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Lichen, moss and soil in resolving the occurrence of semi-volatile organic compounds on the southeastern Tibetan Plateau, China

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HIGHLIGHTS

- DDTs, endosulfans, HCHs and hexachlorobenzene predominated in all the samples.
- High detection frequency of HBCDs was only observed in lichen samples.
- Lichen concentrations of OCPs and PCBs increased with elevation in Tibetan Plateau.
- Lichen is more suitable to reveal airborne SVOC contamination than moss.
- SVOCs with log K_{OA} (8–11) and log K_{WA} (2–4) had high mountain contamination potential.

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ABSTRACT

This study investigated a wide range of semi-volatile organic compounds (SVOCs), including 28 persistent organochlorine pesticides (OCPs), 18 polychlorinated biphenyls (PCBs), 13 polybrominated diphenyl ethers (PBDEs), and 3 hexabromocyclododecane (HBCD) congeners in lichen, moss and soil collected from the southeastern Tibetan Plateau, China. This allows research provides insight into elevation gradient distributions and possible cold trapping effects of SVOCs in this high mountain area, and compares lichens and mosses as air passive samplers for indicating SVOC occurrences. DDTs, endosulfans, HCHs and hexachlorobenzene predominated in all of the samples. Source analysis indicted that there were fresh inputs of DDTs and HCHs in the sampling region. Lichens and mosses shared commonalities in revealing the profiles and levels of SVOCs based on their lipid-content-normalized concentrations. The concentrations of 12 OCPs and 14 PCBs in lichens were significantly linearly correlated with altitudes, whereas the correlations for mosses and soil with altitudes were insignificant. Both a frequency distribution diagram and the Mountain Contamination Potential Model indicated that SVOCs with specific values of log K_{OA} (8–11) and log K_{WA} (2–4) had relative high mountain contamination potential on the Tibetan Plateau.

1. Introduction

Semi-volatile organic compounds (SVOCs) are distributed globally through long-range atmospheric transport (LRAT) and have been detected in pristine regions far away from polluted areas such as in high latitude or altitude regions with cold climates (Estellano et al., 2008; Wang et al., 2009). Accompanied by further insight into the adverse effects of SVOCs to humans and the ecosystem, the occurrence and behavior of SVOCs in pristine environments have become a growing concern in recent decades. Considering that electrical power is unavailable and that the access to high latitude or altitude regions is difficult, passive air sampling media, especially of vegetation, have been widely used to investigate the concentrations, distribution patterns and transport mechanisms of SVOCs in those remote regions; their popularity is due to their unique advantages in terms of electrical power savings, sampling convenience, and integration of air contamination over time (Cabrerizo et al., 2012; Daly et al., 2007; Harner et al., 2004; Liu et al., 2010; Ockenden et al., 1998). Various types of vegetation have been used as natural sampling media to evaluate atmospheric pollution of SVOCs since the 1980s (Buckley, 1982; Eriksson et al., 1989). Lichens (Augusto et al., 2009; Blais et al., 1998; Cabrerizo et al., 2012; Schrlau et al., 2011; Yogui et al., 2011), mosses (Cabrerizo et al., 2012; Cipro et al., 2011; Wang et al., 2012; Yogui et al., 2011), tree bark (Salamova

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and Hites, 2010; Tarcau et al., 2013) and pine needles (Blais et al., 1998; Schrlau et al., 2011; Yang et al., 2008) are the most commonly used vegetation because of their high lipid content, large surface area and great seasonal availability. Lichens and mosses, due to lack of barrier structures and root-like structures, can directly absorb gas-phase, aerosol and particle-bound pollutants from the atmosphere (Kansri et al., 1990; Madl et al., 2010; Yogui et al., 2011) and integrate air contamination over time (Simonich and Hites, 1995). Some research has reported an accumulation difference among the various air samplers (Schrlau et al., 2011; Tarcau et al., 2013; Yang et al., 2013). Schrlau et al (2011) compared the accumulation difference of SVOCs in lichen and XAD-passive sampler, and indicated that lichens could accumulate more SVOCs with octanol-air partition coefficients of log Koa > 10, whereas XAD mainly accumulated gas-phase SVOCs.

The Tibetan Plateau is often called the roof of the world, with an average altitude at 4000 m above sea level. It is one of the coldest and most remote regions in the world. The sparse human population, minimal to nonexistent industrial activities and hardly any identified or reported local sources of SVOCs, except for some organic chlorinated pesticides (OCPs), this high mountain region is considered to be an ideal natural setting for researching environmental fate and long-range atmospheric transportation of SVOCs. Previous researches have indicated the existence of some SVOCs with topographic cold trapping effect (Liu et al., 2010; Wang et al., 2009; Yang et al., 2008) in the Tibetan Plateau.

The purpose of this study was to use lichen (*Usnea longissima*), mosses (Hypnaceae and Pottiaceae) and corresponding soil samples to comprehensively investigate the spatial distributions, contamination level, source and cold trapping effect of SVOCs on the southeastern Tibetan Plateau, to gain further insight into the main differences and similarities between lichens and mosses as passive samplers indicating the occurrence of SVOCs in the atmosphere. The target compounds included 28 organochlorine pesticides (OCPs), 18 polychlorinated biphenyls (PCBs), 13 polybrominated diphenyl ethers (PBDEs), and 3 hexabromocyclododecane (HBCD) isomers.

2. Material and methods

2.1. Sampling

A sampling area was chosen on the southeast of the Tibetan Plateau. Compared with other parts, the southeast region is characterized by mountain–valley topography, containing the densest pristine forests. The large moisture passage of the Yarlung Tsangpo Valley nearby provides a constant stream of moisture to this region. The climate there is dominated alternatively by an Indian monsoon in summer and westerly wind in winter, likely bringing SVOCs from potential sources nearby onto the Tibetan Plateau (Sheng et al., 2013; Wang et al., 2010; Zhu et al., 2014). In this study, a total of 140 samples (consisting of 45 lichen, 49 moss and 46 soil samples) were collected from 75 sampling sites at a range of 920 km × 228 km on the southeast of the Tibetan Plateau (Fig. S1, Table S1) in late June 2010 and 2011. The moss and soil samples were nearly all collected at the same sites during the same field trip as paired samples; however, only 19 lichen samples were collected from the same sites as the moss and soil samples during the same field trip. Detailed information about the sampling can be found in Table S1 in the Supplementary content.

Because of the geographical restrictions and species distribution, two families of moss, i.e. Pottiaceae and Hypnaceae, were collected from the southeastern Tibetan Plateau. All of the collected lichen samples belong to *U. longissima* (Table S1). The composite lichen samples were taken from heights between 1.5 and 2.0 m above the ground from six different spots on the sampling tree. For the moss and surface soil (0–5 cm), each sample included a blend of six portions collected from six different segments within 30 m of the sampling sites. The samples were wrapped in aluminum foil, sealed in plastic bags, stored in insulation ice-boxes (polyester), and immediately taken back to the laboratory after sampling. After being rinsed with deionized water, the lichen and moss samples were lyophilized, ground, and then kept at −20 °C in sealed plastic bags until the sample treatment. The soil samples were also freeze-dried, screened, and kept at −20 °C in sealed plastic bags until sample treatment. Anhydrous sodium sulfate aliquot was included as a blank for this procedure.

2.2. Sample preparation and instrumental analysis

An isotope-dilution method was used to analyze the target compounds in this research. Two pretreatment methods, reported previously (Botaro et al., 2011; Wang et al., 2009; Zhu et al., 2012), were used to extract and concentrate OCPs and the three other types of organic pollutants (PBDEs, PCBs and HBCDs) from the samples. A detailed description of the pretreatment methods can be found in the Supplementary content.

Twenty-eight pesticides were identified with a GC–MS system composed of a gas chromatograph (Agilent 5890) and a mass spectrometer (Finnigan MAT 95). Thirteen PBDEs and eighteen PCB congeners were quantified using a HRGC-HRMS (Agilent 6890N/AutoSpec Ultima) system. Three HBCD isomers were analyzed with a HPLC–MS/MS system composed of high performance liquid chromatography (Waters 2695) and triple–quadrupole mass spectrometer (Waters Micromass). Detailed information about the instrument configuration, operational procedures and conditions for analyzing OCPs, PCBs and PBDEs, and HBCDs could be found in previous research (Feng et al., 2010; Wang et al., 2009; Zhu et al., 2014).

The total organic carbon (TOC) content of the soil samples was determined with a TOC Analyzer (OI Analytical, USA).

2.3. Quality assurance/quality control

A procedural blank was included and processed in parallel with each batch of 11 samples to check for interference and cross-contamination. The average recoveries of ^{13}C-labeled internal standards for OCPs, PCBs, PBDE, and HBCDs in all of the lichen samples were 73 ± 16%, 77 ± 21%, 62 ± 9.0%, and 83 ± 16%, respectively. Similarly, they were, respectively, 84 ± 18%, 88 ± 23%, 76 ± 5.0%, and 93 ± 14% in mosses, and 65 ± 12%, 78 ± 9.0%, 68 ± 13%, and 82 ± 12% in soil. The method detection limits (MDLs), defined as 3 times signal-to-noise ratio (S/N), for OCPs, PCBs, PBDEs and HBCDs were 0.57–17 pg/g, 0.10–0.62 pg/g, 0.21–3.6 pg/g, and 0.29–0.38 ng/g in the lichen samples, 1.7–42 pg/g, 0.090–0.45 pg/g, 0.21–4.2 pg/g, and 0.31–0.43 ng/g in the moss samples, and 0.16–4.6 pg/g, 0.19–0.83 pg/g, 0.10–1.3 ng/g, and 0.29–0.37 ng/g in the soil samples, respectively. The quantification limits were defined as 10 times the S/N. The resulting data were adjusted using blank values in light of the following rules: the resulting value (R) = the sample value − the average blank value (X); if the R was larger than 3 times the standard deviation of X, the value of R was deemed valid and reported as a result, otherwise the R was reported as not detectable, and valued as zero to calculate the related medians and means. Statistical tests were performed using SPSS (Statistical Product and Service Solutions, V. 16.0, SPSS Inc., CHI, USA). Independent-sample T-tests were used to determine the significant difference between samples, with a significance level of 0.05. Two-tailed Pearson's correlation tests were processed to determine the correlations among samples.

3. Results and discussion

3.1. Concentrations and profiles of SVOCs in lichen, moss and soil samples

Data summaries of the SVOC concentrations and detection frequencies in the three different matrices were shown in Tables S2, S3 and S4 in the Supplementary content. Independent-sample T-test indicated that there were no significant differences ($p > 0.05$) between the SVOC concentrations of the two families (Pottiaceae and Hypnaceae) of moss.