fungal pathogens (Kunst and Samuels, 2003).

An advantage of conifers as evergreen species is that – unlike broadleaf species – they can accumulate atmospheric pollutants for several years (Di Guardo et al., 2003). A major disadvantage is a poor characterization of a performance of such sampler. Many species with different uptake characteristics are used for the passive air sampling e.g. *Picea abies*, *Pinus nigra* (Di Guardo et al., 2003), *Pinus uncinata* (Grimalt and van Drooge, 2006), *Pinus pinaster* (Piccardo et al., 2005), *Pinus sylvestris* (Holoubek et al., 2000; Keymeulen et al., 2001) or *Cedrus deodara* (Chen et al., 2006). A sampling rate as well as an extent to which the plant sequesters certain chemicals depends on the plant species, age of needles, their structure (number and accessibility of resin channels, for instance) (Di Guardo et al., 2003), or a terpene content of the wax.

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The external stresses such as acid rains or mechanical abrasion, low humidity or a presence of moulds may cause important reductions or alterations of the wax layers similar to the natural process of the needle aging, and such needles exhibit much lower uptake rates. Moreover, a degradation and loss of the cuticle leads to the loss of previously accumulated compounds (Piccardo et al., 2005). Geographical and meteorological factors are influential, too. More volatile organochlorines as α-HCH, γ-HCH, aldrin and α-endosulfan positively correlated with the altitude, while DDTs were inversely correlated (Wang et al., 2006), and Ockenden et al. (1998) demonstrated that lower temperatures enhanced the accumulation rates of PCBs.

Pine needles are probably the most frequently used biomonitoring tool because needles from 1 to 3 years old are found at the same branch and their age can be easily determined (Piccardo et al., 2005). Physicochemical properties of investigated POPs and their ambient air concentrations in both, gaseous and aerosol phases (Di Guardo et al., 2003) are also important. Piccardo et al. (2005) investigated an accumulation of nine polycyclic aromatic hydrocarbons (PAHs) in pine needles of different ages (6–30 months). The bioconcentration of more volatile compounds (phenanthrene, anthracene, fluoranthene, pyrene) was more efficient than the one of less volatile PAHs (benzo(*a*)anthracene, chrysene, benzofluoranthenes, benzo(*a*)pyrene). Low molecular weight PAHs diffuse and accumulate more readily in the inner compartments, while particle associated chemicals very likely linger in the surface compartment where they are exposed to the effects of external environmental factors like temperature, solar irradiation or atmospheric ozone. Liu et al. (2006), however, manifested that pine needles accumulated higher molecular weight PAHs as well. A time-dependent accumulation behavior of organochlorines was also investigated in the field experiments with pine needles of different ages (4, 16 and 22 months) in the vicinity of various emission sources (Wenzel et al., 2000). The concentration increased with the age of needles for low chlorinated PCBs. For highly chlorinated PCBs, HCH isomers, DDT and its metabolites, however, the bioconcentration was not related to the age of needles. Explanation of this surprising result can be found in the work of Kylin and Sjodin (2003) who observed differences in accumulation behavior of HCHs and *p*,*p*′-DDT. He demonstrated that levels of POPs accumulated in needles are consequently a subject of seasonal fluctuations due to the annual cycle of terpene content in the wax with winter minima (1%) and summer maxima (10%). Observed seasonal variation of POP concentrations in needles was significantly larger than the overall accumulation. Underlying the prominent seasonal variation there still was a clear continuous accumulation of POPs which could, however, be easily overlooked if needles from several years were not analyzed in parallel (Kylin and Sjodin, 2003). This natural process could be responsible for the false conclusions about the rapid equilibria and exhausted hydrophobic capacity in older needles reported earlier. In fact, Kylin and Sjodin (2003) observed an accumulation of HCHs and *p*,*p*′-DDT in Scots pine during the entire life span of the needles and hydrophobic capacity did not seem to be exceeded at any time.

Even though needles are undoubtedly useful as an indicator of the atmospheric pollution, a quantitative data interpretation is complicated by the lack of comparative studies. A quantitative statement can be made if the same methods have been used. A variety of employed coniferous species and needle ages, sampling, analytical and reporting techniques, however, prevent a reasonable comparison of the results from various studies. A standardization of the methods and approaches is highly desirable. The biological processes in the plants further complicate the matter and cause such difficulties that we may never be able to calculate absolute air concentrations of the contaminants (Hellstrom et al., 2004) from their levels in needles. A question, whether these levels can be used for establishment of the long-term trends of atmospheric contamination, still has to be answered. To do so, a long-term study has to be designed where needles are collected and analyzed yearly, at exactly the same time of the year. Concentration levels and patterns have to be compared to the continuous air pollution data derived from the high volume air monitoring.

The attempts to compare the sampling efficiency of spruce needles (*P. abies*) to the results of active and passive air measurements have been made recently (Kirchner et al., 2006; Levy et al., 2007). The homologue patterns of polychlorinated dibenzo-*p*-dioxins and furans accumulated in 0.5, 1.5 and 2.5 year-old needles were compared to the ones in semipermeable membrane devices and high volume air samples. Needles were capable of the uptake from both, gas and particulate phases, and the fingerprint of PCDDs/Fs captured in needles correlated very closely with the one obtained from the active sampler. On the other hand, SPMDs appeared to be a very sensitive tool for lower chlorinated PCDDs/Fs due to their ability to sequester compounds from the gas phase. Such data are, however, not yet available on polyurethane foam (PUF) based devices that are capable of fine particle sampling (Klanova et al., 2008).

In the attempt to fill these gaps, data from the long-term integrated monitoring project in the background observatory Kosetice, Czech Republic (Holoubek et al., 2007a; Váňa and Holoubek, 2007) were analyzed. A multimedia sampling of ambient air (active and passive), wet deposition, surface water, sediment, soil, and biota, as the key components of the environmental system, has been performed since 1988 as a part of the European Monitoring and Evaluation Programme (EMEP) and provided an extensive data base. Results of the comparative study focused on polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polyaromatic hydrocarbons (PAHs) and the efficiency of their sequestration in the pine needles, active and passive samplers are reported here.

## 2. Materials and methods

### 2.1. Sampling methods

Air samples have been collected in the background station once a week (52 samples per year) since 1996 using a high volume ambient air sampler PS-1 (Graseby-Andersen, USA, flow: 12–18 $m^3\ h^{-1}$, volume: 250–400 $m^3$ per 24 h) and two types of adsorbents: a Whatmann quartz filter (fraction $d_{ae} < 50\ \mu m$) for collection of particles, and a polyurethane foam (PUF) filter (Gumotex Břeclav, density 0.03 g $cm^{-3}$) for collection of the gaseous phase. Duration of sampling was 24 h; quartz filter field blanks and PUF filter field blanks were collected each month (Holoubek et al., 2007a).

Passive air samplers consisting of the polyurethane foam disks (15 cm diameter, 1.5 cm thick, density 0.030 g $cm^{-3}$, type N 3038; Gumotex Breclav, Czech Republic) housed in protective chambers were employed with the sampling duration of 28 days (13 samples per year) since 2003. All PUF disks were pre-washed, cleaned (8 h Soxhlet extraction in acetone and 8 h in dichloromethane), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in a freezer prior to deployment. Field blanks were obtained by installing and removing the PUF disks at all sampling sites (Klanova et al., 2008).

Pine needles (*P. sylvestris)* used in this project were collected annually in early September from five sampling sites in the vicinity of the background station. 3.5-year-old needles (*P. sylvestris*) were handpicked, transported to the laboratory wrapped in the aluminum foil (Holoubek et al., 2007b), and air-dried before the analysis.

### 2.2. Chemical analysis

All filters as well as needles were extracted with dichloromethane in a Bühi System B-811 automatic extractor. Surrogate recovery standards ($d_8$-naphthalene, $d_{10}$-phenantrene, $d_{12}$-perylene for PAH analysis; PCB 30 and PCB 185 for PCB analysis) were spiked on each sample prior to extraction. Terphenyl and PCB 121 were used as internal standards for PAH and PCB analyses, respectively. The volume was reduced after the extraction under a gentle nitrogen stream at ambient temperature, and fractionation was achieved on a silica gel column; a sulfuric acid modified silica