

## BIOACCUMULATION OF POLYBROMINATED DIPHENYL ETHERS IN FISH FROM THE NORWEGIAN LAKE MJØSA.

Espen Mariussen<sup>1</sup>, Eirik Fjeld<sup>2</sup>, Martin Strand-Andersen<sup>1</sup>, Marianne Hjerpset<sup>1</sup> and Martin Schlabach<sup>1</sup>

<sup>1</sup>Norwegian Institute for Air Research, P.O.Box 100, N-2027 Kjeller, Norway.

<sup>2</sup>Norwegian Institute for Water Research, Postboks 173 Kjelsås, N-0411 Oslo, Norway.

### Introduction

The worldwide use of brominated flame retardants (BFRs) is extensive and there are significant release of these components to the environment<sup>1</sup>. The last twenty years the levels of the polybrominated diphenyl ethers (PBDE) in biota have increased and in some areas the levels are comparable or even higher to what is reported for the polychlorinated biphenyls (PCB)<sup>2-5</sup>. It has also been reported that some of the lower brominated PBDEs have an higher bioaccumulation factor than PCBs with similar lipophilicity<sup>6</sup>.

In Lake Mjøsa, which is the largest lake in Norway located in the south-eastern part of Norway, we have found especially high levels of PBDEs in trout (Mariussen et. al., this issue). On the basis of these findings we have in this study collected five different fish species to evaluate the levels of PBDE. The fish collected were trout (*Salmo trutta*), burbot (*Lota lota*), smelt (*Osmerus eperlanus*), common whitefish (*Coregonus lavaretus*) and european whitefish (*Coregonus albula*), which represent different trophic levels of the Lake Mjøsa food web.

With the exception of smelt these species are also used for human consumption among people living near the lake. Relatively little is known about the toxic effects of chronic exposure of this compound group. It is therefore of importance to achieve knowledge of the PBDE levels, and the levels of other environmental contaminants, in different fish species in a rather heavily polluted lake such as Lake Mjøsa.

### Methods and Materials

#### *Sample collection*

Samples of five different fish species were collected from Lake Mjøsa, the largest lake in Norway. The fish species collected were trout (*Salmo trutta*), autumn 2001, burbot (*Lota lota*), spring and summer 2002, smelt (*Osmerus eperlanus*), autumn 1998, common whitefish (*Coregonus lavaretus*), autumn 1998, and european whitefish (*Coregonus albula*), autumn 1998. Burbot usually have their habitats attached to one locality, whereas the trout is a migrating species. Burbot from two different localities where analysed, from the city of Lillehammer and the city of Hamar respectively, for investigating spatial differences in the PBDE content. With the exception of the burbot samples, which are whole fish samples, the content of the PBDEs in the samples was analysed in fillet. The samples were kept frozen at -20°C until analysis.

#### *Extraction and clean up*

Fillets from the trout were homogenized in  $\text{Na}_2\text{SO}_4$  to remove water. Fish representing 0.1-0.25g fat were then spiked with internal standard (BDE-71 and BDE-77) and subjected to cold extraction with cyclohexane and ethylacetate (1:1). The crude solvent extract where cleaned by eluting the extract through a column with acid treated silica with 3% ether in hexane. The purified extracts with a final volume of 100 $\mu\text{l}$  were then added recovery standard (1234-TCN) and subjected to GC/LRMS-NCI or GC/HRMS-EI analysis.

#### *Analysis of PBDE by GC/LRMS-NCI*

Analysis of the PBDEs (BDE-28, -47, -99, -100, -153, -154, -183) in trout, smelt, and whitefish where performed by GC/LRMS in the NCI mode. The PBDE were separated by a fused silica capillary column from J&W Scientific (Ultra 2, 25m, 0.2mm id, 0.11 $\mu\text{m}$  film thickness). The PBDEs were detected by negative chemical ionisation monitoring at  $m/z$  79 and 81 with methane as the chemical ionisation gas.

#### *Analysis of PBDE by GC/HRMS-EI*

Analysis of the PBDE in burbot where performed by GC/HRMS in EI mode. The PBDE were separated by a fused silica capillary column from HP (HP5, 20m, 0.25mm id, 0.10 $\mu\text{m}$  film thickness). The HRMS were operated in EI mode with a mass resolution of more than 10000 (5% valley). PBDE were detected by monitoring at  $m/z$  of the molecular ions with C13PCB 101 as internal standard.

### **Results and Discussion**

This study is a part of a project to analyze levels of brominated diphenylethers in Norwegian terrestrial and limnic biota. Previous reports of high levels of environmental contaminants such as PCB in trout and burbot collected from Lake Mjøsa<sup>5</sup> prompted us to investigate the level of PBDE in different species of fish from the lake. These fish species represent different trophic levels of the lake's food web, and are, with the exception of smelt, also used for human consumption.

PBDE were found in high amount in all species of fish (Table 1). The variation of the results within sample groups was high (Table 2). With the exception of the smelt sample, the congener pattern of the PBDE was similar. The smelt sample had relatively much higher concentration of BDE-47 and the higher brominated BDE-183 compared to the other species. It is known from previous studies of PCBs that the PCB congener pattern may differ between organisms<sup>7</sup>. This discrepancy in the congener pattern may be due to a preference to certain kind of food, due to the preferred habitat or due to difference in the metabolism of the compounds. A discrepancy in the congener patterns may also be due to release of different mixtures of contaminants. E. g. more of "octa-" rather than the "penta-mixture".

Table 1: Mean concentration (*ng/g wet weight*) of PBDE congeners in five different species of fish from Lake Mjøsa.

PBDE	BDE-28	-47	-99	-100	-153	-154	-183	SUM
Fish								
Com whitefish	0.005	0.65	1.1	0.42	0.19	0.24	n.d.	2.6
Smelt	0.018	3.7	0.96	0.87	0.24	0.29	0.30	6.4
Euro whitefish	0.079	9.5	11.4	3.5	0.81	0.99	0.01	26.3
Trout*	0.87	144	126	52.5	14.8	15.7	n.d.	353
Burbot, Lillehammer	1.7	339	356	203	35.7	44.8	0.072	982
Burbot, Hamar	0.71	135	55.2	34.4	8.6	13.8	0.02	247

\* Mariussen et. al. 2003, this issue

Table 2 Mean, media and range of SUM PBDEs in burbot and trout from Lake Mjøsa

Fish	PBDEs <i>ng/g wet weight</i>			PBDEs <i>ng/g fat weight</i>		
	Mean	Median	Range	Mean	Median	Range
Burbot, Lillehammer	982	849	261-2265	22395	18710	7066-45144
Burbot, Hamar	247	284	114-347	18714	19485	14235-25794
Trout*	353	161	72-1120	5283	4461	1496-7915

\* Mariussen et. al. 2003, this issue

To compare the difference in the levels of PBDEs between trophic levels it is most convenient to compare the levels on lipid weight basis (Table 3). As expected trout and burbot had the highest levels of PBDE indicating bioaccumulation of PBDE through the food web. Trout and burbot are both fish eating predators whereas smelt and whitefish mainly eat shellfish, zooplankton and insect larvae. The burbot sample had much higher levels of PBDE than trout, which may be due to its preferential habitat closer to the sediments. The flame retardants and other organohalogens have a very low water solubility and are mainly tied up in the sediments.

Based on lipid weight basis, there was no apparent spatial difference in PBDE concentration between burbot caught from the Lillehammer area and the Hamar area (Table 3). The distance between these two cities is approximately 50 kilometers. Since the burbot is expected to have a habitat attached to one locality, this observation indicates a more uniform pollution of the PBDEs rather than a local hot spot. However, more investigation has to be performed to make a more certain conclusion.

Although the burbot had the highest level of PBDE among the analyzed fish species, most of the contaminants are stored into its liver. The fish muscle is very lean compared to trout, which have high lipid content in the muscles. Most of the burbot's fat deposits are stored in its liver. This is of major importance regarding recommendations for food consumption.

Table 3: Mean concentration (*ng/g lipid*) of seven PBDE congeners in five different species of fish from Lake Mjøsa.

PBDE	BDE28	-47	-99	-100	-153	-154	-183	SUM
Fish								
Com whitefish	1.1	135	227	86.9	39.9	50.1	n.d.	540
Smelt	3.0	627	164	148	41.2	50.0	51.2	1084
Euro whitefish	12.3	1475	1767	543	126	154	2.1	4079
Trout*	13.3	2197	1763	807	242	260	n.d.	5283
Burbot, Lillehammer	37.0	7815	8151	4587	805	1000	0.77	22395
Burbot, Hamar	49.0	10353	4032	2585	661	1033	1.5	18714

\* Mariussen et. al., 2003, this issue

This study shows that Lake Mjøsa is heavily contaminated by PBDE. Lake Mjøsa is located at a rather densely populated (a population of approximately 200 000 inhabitants) and industrialized area with some textile industry and manufactures of electronic equipment. One could also expect leakage from municipal sewerage systems and landfills. However, at present there is no certain information regarding the sources of the pollution.

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