

Pollution of Lake Mjøsa by Brominated Flame Retardants

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Introduction

The worldwide use of brominated flame retardants (BFRs) is extensive and there are significant release of these components to the environment. 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).

This study was focused on the pollution of PBDEs in Lake Mjøsa, where unusually high concentrations have been found in fish (Fjeld et al., 2001, Mariussen et al. 2003, Fjeld et al., 2004). The objective of this part of the survey was to make a broader documentation of the PBDE levels in sediments and fish, and to localize areas with point sources of PBDEs.

Methods and Materials

Sample collection

Lake Mjøsa is situated in Southeast Norway (see Figure 1) and is the country's largest lake (365 km², average depth: 153 m, max depth: 449 m). Surface sediment samples (0–2 cm) were collected from 14 stations. One sediment sample was also collected from the main inlet river at Lake Losna, 25 km north of lake Mjøsa. Fish were collected from the inlet river at Lake Losna, from Lake Mjøsa, from the outlet river Vormå, and from Lake Øyeren further down the watercourse. Fish samples were homogenates of whole body or muscle fillets (pooled samples, typically 7–20 individuals per sample). The indicator species were brown trout (*Salmo trutta*), perch (*Perca fluviatilis*), pike (*Esox lucius*), burbot (*Lota lota*), vendace (*Coregonus albula*) and smelt (*Osmerus eperlanus*). Archived samples of vendace fished during 1993–2002 were also included.

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.

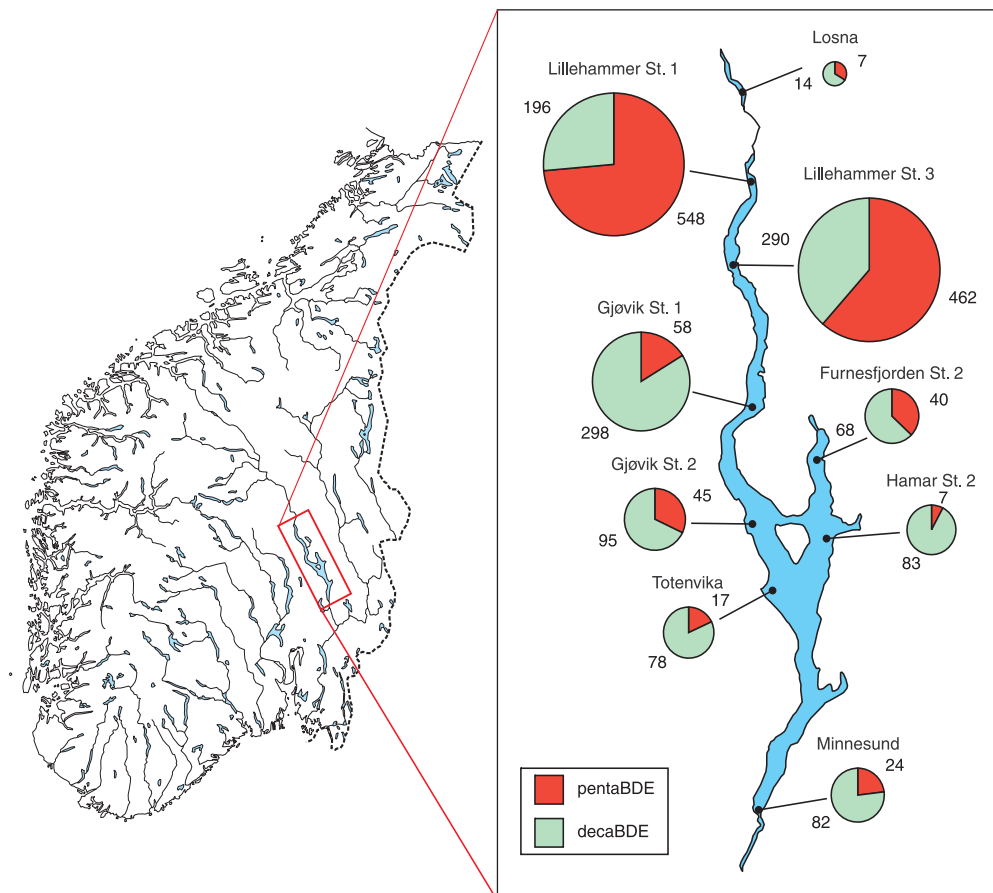


Figure 1: Lake Mjøsa, the largest lake in Norway. A selection of some representative stations with the concentrations of congeners found in technical pentaBDE and decaBDE in sediment samples.

Extraction and clean up

All the samples were added internal standards (^{13}C -PBDEs, ^{13}C -TBBPA and ^{13}C -PCB 118) prior to the sample preparation. The sediment samples were filtered, and then Soxhlet extracted two times: First with acetone and second with acetone/hexane. The biological samples were homogenised with Sodium sulphate prior to cold extraction with hexane/acetone and ethyl acetate/cyclohexane respectively. All the samples were further cleaned on a GPC system. For PBDE, TBBPA and CP analyses the samples were sulphuric acid treated and then concentrated prior to the GC/MS analyses. In addition TBBPA was derivatised using MSTFA. The solvent in the extracts for HBCD analysis were after GPC and sulphuric acid treatment shifted to methanol prior to analysis by LC/MS.

Analysis

An HP5890 GC coupled to a VG AutoSpec, high resolution mass spectrometer was used for all of the GC/MS analyses. For PBDE and TBBPA the MS was operated in EI mode, and for the CPs the MS was operated in ECNI mode. For the HBCD analyses an Agilent 100 HPLC was coupled to a Micromass LCT in electrospray mode, negative ions.

Results and Discussion*Polybrominated diphenyl ethers, PBDEs*

The concentrations of PBDEs in sediments (see Table 1) from Lake Mjøsa were in the range 0.6–27 ng/g d.w. The levels were highest in the northern part (the inlet basin, close the town of Lillehammer) and lowest close to the outlet in the south. Based on the content of organic carbon (TOC), the concentrations outside Lillehammer were 600–740 ng/g TOC, whereas the concentrations elsewhere varied between 50–350 ng/g TOC. Tri- to hexa-BDEs (BDE-47, -99, -100, -153 and -154) constituted 60–70 % of the sum PBDEs in sediments from the northern part. Elsewhere, BDE-209 was the dominating congener with 50–90 %. The concentration in sediments from Lake Losna (the lake in the inlet river) was 21 ng/g TOC, with a BDE-209 percentage close to 67 %. We conclude that the high concentrations of PBDEs in sediments close to Lillehammer, together with the high percentage of tri- to hexa-BDEs, strongly indicate that the technical product “pentaBDE” has been discharged to the lake here.

The concentrations of sum PBDEs in pooled fish samples from Lake Mjøsa (

Table 2) were in the range 50–90 ng/g wet-weight (w.w.) or 1 200–22 000 ng/g lipid. The lowest levels were in vendace and smelt (zooplankton-feeding species), whereas the highest levels were in perch, pike, trout and burbot (fish-eating species). Average concentration of 10 individual trout samples (mean weight: 3.5 kg) was 5 450 ng/g lipid, with individual concentrations in the range of 3 300–17 500 ng/g lipid. These are the highest concentrations in free-living salmonids reported internationally. Average concentration of 10 individual burbot samples from Lillehammer (mean weight: 1.5 kg) was 22 000 ng/g lipid, with individual concentrations in the range of 7 100–45 000 ng/g lipid. This is close to the highest concentration ever reported internationally in fish (47 000 ng/g lipid). The concentration of sum PBDE in burbot from Lake Losna (in the inlet river) was 49 ng/g lipid, whereas the concentrations in two trout samples from the outlet river Vormå was 5 750 and 7 900 ng/g lipid. BDE-99 was the dominating congener (21–45%), with BDE-47 as number two (24–35%) and BDE-100 as number three (8–15%).

The concentrations of PBDEs in archived samples of vendace showed a significant increase after 1995 and a maximum in 2002 (Table 3).

Hexabromo cyclododecane, HBCD

Of the sediment samples from Lake Mjøsa and Lake Losna (Table 4), the only detectable level was found outside the town of Lillehammer in the northern part of Lake Mjøsa. Only β -HBCD was found here, with a concentration of 7.9 ng/g d.w.

HBCD was found in fish from Lake Mjøsa and further down the watercourse in the river Vormå and Lake Øyeren (Table 5). The levels were in the range of 90–880 ng/g lipid. The α -isomer dominated the concentrations. The highest level was found in a pike sample from Lake Mjøsa.

Tetrabromo bisphenol A (TBBPA)

In sediments from Lake Mjøsa and Lake Losna (Table 5), low concentrations of TBBPA were found (0.04–0.13 ng/g d.w.).

The concentrations of TBBPA in fish samples from Mjøsa, Vormå and Øyeren were low 0,01-0,18 ng/g w.w. and 0,2-9 ng/g lipid (Table 5).

Conclusion

The rapid increase of PBDEs in archived samples of vendace, the high concentrations of the lower brominated PBDEs in sediment samples from Lillehammer, and the internal reports on use of technical PentaBDE point to a textile factory as one major emission source. However, there must be additional unidentified source for BFR emissions, since the concentration of PBDEs in vendace was already elevated compared to fish from other lakes before the emission from the textile factory started in 1995 and since neither decaBDE nor HBCD were used by this factory.

Table 1. Concentration of the sum of the detected polybrominated diphenylethers (Σ PBDE, dry weight = d.w. and total organic carbon (TOC)) and the single congeners in sediment samples from Mjøsa and Losna. In addition the content of total organic carbon (TOC) is listed. For the calculation of Σ PBDE results below the limit of detection are set to half the limit of detection. Results below the limit of detection are marked with <.

BROMINATED COMPOUNDS: ANALYSIS, LEVELS, TRENDS

stasjonsnavn	TOC	ΣPBDE		PBDE, ng/g d.w.									
	µg C/mg	ng/g d.w.	ng/g TOC	BDE-28	BDE-47	BDE-49+71	BDE-99	BDE-100	BDE-138	BDE-153	BDE-154	BDE-183	BDE-209
Losna	16,8	0,36	21	<0,01	0,03	<0,01	0,03	0,02	<0,01	<0,01	<0,01	<0,01	0,23
Lilleham. St. 1	30,3	22,59	727	0,07	4,14	0,55	8,03	1,70	0,15	1,03	0,85	0,05	5,95
Lilleham. St. 2	36,8	22,51	595	0,06	3,55	0,61	6,61	1,44	0,15	0,96	0,78	0,04	8,30
Lilleham. St. 3	35,7	26,95	740	0,05	4,36	0,51	7,51	1,78	0,13	1,16	0,98	0,09	10,37
Gjøvik St. 1	35,5	12,65	354	0,02	0,77	0,07	0,76	0,10	<0,02	0,13	0,17	0,02	10,59
Gjøvik St. 2	58,9	8,25	139	0,01	0,58	0,04	1,35	0,30	<0,03	0,17	0,16	0,03	5,58
Gjøvik St. 3	45,6	13,97	306	0,01	0,61	0,03	1,20	0,31	<0,01	0,17	0,16	0,03	11,44
Gjøvik St. 4	26,6	3,86	144	<0,01	0,17	0,03	0,20	0,06	<0,01	0,03	0,03	0,01	3,30
Totenvika	45,6	3,52	95	0,01	0,30	0,04	0,28	0,08	<0,01	0,03	0,04	0,01	3,57
Furnesfj. St.1	56,1	5,99	61	0,02	0,67	0,07	0,63	0,18	<0,02	0,06	0,08	0,04	1,75
Furnesfj. St. 2	55,1	3,73	107	0,03	0,89	0,07	0,74	0,25	<0,02	0,10	0,11	0,02	3,76
Furnesfj. St. 3	47,3	3,37	78	0,02	0,52	0,03	0,36	0,15	<0,01	0,05	0,07	0,02	2,48
Hamar St. 1	65,5	2,12	51	0,02	0,54	0,04	0,61	0,16	<0,01	0,08	0,07	0,02	1,83
Hamar St. 2	23,6	4,36	89	<0,01	0,06	0,01	0,05	<0,01	<0,01	<0,01	<0,01	<0,01	1,96
Minnesund	5,8	0,64	109	0,01	0,30	0,04	0,28	0,08	<0,01	0,03	0,04	0,01	3,57

BROMINATED COMPOUNDS: ANALYSIS, LEVELS, TRENDS

Table 2: Concentration of the sum of the detected polybrominated diphenylethers (Σ PBDE, wet weight = w.w. and lipid weight) and the most abundant congeners in fish from Mjøsa, Losna, Vorma og Øyeren. In addition the average weight of the fishes in each sample (Av.weight) and the fat content in percent (Lipid) is listed. The samples are pooled from whole homogenized fish or from fish muscle (m). For Σ PBDE results below the limit of detection are set to half the limit of detection.

Location	Sample	Av. weight	Lipid %	Σ PBDE		PBDE in ng/g w.w.					
				ng/g w.w.	ng/g lipid	BDE-47	BDE-49	BDE-99	BDE-100	BDE-153	BDE-154
Losna	Burbot	0,7 kg	4,92	2,4	49	0,8	0,1	0,9	0,2	0,1	0,1
Lillehammer	Burbot*	1,5 kg	4,48	981,6	21911	339,6	-	356,3	203,2	35,3	45,2
Gjøvik	Perch	0,2 kg	2,40	261,2	10883	101,6	8,1	66,1	54,9	13,1	15,4
Gjøvik	Pike	1,8 kg	2,94	289,8	9857	111,6	9,0	84,6	51,9	13,3	16,5
Furnesfj.	Perch	0,3 kg	2,64	150,1	5686	59,8	5,8	41,3	26,7	6,7	8,6
Furnesfj.	Pike, m	2,1 kg	0,53	39,3	7415	17,6	1,6	9,8	6,6	1,5	1,8
Mjøsa	Trout, m	0,3 kg	1,26	73,2	5810	34,7	1,6	13,7	15,3	3,1	4,2
Mjøsa	Trout, m	3,5 kg	5,81	317,0	5456	133,5	-	107,1	47,2	13,6	14,9
Mjøsa	Trout, m*	10,2 kg	9,75	363,3	3726	130,1	16,7	126,8	54,1	15,3	17,4
Mjøsa	Smelt	10,3 g	2,34	56,9	2432	13,5	2,9	9,3	21,8	3,9	4,9
Mjøsa	Vendace	60,3 g	4,10	49,8	1215	17,3	2,0	20,5	5,7	1,7	1,9
Vorma	Trout, m	6,0 kg	3,04	240,2	7901	53,3	16,1	95,1	42,8	17,8	14,9
Vorma	Trout, m	1,8 kg	0,75	43,1	5747	7,2	5,3	12,0	6,1	5,5	6,0
Øyeren	Perch	0,5 kg	3,60	16,1	447	8,8	0,2	3,6	1,8	0,8	0,7
Øyeren	Pike	1,8 kg	1,38	13,1	949	7,3	0,1	2,8	1,6	0,6	0,6

*) These concentrations are the average of 10 individual samples. The individual concentrations are between 3 300–17 500 ng/g lipid for trout and 7 100–45 100 ng/g lipid for burbot.

Table 3: Time trend of the concentration of the sum of the detected polybrominated diphenylethers (Σ PBDE, wet weight = w.w. and lipid weight) and of the most abundant congeners in vendace from Mjøsa. In addition the fat content in percent (Lipid) is listed. The samples are pooled from fish muscle (m). For Σ PBDE results below the limit of detection are set to half the limit of detection.

Year	Lipid %	Σ PBDE		PBDE in ng/g w.w.								other
		ng/g w.w.	ng/g lipid	BDE-47	BDE-49	BDE-99	BDE-100	BDE-153	BDE-154	BDE-209		
1993	0,65	5,9	908	1,4	0,4	1,2	0,5	0,1	0,2	2,0	0,1	
1995	1,23	3,9	317	1,4	0,2	1,5	0,3	0,1	0,1	0,1	0,1	
1997	2,24	15,3	683	4,8	0,8	6,9	1,6	0,6	0,5	0,0	0,1	
1998	0,69	24,3	3522	7,9	3,0	9,3	2,5	0,8	0,7	0,0	0,1	
1999	4,42	52,6	1190	15,4	3,4	23,9	5,1	2,3	2,0	0,1	0,5	
2000	2,94	45,2	1537	10,7	2,2	21,3	6,7	1,9	1,9	0,1	0,4	
2002	4,68	83,3	1780	25,8	5,8	33,4	10,0	3,7	3,6	0,2	0,7	
2003	4,10	49,8	1215	17,3	2,0	20,5	5,7	1,7	1,9	0,2	0,3	

BROMINATED COMPOUNDS: ANALYSIS, LEVELS, TRENDS

Table 4. Concentrations of α -, β - and γ -hexabromo cyclododecane (α -, β - and γ -HBCD) and tetrabromo bisphenol A (TBBPA) in sediment samples from Mjøsa and Losna given in dry weight (d.w.). In addition the content of total organic carbon (TOC) is listed. Results below the limit of detection are marked with <.

Location	Sample	TOC $\mu\text{g C/mg}$	Concentration in ng/g d.w.			
			α -HBCD	β -HBCD	γ -HBCD	TBBPA
Losna	Losna	16,8	0,1	<0,3	0,05	0,04
Mjøsa	Lillehammer St.1	30,3	<0,3	7,91	<0,4	0,04
Mjøsa	Gjøvik St. 2	58,9	<0,3	<0,2	<0,4	0,08
Mjøsa	Furnesfj. St. 1	56,1	<0,3	<0,2	<0,4	0,13

Table 5. Concentrations of α -, β - and γ -hexabromo cyclododecane (α -, β - and γ -HBCD) and tetrabromo bisphenol A (TBBPA) in fish from Mjøsa, Vorma and Øyeren. The samples are pooled from whole homogenized fish or from filleted muscle (m). The fat content of the samples are given in percent (lipid %). Results below the limit of detection are marked with <.

Location	Sample	Lipid %	Concentration in ng/g w.w.			
			α -HBCD	β -HBCD	γ -HBCD	TBBPA
Mjøsa, Gjøvik	Perch	2,40	6,73	<0,04	0,37	1,4
Mjøsa, Gjøvik	Pike	2,94	9,25	<0,05	0,92	13,7
Mjøsa, Furnesfj.	Perch	2,64	8,12	<0,04	<0,07	7,7
Mjøsa, Furnesfj.	Pike (m)	0,53	4,41	<0,04	0,22	4,3
Mjøsa	Smelt	2,34	2,1	0,03	0,25	2,0
Mjøsa	Vendace	2,94	3,15	0,4	0,62	5,8
Mjøsa	Trout small (m)	1,26	2,3	0,06	0,24	2,67
Mjøsa	Trout big (m)	9,75	13,3	0,44	1,73	6,4
Vorma	Trout big (m)	3,04	7,33	1,12	3,73	6,1
Vorma	Trout medium (m)	0,75	2,28	0,183	0,516	10,4
Øyeren	Perch	3,60	3,14	<0,1	<0,1	1,2
Øyeren	Pike	1,38	1,02	<0,02	0,03	1,0

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