HUMUS FROM CONIFEROUS FORESTS A RESERVOIR FOR PBDE FROM AIR AND DEPOSITION – ANALYSIS AND QUALITY CONTROL

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Introduction

Spruce needles are efficient receptors of lipophilic semivolatile organic compounds (SVOC) from air due to their highly absorbing epicuticular wax. Soil in coniferous forests, especially the high organic carbon containing humus layers, accumulate organic compounds from deposition and fall of needles over a long period of time.

Polybrom-diphenylether (PBDE) analysed in this indicator samples are heavily used as flame retardants in polymers and textiles and have become ubiquitous. Because of exponentially increasing levels in human blood and milk, technical Penta- and OctaBDE are banned in the European Union,[4] California and Maine,[8] and industry voluntarily ceased production.[12] DecaBDE is not included in these bans. Total market demand of DecaBDE was 56,418 tons in 2003.[3] Industry tries to reduce its emission throughout the live-cycle and sponsors a deca-monitoring program.[2]

Until now only a few data on PBDE levels in vegetation have been published. Spinach, potatoes and carottes from Japan,[9] pine needles from Tokyo Bay, Japan,[10] moss (*Hyolocomium splendens*) from the Norwegian environment[7] and archived U.K. herbage[5] were analysed.

The analytical method described in this paper was developed for MONARPOP (**Mo**nitoring **N**etwork in the **A**lpine **R**egion for **P**ersistent **O**rganic **P**ollutants). The major goal of this study is to get information about the levels and long-range atmospheric transport potential of POPs to high mountains.[1] For DecaBDE (BDE 209) four multimedia models predicted a very low potential to reach remote areas.[13] Therefore the method emphasizes on the analysis of very low PBDE concentrations (0.5-75 ng kg^{-1} d. m.) in humus and spruce needles with special efforts to identify and quantify BDE 209. 32 humus samples from MONARPOP are analysed so far. Total number of samples finally will be 56 humus and 55 spruce needle samples.

Materials and Methods

Reduction of Blanks

In indoor dust high concentrations of PBDE were detected.[6] Therefore, a clean laboratory environment is essential for the analysis of PBDE, in particular for the analysis of DecaBDE.

Polymer material (e.g. red rubber septa) were tested before use. Silica, sodium sulfate and glass wool were extracted with dichloromethane. After evaporation of the solvent, silica and sodium sulfate and all laboratory glassware used for the clean-up procedure were baken out for 16 hours at 450°C. Glass fiber extraction thimbles and filters, Pasteur pipettes and glass wool, which became brittle if heated to long, were immediately cooled down after heating up. After cooling down the glassware was immediately capped with aluminium foil or stored in metal boxes until usage. Sodium hydroxide water solution for the preparation of SiO_2-NaOH was extracted 3 times with hexane. To avoid cross contamination the vapour tubes of the rotary evaporators were changed after each sample.

Extraction and baking out of all for sample clean-up used chemicals and laboratory glassware and avoiding dust contamination reduced the laboratory blanks (May 2005 set 100%) for BDE 209 to 4% and for BDE 47 and BDE 99 to 33 and 27% (March 2006) (Fig. 4).

Analytical Method

20 g freeze-dried humus sample was spiked with the $^{13}C_{12}$-BDE standard mixture (1 ng BDE 28, 47, 99; 2 ng BDE 153, 154, 183 and 5 ng BDE 209) and extracted by Soxhlet extraction (Knöfler-Böhm hot extractor). Residual water (0-11%) was simultaneously distillated with Dean-Stark water separator with toluene. The extract was cleaned by a four column clean-up (1. Multi-layer SiO_2-H_2SO_4, NaOH. 2. Macro alumina. 3. GPC bio-beads S-X3. 4. Mini alumina), spiked with the injection standard (1 ng $^{13}C_{12}$-BDE 138) and reduced to 50 µl. 1 µl was injected on-column (guard column 2 m x 0.32 mm, uncoated, deactivated) and analysed by GC-SIM(EI+)HRMS (TRACE GC-MS MAT 95 XP, ThermoFinnigan, Bremen) using a DB-5MS (15 m x 0.25 mm, 0.1 µm). The two

most intense masses of the bromine cluster (Tri- and TeBDE: M^+. Te- to DeBDE: M^+-2Br) were measured for each homologue group. The identification of PBDE was based on retention time and correct isotope ratio for both fragments recorded. Quantification was performed by means of the $^{13}C_{12}$-labelled internal standards. All congeners except BDE 100 were quantified based on their corresponding $^{13}C_{12}$-labeled analogues used as internal standards. BDE 100 was quantified using the $^{13}C_{12}$-BDE 99 internal standard. The laboratory took part in the BSEF/QUASIMEME interlaboratory study on brominated flame retardants December 2001 to March 2002. Method blanks were spiked on a plug of glasswool in a Soxhlet extraction thimble and extracted and clean-up processed like samples. Blanks were analysed every four samples. The blank concentrations were calculated on a fictive sample weight of 20 g (Fig. 5).

Results and Discussion

Recovery of $^{13}C_{12}$-labeled internal standards

The mean recovery of the $^{13}C_{12}$-labelled internal standard from 32 humus samples ranges from 68-100%. For BDE 154 (68%) and BDE 183 (86%) the lowest mean recoveries were found (Fig. 1).

Duplicate analyses

One sample was analysed in duplicate (totally separate PBDE determination of two aliquots of humus from the same sample). The repeatability of the method for the Tri- to HeptaBDE 28-183 is good. For the difficult to analyse DecaBDE 209 different concentrations of 2641 and 5012 ng kg^{-1} d. m. were detected (Fig. 2).

PBDE concentrations in humus and blanks

The contribution to the total blank of every clean-up column was separately tested. These blanks are dominated by BDE 209 followed by BDE 47, 99 and 100. Only minor amounts of BDE 28, 153, 154 and 183 were detected. The contribution of multi-layer and macro alumina to total blank is 4-5 times the contribution of bio-beads S-X3 and mini alumina column (Fig. 3). A lower recovery for $^{13}C_{12}$-BDE 154 as for the total humus sample clean-up (Fig. 1) was also observed for the multi-layer, macro alumina and mini alumina but not for the bio-beads S-X3 column. A contribution of rotary evaporators to blank concentrations as recently reported was not observed. The minimum amount of PBDE present in the humus samples was 3-48 times higher than in the blanks and therefore no corrections were applied (Fig. 5).

References

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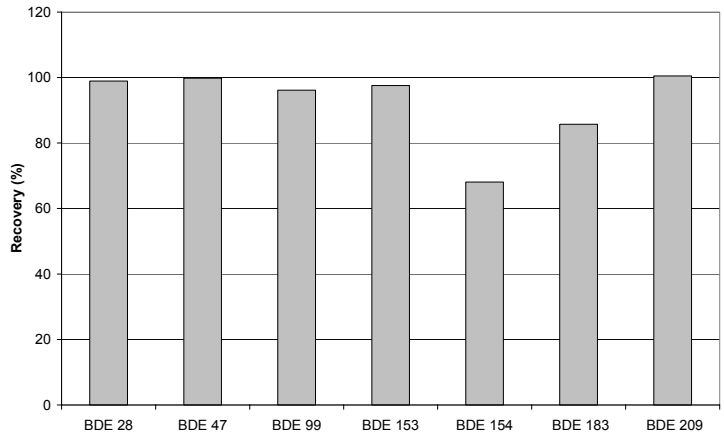

Fig. 1. Mean recovery rates of the PBDE determination in spiked humus samples (n=32). Standard addition 1 ng $^{13}C_{12}$-BDE 28, 47, 99; 2 ng $^{13}C_{12}$-BDE 153, 154, 183 and 5 ng $^{13}C_{12}$-BDE 209/20 g d. m. humus.

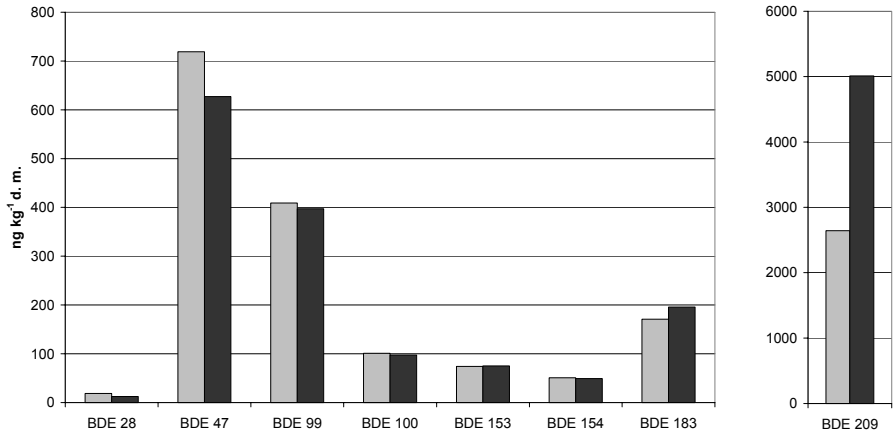

Fig. 2. Duplicate analyses of PBDE in a humus sample.

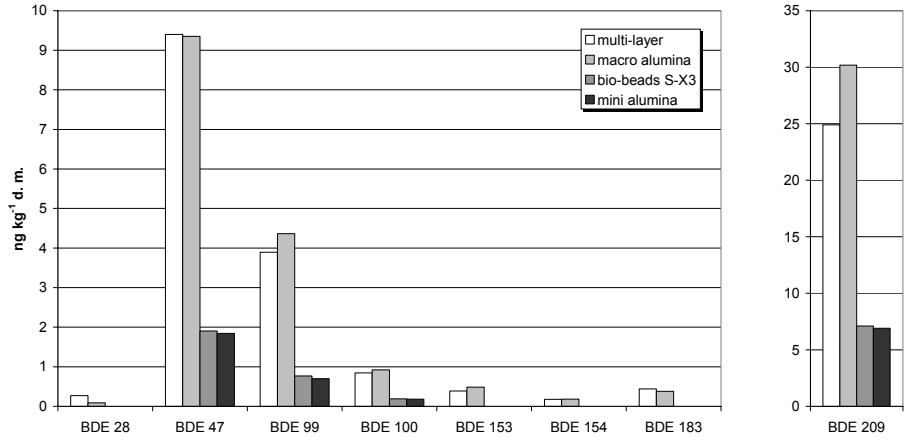

Fig. 3. Mean blank concentrations (n=2) of PBDE after multi-layer, macro alumina, bio-beads S-X3 and mini alumina clean-up column. The blank concentrations are calculated on a fictive sample weight of 20 g.

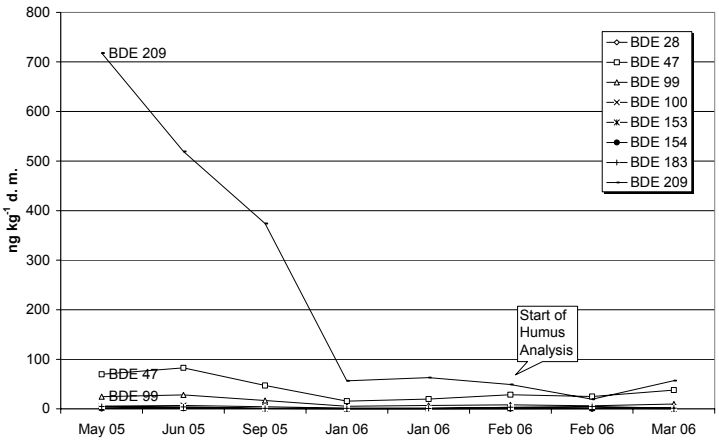

Fig. 4. Decrease of PBDE blank concentrations from May 2005 to March 2006.

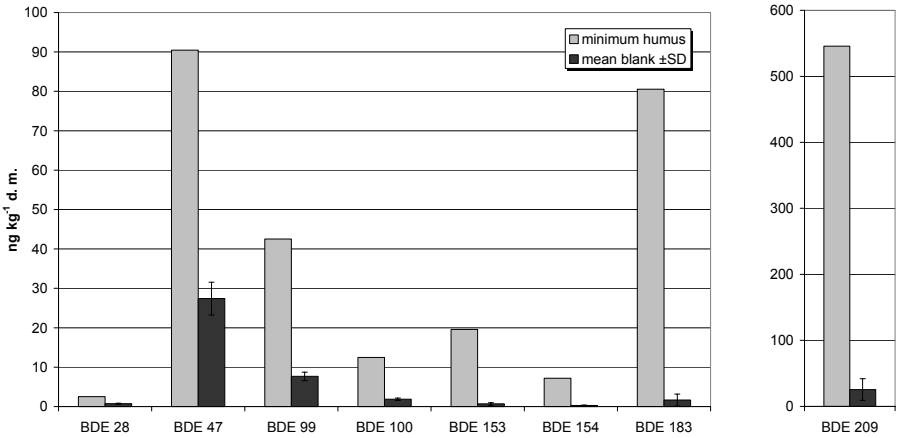

Fig. 5. Minimum PBDE humus (n=31) and mean blank concentrations ±standard deviation (n=9). The blank concentrations are calculated on a fictive sample weight of 20 g.