ANALYSIS OF POLYBROMINATED DIPHENYL ETHERS IN MOSS (Hylocomium splendens) FROM THE NORWEGIAN ENVIRONMENT

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Introduction

The environmental levels of the brominated flame retardants (BFRs) are increasing and as previously shown for the polychlorinated biphenyls (PCB) the BFRs have now a worldwide distribution[1,2]. Relatively little is known about the toxicology[3] of the BFRs and the observed increase in the environment is of major concern. The polybrominated diphenyl ethers (PBDEs) are used as additive flame retardants and annual demand has now reach approximately 65 000 ton[2] of which the use of the decaBDE mixture constitute of approximately 85%. Much emphasize are performed regarding environmental spread of the polychlorinated biphenyls (PCBs) showing that this compound group are attributed to atmospheric spread[4,5]. The PBDEs have similar chemical and physical properties suggesting that the PBDEs behave similar as to the PCBs in the enviroment. This view was strengthen by Wania and Dugani[6] who reported that the lower brominated PBDEs behave similar to the higher chlorinated PCBs, whereas the heavy brominated PBDEs, such as the decaBDE, primarily is attributed to particulate spread. The potential of particulate spread of this compound group was, however, not discussed. In this study we have collected moss (*Hylocomium splendens*) from twelve different localities in Norway, expected to be non-contaminated areas with little influence from industry and human population. Moss has been used as a natural passive sampler and is a good indicator of atmospheric spread of environmental contaminants[5].

Materials and Methods

Sample collection

Samples of moss (*Hylocomium splendens*) from twelve different localities in Norway were collected in summer 2004 (Fig. 1). The moss samples were sampled in cleaned glass containers, in the field, and stored at -20°C until analysis. The extraction and clean up procedure were performed in a “clean-room” (class 200-1000) to avoid contamination of laboratory dust.

Extraction and clean up

The moss samples were dried in paper bags at 40°C for approximately 24 hours. The samples were first soxhlet extracted for 8 hours in hexane. The crude solvent extract where then cleaned by eluting the extract through a column with acid treated silica (sandwich column with activated silica and 33% sulphuric acid treated silica) with 10% toluene in hexane preconditioned with hexane. The purified extracts with a final volume of approximately 100µl were then added recovery standard (1234-TCN) and subjected to GC/HRMS-EI analysis.

Analysis of PBDE by GC/HRMS-EI

Analysis of 14 different PBDE congeners (BDE-28, -47, -49, -66, -85 -99, -100, -119 -153, -154, -183, -196, -206 and -209) where performed by GC/HRMS in the EI mode. The PBDEs were separated by a fused silica capillary column from Zebron (ZB-1, 15m, 0.25mm id, 0.1 µm film thickness). The PBDEs were detected in the EI mode with their respective molecular ion masses as target ions $[M]^+$, with the exception of BDE-206 and BDE-209, $[M-2Br]^+$.

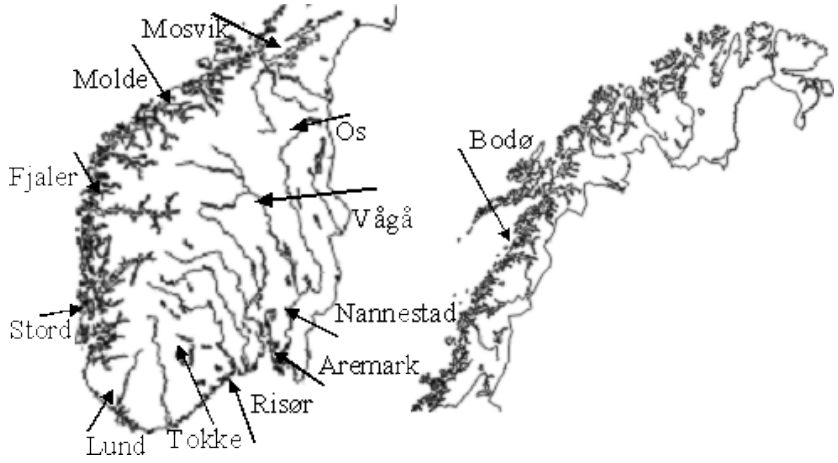

Fig 1. Twelve moss (*Hylocomium splendens*) samples were collected from different locations in Norway

Results and Discussion

Moss collected from 12 different localities in Norway was analysed for the presence of. PBDEs. The recovery of the internal standards is summarized in table 1. Most of the congeners analysed were detected in the samples with the exception of BDE-196. BDE-85 and BDE-206 were only detected in two and one samples respectively. The levels of the eight major PBDEs in the moss samples are summarized in table 2. The decaBDE was the dominating congener contributing to approximately 85% of the total (85%±6, mean ± SD). The low presence of the octa brominated BDE-196 and BDE-206 indicates that the decaBDE do not decompose to these congeners in considerable amounts in the environment.

Table 1: Recovery of the C13-labelled internal standards (percent recovery)

	BDE28	BDE47	BDE99	BDE153	BDE183	BDE209
Mean	89	66	67	67	61	64
SD	22	27	19	18	17	13
Median	86	58	57	60	61	67

Table 2: The concentration *(pg/g dry weight)* of eight PBDE congeners in moss from 12 different localities in Norway

	BDE28	BDE47	BDE99	BDE100	BDE153	BDE154	BDE183	BDE209	SUM PBDE*
Lund	2	48	92	13	21	14	21	1107	1380
Risør	2	67	45	11	13	11	23	1593	1783
Aremark	2	34	55	9	11	8	15	801	948
Tokke	1	22	21	5	14	5	37	426	531
Stord	2	29	45	9	13	7	10	794	924
Nannestad	2	28	28	5	nd*	nd	12	1198	1272
Fjaler	1	25	38	5	9	6	11	347	449
Vågå	2	41	13	5	4	5	nd	746	822
Os	1	8	10	2	4	2	3	105	139
Molde	nd	11	16	3	nd	nd	nd	133	168
Mosvik	nd	5	5	1	nd	nd	nd	133	145
Bodø	1	9	12	2	3	3	3	640	677

* SUM PBDE includes all PBDEs analyzed, BDE-28, -47, -49, -66, -85 -99, -100, -119 -153, -154, -183, -196, -206 and –209; nd, not detected.

The PBDEs found in the samples were not due to background contamination from the laboratory environment although some contamination was revealed. Procedure blanks were prepared simultaneously to elucidate background contamination revealing that 8 out of 12 moss samples were at least 2 times higher in total BDE-209 concentration than the highest amount of decaBDE measured in a procedure blank. In two of the blanks BDE-209 was not detected (Table 3). Also BDE-28 and BDE-47 were revealed in considerable amounts in the procedure blanks, whereas the higher brominated congeners such as BDE-153 and BDE-154 were not detected.

Table 3: Total amount of eight different PBDEs (pg) in the moss samples and the procedure blanks

	BDE28	BDE47	BDE99	BDE100	BDE153	BDE154	BDE183	BDE209
Lund	13	270	517	74	118	81	120	6234
Risør	12	460	313	74	93	75	160	10992
Aremark	12	247	395	64	81	61	108	5770
Tokke	8	168	161	37	109	41	292	3320
Stord	10	182	282	54	82	41	63	5002
Nannestad	10	138	138	26	nd	nd	59	5988
Fjaler	8	140	208	28	49	31	62	1907
Vågå	12	278	87	33	26	31	nd	5008
Os	6	53	66	15	30	10	20	706
Molde	nd	73	110	21	nd	nd	nd	893
Mosvik	nd	42	43	10	nd	nd	nd	1107
Bodø	5	69	93	16	25	21	26	5057
Blank 1	nd	29	15	4	nd	nd	nd	nd
Blank 2	6	48	14	4	nd	nd	nd	1679
Blank 3	5	47	nd	nd	nd	nd	12	397
Blank 4	nd	43	22	4	nd	nd	nd	nd

These findings show that most PBDEs, including the decaBDE, may be spread into a terrestrial environmental and that the decaBDE is the dominating compound. This is reasonable since this congener constitutes of more than 85% of the total worldwide use of PBDEs. The appearance of the BDE-209 congener in the moss samples is most likely due to particulate spread. There was no clear evidence of a spatial distribution of the PBDE levels in the samples. In Europe the use of the pentaBDE mixture is now prohibited and it is indications of a stabilisation in the environmental levels of this compound group in some European countries[7]. Recent studies from the United States have, however, revealed that the levels of PBDEs are increasing and are at least one orders of magnitude higher in mother's milk collected from US women compared to their European counterpart[7,8]. The worldwide use of the decaBDE is extensive and it is therefore of importance to investigate its environmental fate.

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