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Short communication

Levels of short chain chlorinated paraffins in pine needles and bark and their vegetation-air partitioning in urban areas

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ABSTRACT

Short chain chlorinated paraffins (SCCPs) have been of considerable concern in recent years due to their high production volumes, environmental persistency and potential for long range atmospheric transport. Vegetation can take up considerable amounts of semivolatile organic compounds from the atmosphere and can act as indicators of local contamination. Paired pine needles and bark were sampled around Beijing during winter and summertime to investigate the distribution of SCCPs in urban areas. Levels in bark samples ranged 5.79–37.5 μg/g on a lipid normalized basis (lw) with a geometric mean (GM) of 16.9 μg/g lw whereas levels were 3.03–40.8 (GM 11.8) μg/g lw for needles. Average congener group abundance profiles showed equal contribution of all four carbon groups (C_{10-13}) in wintertime whereas higher abundances of C_{10} and C_{11} groups were found during summer. Uptake of SCCPs occurred mainly via kinetically limited gaseous deposition and particle bound deposition in the investigated area.

1. Introduction

Chlorinated paraffins (CPs) are industrial chemicals that have been produced in large amounts during the past decades and used as additives in metalworking fluids and drilling oil, and as secondary plasticizers and flame retardants in plastics and sealants (Bayen et al., 2006). Their molecular formula is $C_xH_{(2x-y+2)}Cl_y$, and they are also subdivided into three groups according to their carbon chain length; short chain chlorinated paraffins (SCCPs) with 10–13 carbon atoms, medium chain chlorinated paraffins (MCCPs) with 14–17 carbon atoms, and long chain chlorinated paraffins (LCCPs) with 18–30 carbon atoms. It has been found that CPs, mainly SCCPs, can be persistent in the environment, are prone to long-range atmospheric transport due to their semivolatile properties, have the potential to bioaccumulate and are toxic to certain animals (Bayen et al., 2006). Several actions have been taken to regulate SCCPs but more research is urgently needed to provide better understanding on their environmental distribution and fate. Scarcity of data on the environmental levels of SCCPs is mainly due to the great challenges associated with their analysis and quantification (Sverko et al., 2012).

Monitoring the atmospheric levels of semivolatile organic compounds (SVOCs) is important to understand their environmental fate. Active air samplers and passive air samplers are frequently used to investigate the atmospheric levels and distribution of SVOCs (Hayward et al., 2010), but these need to be deployed at each site and revisited during collection. These sampling methods have also been previously used for evaluating the levels of SCCPs in the atmosphere (Wang et al., 2012, 2013; Li et al., 2012). On the other hand, vegetation can also accumulate considerable amounts of SVOCs from the atmosphere by gas-phase partitioning process and/or deposition of particle bound residues. For example, conifer needles are covered by a protective epicuticular wax layer and have been previously found to effectively accumulate atmospheric SVOCs (Kylin et al., 1994). Similarly, tree bark can also accumulate SVOCs due to their large surface area and high lipid content and can show the integrated levels of lipophilic compounds over a period of several years (Simonich and Hites, 1997). Therefore, tree bark and pine needles have been widely used as natural passive air samplers to investigate the atmospheric levels of SVOCs. Furthermore, due to their effective scavenging of atmospheric SVOCs, vegetation can also be an important sink/depository of these compounds and greatly affect their transport potential.

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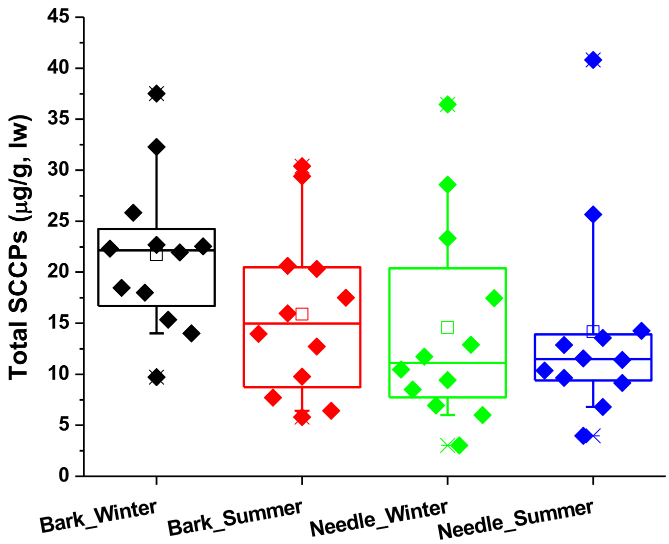

Fig. 1. Boxplot of SCCP levels grouped by matrices and winter and summer periods. Individual samples are shown as diamonds. The range of each box represents the 25th and 75th percentile, whereas the whiskers represent the 10th and 90th percentile. Maximum and minimum levels are marked with "x".

To our knowledge, only one previous study has investigated the levels of CPs in foliage, which reported the total CP levels (SCCPs + MCCPs + LCCPs) in spruce needles at the European Alpine region (Iozza et al., 2009). More studies are therefore needed to investigate the levels of SCCPs in vegetation and to determine their suitability as indicator of atmospheric SCCPs. We aim with this study to: investigate the levels of SCCPs in pine needles and bark around Beijing; compare the levels and congener group distribution; and investigate the partitioning mechanisms of SCCPs between air and vegetation.

2. Method section

2.1. Sampling procedure

Sampling was conducted in February 2011 (winter) and September 2011 (summer) at twelve sites distributed around Beijing (sites S1–S12, see Fig. S1). The samples were collected within residential areas and university campuses. At each site, the needles and bark of pine trees were sampled. The most recent growing buds of pine branches were sampled during each campaign. These therefore represented about 10–11 month old needles for the winter samples and about 5–6 months for the summer samples since bud burst occurred around April–May. Current year needles from two to four individual pine trees per site were collected, wrapped in aluminum foil and placed in zipper bags. Approximately 5 cm^2 of bark (thickness around 2–5 mm) was chiseled from two spots at a height of about 1.5 m for the same trees as for the collected needles. Parts with visible signs of epiphytes were not sampled. In order to study the vegetation-air partition, additional composite pine bark and needles ($n = 4$) were sampled again in site S2 in September 2013, where a high volume sampler (Sibata HV1000R) was concurrently operated for 24 h during a five day period prior to the vegetation sampling. The samples were taken to the laboratory during the same day and kept in a freezer. They were then lyophilized, ground to powder and stored at −20 °C.

2.2. Sample pretreatment, instrumental analysis and quantification

Sample pretreatment follows our previous protocols (Zeng et al., 2011) with some minor modification and the details can be found in the Supplementary material (SM) together with the QA/QC. A gas chromatograph coupled with a low resolution electron capture negative ionization mass spectrometer (GC/ECNI-LRMS, Agilent 7890A/7000A) was used for the analysis of SCCPs. Qualitative identification of different SCCP congener groups was performed by monitoring selected $[M-Cl]^-$ ions and by comparing retention

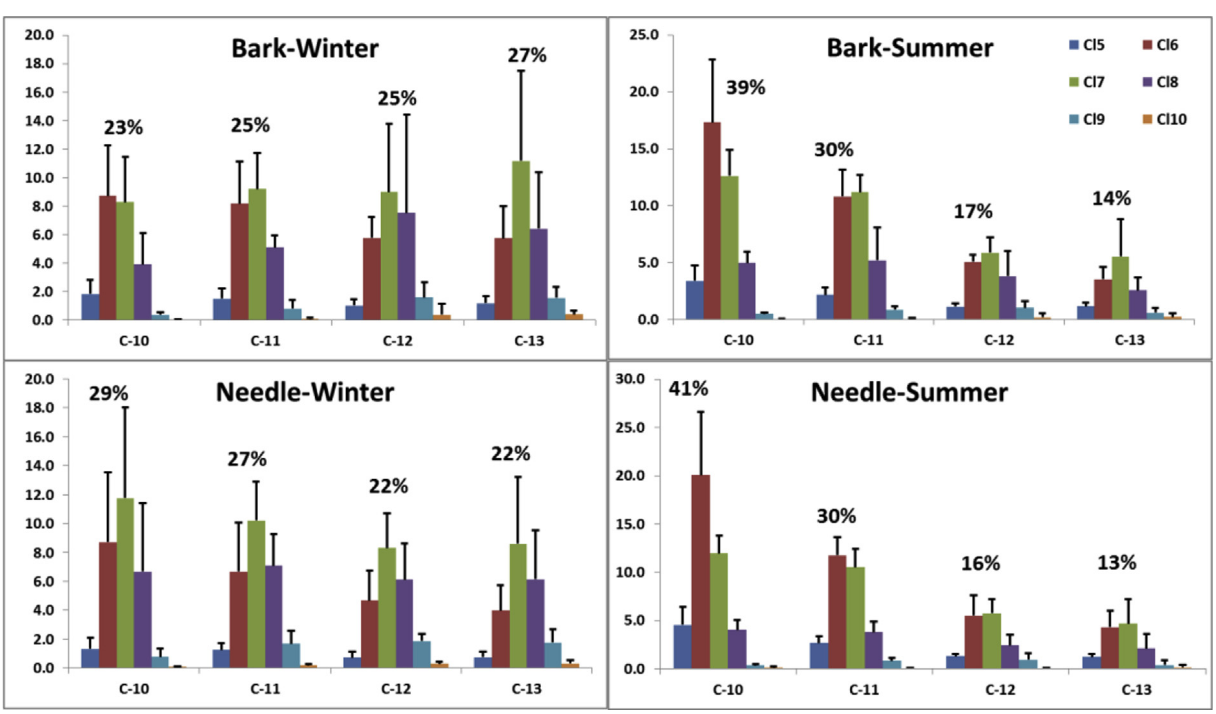

Fig. 2. Average congener group abundance profiles (in percent and with standard deviations) of pine bark and needles during winter and summer in Beijing.