BFR CONTAMINATION OF THE MARINE ENVIRONMENT AROUND THE CITY OF ÅLESUND, NORWAY

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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) and hexabromcyclododecane (HBCD) in biota have increased and in some areas the levels are comparable or even higher to what is reported for the polychlorinated biphenyls (PCB)[1].

On behalf of the Norwegian Pollution Control Authority (SFT) several screening studies covering both the Norwegian freshwater and marine environment have been performed during the last years. The focus has mainly been on brominated flame retardants (BFR) [2-4] and addition also on other emerging compounds like PFAS and biocides. In general low to moderate levels are found in marine sediments and biota like blue mussels, edible crab and cod liver. However, in the area of Ålesund the marine environment of the fjords are much higher contaminated with both polybrominated diphenylethers (PBDE) and hexabromcyclododecane (HBCD). The major source of HBCD contamination seems to be the production polystyrene polymer products. However, the source(s) of the high PBDE levels are yet not identified.

Materials and Methods
From several field campaigns during the years 2004 and 2005 the following samples were taken in the fjord system (Åsefjord, Borgundfjord, Hessafjord, Spjelkavika and Aspevågen) near the city of Ålesund on the West coast of Norway: marine sediments, blue mussels (*Mytulis edulis*, pooled samples of all soft tissue inside the shell), the edible crab (*Cancer pagurus*, pooled samples of hepatopancreas and gonads), cod (*Gadus mohrua*, pooled samples of either muscle or liver), ballan wrasse (*Labrus bergylta*) and two species of flatfish (*Limanda limanda* and *Pleuronectes platessa*) pooled samples of muscle.

Extraction and clean up
All the samples were spiked with internal standards (^{13}C-PBDEs and ^{2}D-HBCDs) prior to the sample preparation. The sediment samples were dried and then Soxhlet extracted with acetone/hexane. The biological samples were homogenised with Sodium sulphate prior to cold extraction with ethyl acetate/cyclohexane (1/1). All the samples were treated with concentrated sulphuric acid and further cleaned on a 4 g silica column with n-hexane/diethyl ether (9/1). The following brominated flame retardants were analyzed with GC/HRMS: polybrominated diphenyl ethers (PBDE). Hexabromocyclododecanes (HBCD) were analyzed with LC/MS.

Results and Discussion
The concentrations of the most prominent PBDE congeners, the sum of all detected PBDEs, together with the concentrations of α-, β-, and γ-HBCD and the sum of all detected HBCD-isomers are given in table 1 for all samples.

Table 1: Concentrations of the most prominent PBDE congeners, the sum of all detected PBDEs, α-, β-, and γ-HBCD and the sum of all detected HBCD-isomers given in ng/g dry weight (d.w.) for sediments and wet weight (w.w.) for biota.

Station	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-209	Σ PBDE	α-HBCD	β-HBCD	γ-HBCD	ΣHBCD
Sediment in ng/g d.w.											
Hessafjorden	0.16	0.20	0.05	< 0.10	< 0.06	69.40	71.0	2.66	0.08	9.26	12.0
Borgundfjorden	1.17	1.67	0.29	0.15	0.11	1063	1074	30.7	0.56	86.6	118
Humla vest	0.34	0.46	0.09	< 0.05	0.04	284	287	34.9	0.92	111	147
Aspevågen	1.03	1.49	0.28	0.20	0.15	973	983	49.6	3.28	175	227
Tjørsundet Nord	13.0	17.3	2.56	1.74	1.16	1555	1599	229	27.9	675	932
Åsefjorden, St. 2b								7.47	0.06	16.9	24.4
Åsefjorden, St. 3						242	248	28.9	7.42	87.7	124
Åsefjorden, St. 2						240	254	49.4	18.9	162	230
Åsefjorden, St. 1c						197	328	1993	981	4591	7565
Åsefjorden, St. 1d						220	466	2426	60.8	5996	8483
Blue mussel in ng/g w.w.											
Åsefjorden, St. 4	0.44	0.33	0.12	0.01	0.01	0.16	1.24	36.7	0.64	18.03	55.4
Åsefjorden, St. 5	0.51	0.4	0.16	0.02	0.01	0.12	1.37	78.5	4.78	71.7	155
Åsefjorden, St. 6	0.81	0.79	0.24	0.04	0.03	0.46	2.63	184	14.3	131	329
Edible crab ng/g w.w.											
Tjørsundet Nord	0.50	0.27	0.18	0.08	0.08	0.30	1.52	0.60	< 0.01	< 0.04	0.60
Humla	0.66	0.41	0.22	0.12	0.15	0.83	2.56	0.34	0.03	0.05	0.42
Hessafjorden	0.33	0.14	0.07	0.04	0.05	1.97	2.69	0.14	< 0.02	< 0.04	0.14
Aspevågen/Slinningen	0.92	0.35	0.27	0.11	0.13	0.51	2.85	0.39	< 0.04	< 0.07	0.39
Åse, vest pumpestasjon	0.88	0.30	0.25	0.10	0.13	1.03	2.86	0.60	< 0.02	< 0.04	0.60
Spjelkavik	1.22	0.76	0.38	0.18	0.18	0.98	4.15	4.82	0.05	0.44	5.31
Bogneset	1.01	0.22	0.22	0.07	0.11	3.88	5.80	0.40	< 0.02	< 0.03	0.40
Cod muscle in ng/g w.w.											
Aspevågen/Slinningen	0.09	< 0.01	0.02	< 0.01	< 0.01	0.07	0.19	0.009	< 0.01	< 0.01	0.009
Hessafjorden	0.12	< 0.01	0.02	< 0.01	< 0.01	0.04	0.19	0.010	< 0.01	< 0.01	0.010
Tjørsundet Nord	0.14	0.02	0.03	< 0.01	< 0.01	0.04	0.26	0.011	< 0.01	< 0.01	0.011
Humla	0.10	< 0.01	0.02	< 0.01	< 0.01	0.04	0.18	0.018	< 0.01	< 0.01	0.018
Åse, pumpestasjon	0.15	< 0.01	0.03	< 0.01	< 0.01	0.10	0.29	0.024	0.012	0.015	0.050
Cod liver in ng/g w.w.											
Hessafjorden	20.7	0.49	4.52	0.07	0.67	0.60	33.7	14.8	< 0.14	0.65	15.4
Aspevågen/Slinningen	34.1	0.27	7.20	< 0.53	1.73	< 2.83	49.5	23.7	< 0.09	0.97	24.6
Humla	36.3	0.52	12.3	0.11	1.28	0.71	60.5	36.0	< 0.09	1.02	37.0
Åse, pumpestasjon	64.0	< 0.89	14.7	< 1.58	2.15	< 10.3	86.6	41.5	0.03	1.04	42.6
Tjørsundet Nord	58.3	1.17	18.2	0.13	1.44	0.60	98.9	42.3	0.04	1.80	44.2
Ballan wrasse in ng/g w.w.											
Hessafjorden	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04	0.04	0.17	< 0.01	0.01	0.19
Åse, pumpestasjon	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05	0.05	1.49	< 0.01	< 0.09	1.49
Flatfish in ng/g w.w.											
Aspevågen/Slinningen	0.11	< 0.01	0.02	< 0.01	< 0.01	0.07	0.19	< 0.01	< 0.01	< 0.01	< 0.01
Spjelkavik	0.18	< 0.01	0.02	< 0.01	< 0.01	0.06	0.25	0.06	< 0.01	0.01	0.07

The results from analysis of sediments (ΣPBDE: 71-1599 ng/g dry weight) indicate that all stations have received more PBDE than expected from only diffusely contaminated areas and thus shows the same general trend as for HBCD. The observed levels were considered very high compared to other international data on marine sediments, especially in the samples from Aspevågen, Borgundfjorden and Tjørsundet. Our findings support the notion that the Åsefjord and it margins are severely polluted by PBDE. Even the most westerly station in Hessafjorden has received some PBDE.

The concentration of ΣPBDE observed in blue mussels (1,24-2,63 ng/g wet weight) and in crabs (1,5-5,8 ng/g wet weight) and indicate bioaccumulation (for crabs at least in the samples from Spjelkavik, a bay in the inner part of the Åsefjord and Bogeneset on the West margin of the Åsefjord). It is also possible that crabs outside the Åsefjord are contaminated with PBDE but this can not be clarified before more data from presumptive reference areas are available.

The concentration of ΣPBDE observed in cod liver (34-99 ng/g wet weight) were high compared to results from presumed uncontaminated areas of the Norwegian coast and bioaccumulation of PBDE seems to have taken place. The highest concentration was observed in crabs from an area Southeast in the Åsefjord (Tjørsundet, Nord) were the level were approximately as observed previously in the Oslo fjord

The concentration level of ΣPBDE in filet of ballan wrasse (0,04-0,05 ng/g wet weight) was considerably lower than observed in filet from cod (0,18-0,29 ng/g wet weight). The results indicate that wrasse from Åsefjorden contains only slightly higher or similar concentrations of PBDE than wrasse from the most Easterly station in the Hessafjord. This is very different from what was observed for HBCD, where a considerably higher concentration was observed in Åsefjord compared to Hessafjord.

The results show that sediments from all stations are contaminated with HBCD (ΣHBCD: 12-8483 ng/g dry weight). The main source seems to be East in the Åsefjord. The results show that HBCD is transported also into the deeper part of the Hessafjord west of the investigated area.

The concentration of ΣHBCD observed in blue mussels (composite samples of soft tissue) ranged 55-329 ng/g wet weight and in crab tissue (composite sample of hepatopancreas and gonads) ranged 0,14-5,31 ng/g wet weight and shows that bioaccumulation have taken place. The results indicate that both blue mussels and crabs from stations in the Åsefjord and its margins are contaminated. It is also possible that crabs outside the Åsefjord are contaminated but this can not be clarified before more data from presumptive reference areas are available.

The observed concentrations of HBCD in cod liver (ΣHBCD: 15-44 ng/g wet weight) were somewhat high compared to presumed reference areas (Lista, Bømlo, Færder, Svolvær, Ulsteinvik) along the Norwegian coast (ΣHBCD: 2,5-8 ng/g wet weight). The highest concentrations were observed in the stations in the Åsefjord and its margins (ΣHBCD: 24-44 ng/g wet weigh). The lowest concentration in cod liver was observed in fish from Hessafjord (ΣHBCD: 15 ng/g wet weight). The results show bioaccumulation in cod liver but to a much lesser extent in filet (ΣHBCD: 0,009-0,050 ng/g wet weight). The results from filet of ballan wrasse from Åsefjorden (ΣHBCD: 1,5 ng/g wet weight) do, however, indicate some bioaccumulation in filet from this species

The α-isomer dominated in biota and γ-HBCD in sediments.

The highest concentrations of both HBCD and PBDE were observed in the Southeast part of Åsefjorden and the lowest in Hessafjorden. The ratio between the observed highest and lowest concentrations was much higher for HBCD than for PBDE in both sediments and crabs. This indicates steeper concentration gradients for HBCD than for PBDE. There was no clear linear relation between the concentrations of the two groups of compounds when all five stations are considered, as expected, if the source of the two group's contaminants were located at the same place. One can therefore not exclude the possibility that the main source for the two compounds is different. The major source of HBCD contamination seems to be the production polystyrene polymer products. However, the source(s) of the high PBDE levels are yet not identified.

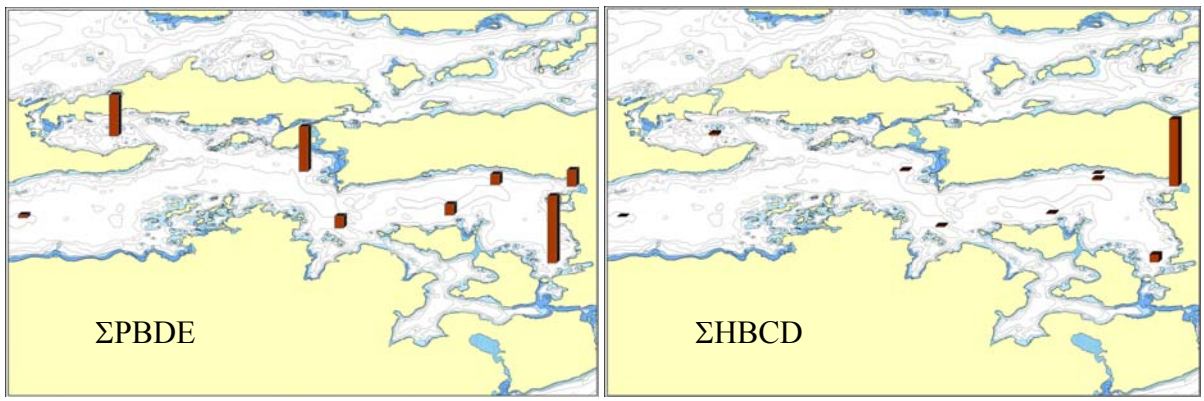

Figure 1: Concentration of ΣPBDE (left map) and ΣHBCD (right map) in sediment samples from the Ålesund area. The highest ΣPBDE value (Tjørsund) represents a concentration of about 1600 ng/g d.w and the highest ΣHBCD value (Åsefjorden) represents a concentration of about 8000 ng/g d.w..

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References

1. de Wit C,. An overview of brominated flame retardants in the environment. *Chemosphere* 2002; 46: 583 – 624.

2. Schlabach M, Mariussen E, Borgen A, Dye C, Enge EK, Steinnes E, Green N, Mohn H, 2002. Kartlegging av bromerte flammehemere og klorerte parafiner. Statlig program for forurensningsovervåkning. SFT rapport TA-1924/2002. 134p (Norwegian).

3. Fjeld E, Schlabach M, Berge JA, Eggen T, Snilsberg P, Källberg G, Rognerud S, Enge EK, Borgen A and Gundersen H, 2004. Kartlegging av utvalgte nye organiske miljøgifter – bromerte flammehemmere, klorerte parafiner, bisfenol A og triclosan. SFT rapport TA-2006/2004 (Niva rapport nr. 4809-2004), 117p (Norwegian with English abstract).

4. Fjeld E, Schlabach M, Berge JA, Green N, Eggen T, Snilsberg P, Vogelsang C, Rognerud S, Källberg G, Enge EK, Dye C and Gundersen H, 2005. Kartlegging av utvalgte nye organiske miljøgifter 2004. Bromerte flammehemmere, perfluoralkylerte stoffer, irgarol, diouron, BHT and dicofol.. SFT rapport TA-2096/2005 (Niva rapport nr. 5011-2005), 97p (Norwegian with English abstract).