Dechloranes in lichens from the southeast Tibetan Plateau: Evidence of long-range atmospheric transport

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HIGHLIGHTS

- The occurrence and distribution of Dechloranes were investigated in the southeast Tibetan Plateau (TP).
- DP concentration in southeast TP was much higher than those in moss from the Arctic region.
- Different altitudinal patterns between DP and Dec 602 were identified.
- Decs are prone to undergo LRAT and cold-trapping by the mountains in the southeast TP.

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ABSTRACT

Dechloranes (Decs) have been recently found to occur widely in the environment even in the remote polar regions. However, the understanding of their environmental fate is rather limited. The Tibetan Plateau (TP) may be an important indicator region to study the long-range atmospheric transport and their fates of these emerging contaminants since it has very limited local sources. In the present study, Dechlorane plus (DP), Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603) and Dechlorane 604 (Dec 604) were analyzed in lichen samples from the southeast TP. The results showed that only DP and Dec 602 were detected, with a detection frequency of 89% and 100%, respectively. The average concentrations (dry weight) of DP and Dec 602 were 318 pg g$^{-1}$ (20–1132 pg g$^{-1}$) and 167 pg g$^{-1}$ (27–843 pg g$^{-1}$), respectively. The DP concentration in this study was much higher than those in moss from the remote Ny-Alesund, Arctic. The concentrations of Dec 602 were found to generally increase with increasing altitude, while DP concentrations seemingly showed an opposite altitudinal trend along the mountain slopes. No stereoselective accumulation or transformation of anti-DP and syn-DP was observed in lichens and the altitudinal behavior of the two isomers was similar. This research documented that Decs are prone to undergo LRAT and cold-trapping by the mountains in the southeast TP.

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1. Introduction

Halogenated (usually bromine- or chlorine-based) flame retardants are extensively used for fire prevention in electronic equipment, furniture, textiles and commercial buildings (Hoh et al., 2006; Na et al., 2015). Dechloranes (Decs) are highly chlorinated flame retardants that include Dechlorane 602 (Dec 602), 603 (Dec603), 604 (Dec 604), Mirex and dechlorane plus (DP, also called as dechlorane 605), which were patented by Hooker Chemical Corporation (Hoh et al., 2006). DP is manufactured by two corporations in the world: Hooker Chemical Corporation in Buffalo, NY, USA (now OxyChem) and Anpon Electrochemical Co., Ltd in Jiangsu province in China (Xian et al., 2011). DP has been identified as a high production volume chemical (HPVC) by the U.S. EPA (Sverko et al., 2011). Apart from the manufacturing plants, other sources of DP might contribute to its emission such as DP-containing e-waste recycling activities and the use of DP-containing products (Syed et al., 2013). Fiberglass-reinforced Nylon-6 is produced with the addition of 18% Dec 602, while Molykote AS-810 silicone grease used for lubrication of metals is produced with the addition of 10–30% Dec 604 (Shen et al., 2010). Dec 604 is also found in the commercial product of Mirex (2%) (Shen et al., 2011). Dec 603 is reported to be an impurity in technical Aldrin and Dieldrin (Shen et al., 2011). However, little information is available on the production volumes for the DP-related compounds (Decs 602, 603 and 604).

Since the first detection of DP in air, fish and sediment sam-
amples from the Great Lakes (Hoh et al., 2006), its ubiquitous presence has been confirmed in various environmental matrices all over the world, as reviewed by Xian and Sverko et al. (Sverko et al., 2011; Xian et al., 2011). By contrast, Dec 602, 603 and 604 were not detected until recently (Yang et al., 2011b). Various studies have shown the presence of Decs in biota samples, thus suggesting their bioaccumulation and biomagnification potential (Tomy et al., 2007). It has been found that Decs can undergo long-range atmospheric transport (LRAT) to remote Arctic and Antarctic regions (Moller et al., 2010; Na et al., 2015). However, to date, there is very limited data on Decs in remote alpine regions, and knowledge on their environmental fate in mountain regions is very limited.

The southeast Tibetan Plateau (TP) has long been considered as one of the most remote and isolated areas on the earth and thus is ideal for the study of LRAT of persistent organic pollutants (POPs). Various kinds of semi-volatile pollutants including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) have been well analyzed in the southeast TP (Yang et al., 2007; Wang et al., 2010b; Yang et al., 2011a; Wang et al., 2013; Yang et al., 2013a). The southeast TP is characterized by mountain-valley topography and monsoon climate, with the valleys acting as pathways of the Indian monsoon in the summer. Lichen is ubiquitously distributed in the southeast TP, and it can be used as a passive sampler to indicate atmospheric contamination. Here we present data on Decs in lichen samples from the southeast TP with the aim to address knowledge gaps regarding the occurrence and levels of Decs in this region. Furthermore, the potential factors that might influence the distribution of Decs are also discussed.

2. Materials and methods

2.1. Study area and sampling

The study area was within the Nyingchi Prefecture in the southeast TP. This region is characterized by mountain-valley topography. Twenty-six lichen samples were collected in July of 2010 along 3 transects of the mountains (Fig. 1); detailed information about the study area and the sampling procedure for lichens were reported in our previous paper (Yang et al., 2013b). Briefly, each lichen sample comprised at least six subsamples from different spots within 30 m of the sampling location. Lichen samples were wrapped in aluminum foil, sealed in plastic bags, placed in an iced cooler, and shipped to the laboratory where they were kept at −20 °C before analysis.

2.2. Chemical analysis

Dechlorane plus, Dec 602, 603 and 604 were purchased from Cambridge Isotope Laboratories (Andover, MA), and were surrogate standard PCB 209 and internal standard octachloronaphthalene (OCN) were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany).

The solvents n-hexane and dichloromethane used for extraction and cleanup were ultra residue-analytical grade and were purchased from J. T. Baker (USA). Alumina (100–200 mesh, Sigma–Aldrich, USA) and Silica gel (100–200 mesh, Qingdao Marine Chemical, China) were baked at 550 °C for 12 h and activated at 180 °C for 2 h. Anhydrous sodium sulfate was baked at 550 °C for 6 h.

Freeze-dried and crushed lichen samples (2 g) were spiked with the surrogate and extracted using mixed solvents of hexane and dichloromethane (DCM) (1:1, v/v) by accelerated solvent extraction ( Dionex ASE 350, U.S.) at a temperature of 150 °C and a pressure of 1500 psi. The thermal equilibration time was 7 min, and the static extractions were performed for 3 cycles. The extracts were concentrated to about 1–2 ml by a rotary evaporator. The cleanup column was packed with 6 g Florisil, 6 g acid silica gel (44% concentrated H2SO4, w/w) and 5 g of anhydrous sodium sulfate from bottom to top. The elution was subsequently conducted using 10 ml hexane and a 50 ml mixture of hexane and dichloromethane (4:1, v/v). The eluates were concentrated to a final volume of 0.5 ml by rotary evaporation and a high-purity nitrogen stream. The internal standard OCN was added before injection.

An Agilent-7890 gas chromatography equipped with an RTX-1614 capillary column (30 m × 0.25 mm × 0.10 μm) was used to separate Decs, while a mass spectrometer with negative chemical ionization (NCI) was used to analyze the target compounds. The oven temperature program was as follows: initial 100 °C for 2 min, 25 °C/min to 250 °C, 1.5 °C/min to 260 °C, 25 °C/min to 310 °C, and finally held for 27 min. The temperature of the injector was set at 250 °C. The ion source, quadrupole and interface temperatures were 150 °C, 150 °C, and 320 °C, respectively. Methane was used as the carrier gas with a constant flow of 1 ml/min. The MS was operated in selected ion monitoring (SIM) mode with the primary/secondary ions being 340.8/613.6 for Dec 602, 635.6/637.6 for Dec 603, 79/81 for Dec 604, 652/654 for both DP isomers, and 340.8/none for Mirex. Quantification was performed by internal standard calibration, using the primary ion of each compound.

2.3. Quality control

Strict quality control and quality assurance measures were conducted during the whole analytical process. A procedural blank was run every set of 10 samples. The recoveries of surrogate standard PCB 209 ranged between 88.6% and 141.1%. The final concentration was corrected using the recovery of the surrogate. The method detection limits (MDLs) were defined as three times the signal-to-noise ratio, and the MDLs for DP, Dec 602, 603, 604 and Mirex were 30 pg g−1, 20 pg g−1, 120 pg g−1, 170 pg g−1, and 180 pg g−1 respectively. The concentration levels in procedural blanks were all below the MDLs.

3. Results and discussions

3.1. Concentrations

All the concentrations are based on dry weight (dw) in this study. Of the six chemicals analyzed, only two isomers of DP and Dec 602 were detected in lichen samples. Similarly, Wang et al. also reported that DPs and Dec 602 were detected in air, soil, and sediment while Dec 603 and Dec 604 were below the detection limit in all the above matrices in Huai’an City, Jiangsu Province (Wang et al., 2010a). In the present study, Dec 602 was detected in all the lichen samples while DPs were detected in 89% of samples. The concentrations of Dec 602 and ΣDP (sum of syn-DP and anti-DP) were in the range of 20–1132 pg g−1 (mean 318 pg g−1) and 27–843 pg g−1 (mean 167 pg g−1), respectively. However, no DP was detected in the air at higher elevation (Nam Co Station) of the TP, which suggested that orographic precipitation may limit the transport of particle-bound DP to high elevations (Xiao et al., 2012).

Vegetation plays an important role in removing organic pollutants from the atmosphere. Amongst plant samples, lichen/moss and tree bark are widely used as natural passive air samplers to indicate atmospheric pollution. The contamination level of this study was compared with those in vegetation from various regions all over the world (Table 1). The ΣDP concentration was comparable but slightly higher than those in tree barks from Shenzhen,
Hangzhou and Tianjin of China (Qiu and Hites, 2007). ΣDP concentration was much lower than those in tree barks from South Korea and New York, United States (Qiu and Hites, 2007) but significantly higher than those in moss from the remote Ny-Ålesund, Arctic (Na et al., 2015). A similar comparison result was obtained when the concentration is normalized to lipid basis (Table 1).

It was reported that DP concentrations were highly influenced by the distance from the potential sources (Salamova and Hites, 2010) and mostly associated with urban and industrial regions (Hoh et al., 2006; Ren et al., 2008). However, the TP is isolated from intensive industrial and commercial activities, so comparatively higher DP concentrations in the southeast TP might be attributed to long-range atmospheric transport (LRAT). Our previous study also confirmed that the high concentrations of OCPs and mercury in this area are largely transported from the sub-Indian Continent by summer Indian Monsoon and then cold-trapped by the high mountains in the southeast TP (Wang et al., 2006; Sheng et al., 2013). No significant linear relationship was observed between concentration of Decs and lipid content, which was similar to our previous study for the OCPs and PAHs (Yang et al., 2013b).

### 3.2. Altitudinal distribution

In order to determine how Decs are distributed along the mountain slopes, the correlation between Log-transformed concentrations of DPs and altitude of the sampling sites was analyzed.

The result showed that generally the concentration of Dec 602 increased with increasing altitude, while the concentration of ΣDP seemed to exhibit the opposite trends along the three transects (Fig. 2). In fact, the physico-chemical properties of the two compounds are different from each other. Although Dec 602 and DP have similar Log \( K_{OA} \) (12.27 and 12.26, respectively), the water sol-
Comparison of Table 1 that the regression between ward slopes of Mt. Shergyla, respectively. It can be easily seen creasing altitude and decreasing temperature. soluble Dec 602 is easily deposited by precipitation with the in-

nounced in the higher altitude sites. In addition, the more water-

port longer in the atmosphere and cold trapping was more pro-

higher volatility of Dec 602. The more volatile Dec 602 can trans-

The distribution patterns could be dominantly attributed to the pollutants and thus providing evidence of mountain cold trapping.

overlaying atmosphere as the dominating input source for these

2013b). This difference was expected because T2 lies windward of (Lavin and Hageman, 2013). The present distribution pattern com-

is more pronounced for the windward slope than the leeward one influenced by the air flow than T1. The Indian monsoon influence

the summer Indian monsoon along the valley and is more strongly

tent with our previous study in which stronger linear correlation

was more pronounced in T2 compared with T1, which was consis-

was 0.71 in the present study, which was within the range

of technical products, possibly reflecting similar behavior during the long-range transport or the similar accumulation patterns by

lichen. The related studies showed that the variations of

the long-range transport or the similar accumulation patterns by

of technical products, possibly reflecting similar behavior during

3.3. Fractional abundance of DP isomers

DP has syn- and anti-DP stereoisomers. The anti-DP fractional abundance \( f_{\text{anti}} \), which is defined as \( f_{\text{anti}} = \text{anti-DP}/(\text{anti-DP} + \text{syn-DP}) \), is generally used to illustrate the different fate and behavior of the two isomers in the environment (Zhang et al., 2013). The \( f_{\text{anti}} \) values ranged between 0.65 and 0.80 in commercial DP produced by OxyChem (Guerra et al., 2011), which was slightly higher than that (0.59) of DP produced by Anpon facility, China (Wang et al., 2010a). The anti-isomer was more frequently detected than the syn-isomer in this study, and the \( f_{\text{anti}} \) value was calculated only when both isomers were detected simultaneously.

The \( f_{\text{anti}} \) value varied between 0.46 and 0.83 with an average value of 0.71 in the present study, which was within the range of technical products, possibly reflecting similar behavior during the long-range transport or the similar accumulation patterns by lichen. The related studies showed that the variations of \( f_{\text{anti}} \) in tree bark from remote regions of the world was not changed sig-

nificantly compared to values in the technical DP (Salamova and Hites, 2012). The \( f_{\text{anti}} \) value in this study was also similar to those

Table 1

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Sampling year</th>
<th>Matrix</th>
<th>( \Sigma \text{DP} ) (dw(^{-1}))</th>
<th>( \Sigma \text{DP} ) (lw(^{-1}))</th>
<th>( f_{\text{anti}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>2010</td>
<td>Lichen</td>
<td>0.027–0.843</td>
<td>0.86–52.7</td>
<td>0.46–0.83</td>
</tr>
</tbody>
</table>

na: not available; nd: not detected.

\( ^{a} \) Dry weight.

\( ^{b} \) Lipid weight.
in bark and reed samples from other parts of the world (Table 1) (Qiu and Hites, 2007; Wang et al., 2012). However, stereoselective enrichment was found in other environmental matrices such as sediment (Qiu et al., 2007), fish (Wu et al., 2009) and water birds (Zhang et al., 2010). It seemed that these two DP stereoisomers exhibited different accumulation behavior between vegetation and other matrices, e.g., water and sediment (Sverko et al., 2008; Ma et al., 2011). The distinct enrichment capacity of the two isomers might result from the different mechanisms of accumulation, degradation, and transformation in different media.

3.4. Correlation analysis and principal component analysis (PCA)

In order to trace the similarities or differences of lichen in accumulating different kinds of organic pollutants, Pearson’s correlation analysis was employed, and the correlation coefficients are listed in Table 2. Data of OCPs and PAHs are derived from our previous study (Yang et al., 2013b).

Besides the fact that HCHs and DDTs were significantly correlated on both the dry weight basis and lipid-normalized basis, and correlation between HCB and PAHs was significant on the lipid-normalized basis, the most significantly correlated pair of compounds was syn-DP and anti-DP. This result is expected because the two isomers constitute technical DP and come from the same emission sources. The same result was also observed in air samples from Northern Lake Victoria (Arinaitwe et al., 2014). The remaining pair of compounds that were significantly correlated was Dec 602 and DDTs. As was discussed above, Dec 602 showed an increasing trend with increasing altitude, which was similar to the altitudinal behavior of DDTs. Thus, their correlation might indicate their similar altitudinal behavior. No correlation was found between Dec 602 and DP isomers.

PCA was also carried out to further explore the relationships. Three components were extracted, which accounted for 32.7%, 27.0% and 16.9% of the variance, respectively. Dec 602, HCHs and DDTs had the highest matrix coefficients for Component 1, syn-DP and anti-DP for Component 2, and HCB and PAHs for Component 3 (Table 3). It is clearly shown that these compounds were separated into three clusters, and HCHs and DDTs were divided into one group because they have similar application in agricultural pest control. Also it is reasonable that HCB and PAHs were classified into another group since they can be produced by incomplete combustion from local or from LRAT in remote areas. It is notable that Dec 602 and DP were included in different clusters (Fig. 3). Because DP and Dec 602 were patented as fire retardants, they may have similar sources. Therefore, the discrepancy between the distributions of DP and Dec 602 possibly indicated their different environmental behaviors, as stated above.

Table 2
Correlation matrices of the concentrations of different kinds of compounds (N = 26).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec 602</td>
<td>1</td>
<td>0.72</td>
<td>0.14</td>
</tr>
<tr>
<td>syn-DP</td>
<td>0.02</td>
<td>1</td>
<td>0.94</td>
</tr>
<tr>
<td>anti-DP</td>
<td>0.14</td>
<td>0.87</td>
<td>1</td>
</tr>
<tr>
<td>HCHs</td>
<td>0.19</td>
<td>0.31</td>
<td>0.13</td>
</tr>
<tr>
<td>DDTs</td>
<td>0.70</td>
<td>0.27</td>
<td>0.05</td>
</tr>
<tr>
<td>HCB</td>
<td>0.09</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.35</td>
<td>0.07</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The upper triangle presents the correlation between compounds on the dry weight basis while the lower triangle presents the correlation on the lipid-normalized basis.

*Correlation was significant at 0.05 level; Bold and **: Correlation was significant at 0.01 level.

4. Conclusions

The concentration of DP in the present study is much higher than those in the Arctic. This research documented that Decs have significant potential for LRAT from source regions and then undergo cold-trapping by the mountains in the southeast TP. The concentrations of Dec 602 generally increased with the increasing altitude, while DP concentration showed a decreasing trend along the mountain slopes. No stereoselective enrichment of two isomers of DP was observed in lichen samples. The occurrence of Decs in remote alpine region highlights the necessity for further investigations. More research is needed to comprehensively understand the transport and deposition processes and environmental risk of Decs in the future.

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References


