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 (C₁₀–C₁₃) in wintertime whereas higher abundances of C₁₀ and C₁₁ groups were found during summer. Uptake of SCCPs occurred mainly via kinetically limited gaseous deposition and particle bound deposition in the investigated area.

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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 cm² 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 $[\text{M}-\text{Cl}]^{-}$ 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.

time, peak shapes and ion ratios with those of standards. The quantification method was based on Reth et al. (2005) and described in more detail in a previous study (Zeng et al., 2011). OriginPro 8 was used for statistical analysis of the results using non-parametric tests.

3. Results and discussion

The total SCCP levels were between 320 and 4270 ng/g on a dry weight basis (dw) for bark samples with a geometric mean (GM) of 980 ng/g dw, and 400–4010 ng/g dw (GM 1090 ng/g dw) for needles. These were higher than total CP levels found in spruce needles in the European Alps (26–450 ng/g dw) by Iozza et al. (2009). The extractable lipid contents in bark and needles ranged 3–23% (GM 5.8%) and 4–13% (GM 9.2%), respectively. Significant correlation was found between the lipid contents and total SCCP levels for bark (Spearman's correlation, $R = 0.62$, $p < 0.01$) but not for needles ($p = 0.91$). This might be due to the longer lifetime and contact period of bark matrices with the air compartment which allows for more time to establish equilibrium, and the potential importance of other plant tissue components such as cutins on the accumulation of SCCPs. In order to make the results more comparable between the different matrices, the concentrations of SCCPs were hereafter presented on a dry weight and lipid normalized (lw) basis. The lipid normalized ranges were 5.79–37.5 $\mu\text{g/g lw}$ (GM 16.9 $\mu\text{g/g lw}$) for bark and 3.03–40.8 (GM 11.8) $\mu\text{g/g lw}$ for needles (Fig. 1). The levels in bark were somewhat higher in winter (GM 20.50 $\mu\text{g/g lw}$) than summer (13.9 $\mu\text{g/g lw}$) although the difference was not statistically significant (Mann–Whitney U , $p = 0.06$), and needle concentrations clearly showed no significant differences between winter (GM 11.7 $\mu\text{g/g lw}$) and summer (GM 11.9 $\mu\text{g/g lw}$). This was in contrast to the ambient air levels of SCCPs in Beijing using active air sampler and also around East Asia using passive air samplers, where higher summer levels were found (Wang et al., 2012; Li et al., 2012).

Site S1 is located in a rural area at the outskirts of Beijing and showed relatively low levels (GM for both matrices combined: 8.78 $\mu\text{g/g lw}$), while levels at site S2 (GM 7.71 $\mu\text{g/g lw}$) were also comparably low (Fig. S2). Some centrally located sites, such as S3 (GM 15.4 $\mu\text{g/g lw}$) and S4 (GM 25.4 $\mu\text{g/g lw}$) displayed somewhat higher levels (Fig. S2). However, a clear trend of lower SCCP concentrations with the increasing distance from the city center could not be found, as shown by relatively high levels at the site S10 (GM 20.0 $\mu\text{g/g lw}$, Fig. S2) which is only about 5 km away from site S1. More research is therefore needed to investigate the underlying reasons for the concentration trends among the sites.

As seen in Fig. 2, the average congener group abundance profiles were quite similar between bark and needles. During wintertime, contributions from all four carbon congener groups were almost equal and Cl₆, Cl₇, and Cl₈ were the predominating chlorine groups. During summertime however, the relative abundances increased for lower carbon groups. This supports previous assumptions that lower molecular weight SCCP congeners are more prone to be volatilized with the increase of ambient temperature (Li et al., 2012; Wang et al., 2012). The congener group abundance profiles for site S2 were further compared to those in the atmospheric gas and particle phase, which showed that the abundance of higher molecular weight SCCPs increased from gas < needles $\leq$ bark < particulate (Fig. S3).

3.1. Estimating the vegetation-air partitioning of SCCPs

Atmospheric SVOCs can be taken up by foliage through three main processes; gas phase equilibrium partitioning, kinetically limited gaseous deposition, and particle-bound deposition (McLachlan, 1999). Concurrent air and vegetation sampling was

conducted at site S2 to study the air-vegetation partition, with the assumption that sampled air levels were representative for the whole growing period. On the basis of the interpretative framework by McLachlan (1999), an investigation on the vegetation uptake mechanisms of the different SCCP congener groups was conducted by plotting the logarithm ratio of needle concentrations (C_v) and gaseous levels (C_g) on a volumetric basis ($\log C_v/C_g$) against $\log K_{oa}$ (octanol–air partitioning coefficient), and $\log C_v/C_p$ (particulate levels) against $\log C_p/C_g$. As experimental K_{oa} values are not available, they were collected or calculated from physical–chemical estimation models (EPI Suite, ACD, SPARC and COSMOtherm) given by Wang et al. (2012), Gluge et al. (2013) and Krogseth et al. (2013). The average ambient temperature (23 °C) during the sampling period was close to the reference temperature (25 °C) usually used for calculating K_{oa} . The calculated K_{oa} values among the different model predictions varied as much as four log-units for the same

Fig. 3. a) Plot of the logarithm ratio of needle concentrations (C_v) and gaseous levels (C_g) on a volumetric basis ($\log C_v/C_g$) against $\log K_{oa}$ (octanol–air partitioning coefficient) for pine needles during summer at sampling site (S2) using predicted K_{oa} values from the physical–chemical property estimation software; SPARC, EPI Suite, ACD and the minimum and maximum values given by COSMOtherm (Gluge et al., 2013; Krogseth et al., 2013; Wang et al., 2012). b) Plot of $\log C_v/C_p$ (particulate levels) vs $\log C_p/C_g$ for summertime. The carbon congener groups are specified by different colors. The chlorination degree (Cl₅–Cl₉) within each carbon group is shown as increasing from left to right (for C₁₃ only Cl₅–Cl₈ were included). (For interpretation of the references to this figure legend, the reader is referred to the web version of this article.)

congener group (Fig. 3a, S4), which displays the high variability among different estimation methods. Despite the large variability among the models, their overall trend was similar. As seen in Fig. 3a, lower chlorinated congener groups are seemingly taken up by needles through kinetically limited gaseous deposition, whereas the steep slope for higher chlorinated congener groups indicate that these were taken up by particle bound deposition. According to McLachlan (1999), a positive slope for the curve of $\log C_v/C_g$ vs $\log K_{oa}$ at $\log K_{oa} > 11$ indicates particle bound deposition. If the vegetation-air partitioning in the investigated area followed that of the ideal behavior, then it would actually be possible to use the operationally defined air-vegetation partitioning trend to verify which of the predicted K_{oa} values are most accurate. From Fig. 3a, it could be inferred that the K_{oa} values were more accurately predicted by SPARC and COSMOtherm since their $\log(C_v/C_g)$ trends are closer to that of the theoretical curve given by McLachlan (1999). The logarithm of the C_p/C_g vs C_v/C_p was also plotted (Fig. 3b) and similar uptake mechanisms were observed. This further validates the observed trends and uptake mechanisms. Fig. 3b further highlights the influence of carbon length and chlorination degree on the uptake mechanism.

This study shows that pine bark and needles could be suitable indicators of SCCPs contamination and that their air-vegetation partitioning trends are similar to those of typical semivolatile organic compounds. A study encompassing a larger geographical scale and including more pronounced source and background sites is warranted to further validate the usefulness of tree bark and needles as indicators of SCCPs contamination. Furthermore, the limited number of days for the air sampling might not be sufficiently representative for the whole growing period. As such, more research is needed to further investigate and validate these trends.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2014.10.025>.

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