CHARACTERIZING THE DISTRIBUTION OF SELECTED PBDES IN SOIL, MOSS AND REINDEER DUNG AT NY-ÅLESUND OF THE ARCTIC

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Introduction

Polybrominated diphenyl ethers (PBDEs) can release into the environments during the production, use and the dismantling of the products due to their weak chemical bond binding. PBDEs can reach soil via wet/dry deposition during their LRAT, and tend to be strongly absorbed in soil owing to their persistence and lipophilicity. Thus, soil has been regarded as an appropriate pollution "snapshot" of the surrounding atmospheric pollution of persistent organic pollutants (POPs). For example, Meijer et al. observed excellent relations of the soil/air partition coefficients of organochlorine pesticides with their octanol/air partition coefficients (K_{OA}) and octanol/water partition coefficients (K_{OW}).

To date, moss have been widely applied for estimating atmospheric POPs as typical natural passive air samplers. Uptake of POPs via lipid-rich cuticula of plant from the ambient atmosphere is one of key reasons for the contamination of aerial plant parts by POPs. Moss accumulates POPs mainly from the ambient atmosphere. In general, compounds with lower subcooled liquid vapor pressure (p°_{L}) are prone to bind with particles, whereas those with higher p°_{L} mainly exist in vapor phase. Thus, the different physicochemical properties of POPs have additional effects on the characteristics of the deposition to plants and soil. Relationships between the vegetation/air partition coefficients and K_{OA} (or p°_{L}) for typical POPs have been reported recently. The distribution of POPs between soil and air (between moss and air) is assumed to be characterized with their physicochemical properties, such as p°_{L} and K_{OA}. Moreover, bioaccumulation of POPs in biota and trophic transfer in food web are influenced by their physicochemical properties. Once POPs are ingested into body by animals, they are hard to be degraded owing to their persistence, and one of main elimination pathways from body is believed to be via feces. Therefore, the distribution of POPs in animal's food and dung is expected to be correlated to their physicochemical properties.[1]

Findings stated above imply similarities in distribution and accumulation trends of POPs between soil and plant (between plant and dung) in relation to the different p°_{L}, K_{OW} and K_{OA} of POPs. However, there have been few reports so far on the application of these physicochemical parameters for describing the distribution of PBDEs in such soil/plant/animal dung.

Materials and methods

Total 32 samples of surface soil (upper 5 cm) (12 samples), moss (12 samples) and reindeer dung (8 samples) were collected in July 2013 from 12 sites at Ny-Ålesund (78°55′N, 11°56′E). The average temperature during sampling is 5 °C. Soil, moss and reindeer dung were collected simultaneously within an area of 50 × 50 m at each sites (there are not reindeer dung samples at 4 sites). Before analysis, soil, moss and reindeer dung samples were freeze-dried, ground, sieved (80 mesh) and stored in sealed glass containers at -20 °C until analysis.

Samples (5 g) were spiked with ^{13}C-labeled surrogate standards (1 ng) and then extracted with a mixture of dichloromethane (DCM) and hexane (v:v, 1:1; 150 mL). Acidic silica (15 g) was added to the extract of moss and reindeer dung samples to remove lipid, and activated copper powder (2 g) was added to soil samples to remove sulfur. Then the extract was concentrated with a rotary evaporator, cleaned with multilayer column filled from the bottom with activated silica gel (1 g), basic silica gel (4 g), activated silica gel (1 g), acidic silica gel (8 g), activated silica gel (1 g), $AgNO_3$ silica gel (2 g) topped with 4 g of anhydrous Na_2SO_4. Samples were eluted with 70 mL hexane and 100 mL DCM/hexane (1:1). The first fraction was discarded and the second fraction was collected and concentrated to 20 μL. Finally, 1 ng of ^{13}C-PCB138 was added as internal standard and mixed completely prior to instrumental analysis.

PBDEs were analyzed using an Ultra GC coupled with a Trace DSQ II MS (Thermo, USA) in selected ion monitoring (SIM) mode with electron capture negative chemical ionization (ECNCI) mode. Analytes were separated on a DB-5MS (30 m × 0.25 mm × 0.25 μm). Helium was used as carrier gas at a flow rate of 1.0 mL/min, methane as reagent gas at a flow rate of 2.0 mL/min, and the injection volume was 2.0 μL in the splitless mode. The following PBDE congeners were analyzed: BDE-17, 28, 47, 66, 71,85, 99, 100, 138, 153, 154, and 183.

Results and discussion

Concentrations (dry weight) of the 12 PBDE congeners (ΣPBDEs) at Ny-Ålesund were 42 ± 23 (11 - 89) pg/g in soil, 122 ± 59 (48 - 259) pg/g in moss and 72 ± 20 (38 - 102) pg/g in reindeer dung, respectively. The difference of PBDE concentrations was not significant ($p > 0.05$) among different sampling sites, that is to say, the influence of local (point) sources on PBDE concentrations at Ny-Ålesund was weak. ΣPBDEs in soil at Ny-Ålesund were compared to the values from the south and east edge of Tibetan Plateau and other remote regions, such as Russian Arctic (16 - 230 pg/g), but much lower than those in Norwegian background soils (median: 970 pg/g). ΣPBDEs in moss were in comparison to the PBDE concentrations in Moss samples (*H. splendens*) collected from Norway (12 - 339 pg/g). However, there are few reports on PBDE levels in reindeer dung. In this study, there was no relationship observed between ΣPBDEs and OM of soil and reindeer dung (and lipid contents of moss).

Fig. 1 shows the mean proportions of PBDE congeners in the three media. Clearly, the congener specific patterns are different in various media. For low brominated congeners (i.e., BDE-17, -28, -47), the proportions were higher in moss than those in soil, whereas for higher brominated congeners (i.e., BDE-138, -154), the values were lower in moss. The observations can be explained with the physicochemical properties of individual PBDE congeners and their different accumulation routes in soil and moss. As stated above, moss accumulate PBDEs mainly from the ambient atmosphere, and PBDEs in soil mainly from dry/wet deposition of particles, thus soil would accumulate more lower p°_{L} or higher K_{OA} compounds, such as BDE-138 and -154, compared to moss.

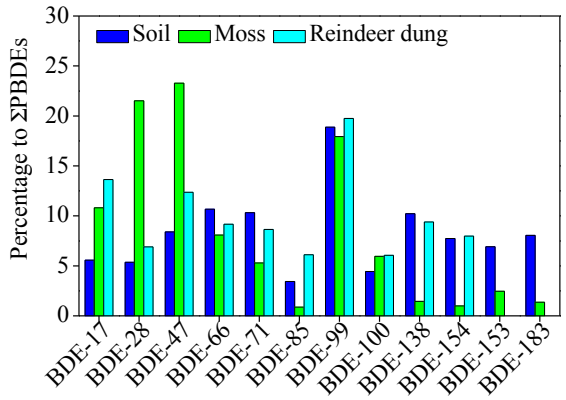

Fig. 1 Percentage of individual PBDE congeners to the total concentration

POPs with lower p°_{L} and/or higher K_{OA} are favored for accumulation in soil, hence, physicochemical properties could be responsible for the observed different profiles of PBDEs in soil, moss and reindeer dung. p°_{L} is often used to describe the relation with the gas/particle partition coefficients (K_P) of PBDEs using the following linear free energy relationship:[2]

$$\log K_P = m_r \log p^{\circ}_{L} + b_r \quad (1)$$

where m_r and b_r are regression parameters. As expected, the distribution of PBDEs in soil, moss and reindeer dung could be described with their physiochemical parameters, such as p°_{L} and K_{OA}. To verify the above hypothesis, the dimensionless soil/moss quotient (Q_{SM}) was defined for each compound:

$$Q_{SM} = C_S/C_M \quad (2)$$

where C_S and C_M are PBDE concentrations in soil and moss (pg/g), respectively. This quotient can effectively reduce the impact of different sampling site loads and organic matter contents both in soil and moss. Due to the concentrations of some PBDE congeners below detection limits in soil and/or moss, the corresponding Q_{SM} of these congeners were not calculated. As shown in Fig. 2, Q_{SM} displayed an excellent log/log-linear relationship with p°_{L} of the 12 PBDE congeners in soil and moss samples collected at Ny-Ålesund:

$$\log Q_{SM} = -0.25 \log p^{\circ}_{L} - 2.24 \quad (5\ ^{\circ}C) \quad (3)$$

Moreover, a significant correlation between $\log Q_{SM}$ and $\log K_{OA}$ was observed as expected ($r^2 = 0.71$, $p < 0.01$). Values of $\log Q_{SM}$ increase significantly with the decrease of $\log p^{\circ}_{L}$ or increase of $\log K_{OA}$, suggesting an increase in accumulation of more hydrophobic PBDEs in soil as compared to moss. The results further confirmed that the physicochemical properties of PBDEs are appropriate for describing their distribution in the terrestrial environments, especially in soil and vegetation.[3,4]

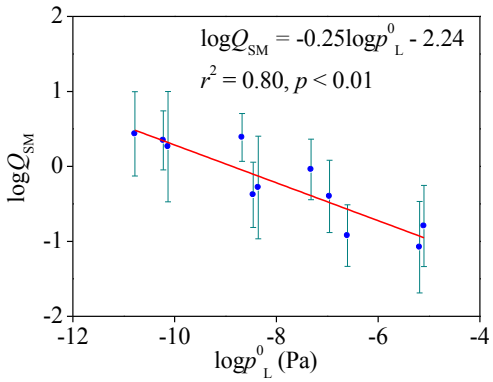

Fig. 2 Significant linear correlation between $\log Q_{SM}$ and $\log p^\circ_L$ of the 11 PBDE congeners (except for BDE-183)

Similar to Q_{SM}, the dimensionless moss/dung quotient (Q_{MD}) was calculated according to the following equation:

$$Q_{MD} = C_M/C_D \quad (4)$$

where C_D is PBDE concentrations in reindeer dung (pg/g). A significant linear relationship between $\log Q_{MD}$ and $\log K_{OW}$ was observed (Fig. 3). $\log Q_{MD}$ of PBDEs increase with the increase of their $\log K_{OW}$, indicating that PBDE congeners with higher $\log K_{OW}$ are prone to accumulation in moss compared to reindeer dung. Similarly, Wang et al. also observed the positive linear correlation between $\log K_{OW}$ and $\log Q_{MD}$ for PAHs in moss and reindeer dung.[3] The trend between $\log Q_{MD}$ and $\log K_{OW}$ can be explained with respect to different absorption and excretion potential for various PBDE congeners.

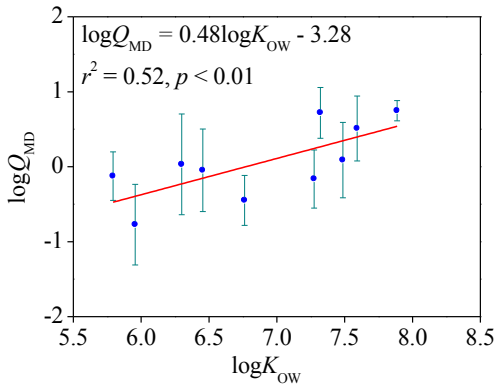

Fig. 3. Correlation between $\log Q_{MD}$ and $\log K_{OW}$ for individual PBDE congeners except for BDE-153 and -183.

Acknowledgements

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