LEVELS OF BROMINATED FLAME RETARDANTS IN FISH FROM SWEDEN

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Abstract
We present results from analyses of brominated flame retardants (BFRs) in eel, brown trout, salmon, herring, sprat, vendace, arctic char, turbot, mackerel, shrimps and mussels from the Baltic sea, the lakes Vänern, Vättern, Mälaren, Hjälmaren, Rebnisjaure and the Swedish west coast. Sum PBDE values (medium bound) were found to be in the range of 0.09-14.1 μg/kg (mean value of 2.8 μg/kg). The concentrations of HBCD were found to be in the range of 0.03-7.8 μg/kg (mean concentration of 1.9 μg/kg). Sum PBDE values generally showed a positive correlation to the fat content in fish from all locations (eels and fish from lakes Vänern and Vättern not included). BDE 47 was found to be the major congener contributing to the sum PBDE. The contribution was on average 61 %. By removing the skin and subcutaneous lipids from herring, it was possible to reduce the levels of PBDEs and HBCD with 38-57 %.

Introduction

For risk assessment purposes, the Swedish National Food Administration (NFA) has during the last years conducted surveys on levels of selected persistent organic pollutants (POPs) in fish from the Baltic region. These studies have included the "traditional" POPs, such as PCBs, PCDD/DFs, and chlorinated pesticides, as well as the brominated flame retardants (BFRs) polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD). The aim with the present survey was to obtain relevant BFR data for the ongoing evaluation of levels and trends of these contaminants in fish.

Materials and Methods

Samples of eel (*Anguilla anguilla*; silver and yellow eel), brown trout (*Salmo trutta*), salmon (*Salmo salar*), herring (*Clupea harengus*), sprat (*Sprattus sprattus*), vendace (*Coregonus albula*), arctic char (*Salvelinus alpinus*), turbot (*Psetta maxima*), mackerel (*Scomber scombrus*), shrimps (*Pandalus borealis*) and mussels (*Mytilus edulis*) from various waters in Sweden, i.e. the Baltic sea, the lakes Vänern, Vättern, Mälaren, Hjälmaren, Rebnisjaure and the Swedish west coast were analysed. The fish were caught in 2000-2003. Generally, the analyses were carried out on muscle tissue except for herring and sprat, where in almost all samples, the muscle including skin was analysed. In the pooled samples, equal amounts of tissue (muscle) were taken from the area around the dorsal fin of each fish, except for herring and sprat where whole fillet with skin was taken. The tissues were pooled and thoroughly homogenised. Analyses of the PBDEs (PBDE congeners 28, 47, 66, 99, 100, 138, 153, 154 and 183) and HBCD were performed at NFA, Uppsala, Sweden. The samples were extracted with mixtures of acetone/n-hexane and n-hexane/diethyl ether. After evaporation the lipid content was determined gravimetrically and the lipids were then removed by treatment with sulphuric acid[1]. The samples were quantified using GC-ECD with dual capillary columns.

Results and Discussion

Table 1 shows the results from the analysis of brominated flame-retardants (BFRs) in fish muscle, fish muscle including skin, fish roe, shrimps and in mussels. For all fish samples, analytical data for BDE 138 and BDE 183 were below the limit of quantification (LOQ). Because of this, these data are not included in the calculations of sum PBDE. BDE 28 is not included due to problems with coelution.

It is important to note that the concentration of organic contaminants can vary considerably in individuals from the same location, depending on factors such as age, fat content, size, etc[2]. Earlier investigations have shown that levels of POPs in fish from a single location can vary from year to year and season to season[3]. The results presented in this report are therefore only representative of the sampling occasion in question.

In the analyses of PBDE congeners 47, 66, 99, 100, 153, and 154, the percentage of samples below LOQ were 0.2 %, 20%, 0.4 %, 0.2 %, 22 % and 20 %, respectively. Values below LOQ for all congeners were set to ½ LOQ in the calculations of sum PBDE and HBCD. For sum PBDE, the percentage difference after adjusting ½

LOQ from values to LOQ or 0 was 0-13 % (median 0.3 %). Exceptions were three samples that had almost all levels of PBDE congeners below LOQ. These are two samples of arctic char from lake Rebnisjaure and one sample of turbot from the waters near Gotland.

Sum PBDE values generally showed a positive correlation to the fat content in fish from all locations ($r = 0.54$, Spearman $p < 0.0001$). However, the eels and the fish from lake Vänern and Vättern are not included in these calculations. The eels have high fat content but quite low levels of PBDEs. Compared to fish from other locations, the fish from lakes Vänern and Vättern have similar fat content but relatively higher levels of PBDEs. BDE 47 was the congener contributing most to the sum PBDE. The contribution was on average 61 % (min 23 % and max 75 %). BDE 47 correlated well with the sum PBDE in all the analysed fish samples ($r = 0.97$, Spearman $p < 0.0001$). BDE 47 also correlates well with the levels of HBCD ($r = 0.93$, Spearman $p < 0.0001$).

A direct comparison of PBDE and HBCD levels in arctic char from lake Vättern (located in the middle part of Sweden) and lake Rebnisjaure (located in the northern part of Sweden) was not done due to large differences in size of the fish sampled in the two locations. However, the data suggest that there are higher levels of flame retardants in lake Vättern compared to lake Rebnisjaure. Furthermore, the levels of PBDE and HBCD in vendace roe from lake Vänern (located in the middle part of Sweden) seems to be elevated as compared to the levels in vendace roe from the Luleå archipelago (northern part of Sweden). For salmon from Baltic Sea, the concentrations of BFRs seem to be in the same range irrespective of where the fish were caught. This is probably due to the migratory behaviour of salmon. Salmons live their first one or two years in the river as parr-smolt, after which they migrate to the Baltic proper. They only return to the river for spawning. This explains why the levels of contaminants in salmon from the Baltic Sea area tend to be in the same range, irrespective of where the salmon were caught.

It is interesting to note the decrease in PBDE and HBCD levels in herring when removing the skin and the subcutaneous lipids (i. e. samples FF20020510-13). It appears as that the removal of skin and subcutaneous lipids, reduces the levels of PBDEs and HBCD with 38-57 %. This is in accordance with earlier results that have showing a significant decrease (approx. 60%) of PCB levels in herring muscle without skin and subcutaneous lipids as compared to herring analysed with skin[4].

Acknowledgements
The study was financially supported by the Swedish Environmental Protection Agency. Lotta Larsson is acknowledged for her excellent technical assistance.

References

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Table 1. Concentrations of sum PBDE (congeners BDE 47, 66, 99, 100, 153, 154) and HBCD in fish muscle, fish muscle + skin, fish roe, shrimps and mussels (µg/kg fresh weight). Location caught marked with * belongs to the Baltic Sea. Values below LOQ were set to ½ LOQ in the calculations of sum PBDE. Please note that there are large differences in age and size within the species reported.

No	Species	Location caught	No of indiv.	Age (years)	Mean weight (g)	Fat (%)	Sum PBDEs	BDE-47	BDE-99	BDE-100	HBCD
FF20020047	Arctic char	N Vättern	10	5.5	707	3.1	4.8	2.5	0.68	0.87	3.9
FF20020010	Arctic char	S.Vättern	10	6.8	1014	2.9	9.8	5.0	1.3	1.9	7.8
FF20020225	Arctic char	Rebnisjaure	11	4.5	379	1.3	0.11	<0.05	0.032	<0.025	0.09
FF20020248	Arctic char	Rebnisjaure	22	3.3	164	0.9	0.09	<0.05	<0.025	<0.025	0.06
FF20010206	B. Trout	Gotland*	1	0	541	2.1	0.55	0.37	0.08	0.06	0.41
FF20010207	B. Trout	Gotland*	1	1	1911	0.8	3.0	1.9	0.48	0.35	1.7
FF20010208	B. Trout	Gotland*	1	0	754	1.1	1.9	1.3	0.27	0.22	1.5
FF20010209	B. Trout	Gotland*	1	1	1190	1.5	0.63	0.44	0.09	0.06	0.64
FF20010210	B. Trout	Gotland*	1	2	1538	0.8	0.99	0.68	0.11	0.14	1.0
FF20010211	B. Trout	Gotland*	1	1	2237	0.6	2.9	1.9	0.44	0.37	2.2
FF20010212	B. Trout	Gotland*	1	3	1722	1.4	4.5	3.0	0.49	0.68	4.2
FF20010213	B. Trout	Gotland*	1	2	2838	2.3	1.9	1.3	0.20	0.25	1.6
FF20010193	B. Trout	N Vänern	9	3.1	4868	1.6	7.3	3.4	1.4	1.4	4.2
FF20020138	B. Trout	Vänern	10	3.0	4013	2.0	4.9	2.1	1.3	0.79	1.6
FF20020167	B. Trout	N Vättern	9	1.4	1168	1.6	3.2	1.3	0.74	0.61	2.2
FF20010227	B. Trout	S.Vättern	7	2	1781	1.2	14.1	5.1	3.5	2.7	6.2
FF20000024	Eel	Valjeviken*	19	-	391	18.3	0.67	0.44	0.03	0.14	0.32
FF20000025	Eel	Marsö*	21	-	369	16.6	0.85	0.56	0.03	0.16	0.55
FF20000026	Eel	Kvädöfjärden*	20	-	339	13.6	0.82	0.50	<0.025	0.16	0.55
FF20000027	Eel	Sturkö*	20	-	360	14.7	0.52	0.31	0.03	0.08	0.31
FF20010181	Eel	Hjälmaren	10	14.9	944	22.1	0.58	0.33	0.06	0.09	1.6
FF20010182	Eel	Mälaren	10	12.8	688	20.2	1.4	0.85	0.09	0.20	1.6
FF20020092	Eel	Gothenburg	10	7.8	85.3	8.6	0.49	0.36	<0.025	0.07	0.70
FF20010018	Herring	Fladen	4	3.5	62.5	7.4	1.3	0.78	0.25	0.16	1.5
FF20010019	Herring	Fladen	4	3.3	52.6	5.8	0.77	0.52	0.13	0.08	1.1
FF20020211	Herring	Kattegatt	59	0.6	36.5	9.4	1.5	0.95	0.22	0.19	0.95
FF20020336	Herring	Rügen*	15	3.7	90.3	9.2	3.2	2.0	0.50	0.33	2.5
FF20020337	Herring	Rügen*	15	3.1	74.2	9.3	3.1	2.0	0.42	0.35	2.6
FF20020338	Herring	Rügen*	17	3.6	62.7	3.4	2.1	1.4	0.24	0.23	1.8
FF20020339	Herring	Rügen*	18	2.4	59.2	5.8	1.3	0.84	0.17	0.15	1.4
FF20020340	Herring	Rügen*	20	2.4	54.2	1.9	1.3	0.78	0.21	0.14	1.3
FF20020341	Herring	Rügen*	15	2.8	69.9	1.6	1.5	0.92	0.23	0.18	1.4
FF20020510	Herring with skin	Rügen*	36	2.9	49.6	6.4	1.2	0.74	0.19	0.12	1.5
FF20020511	Herring without skin	Rügen*	36	2.9	49.6	3.2	0.60	0.40	0.10	0.07	0.73
FF20020512	Herring without skin	Rügen*	30	2.7	48.7	3.2	0.51	0.34	0.09	0.05	0.54
FF20020513	Herring with skin	Rügen*	30	2.7	48.7	6.5	1.1	0.68	0.19	0.11	1.4
FF20020009	Mackerel	Skagerack	20	3.0	393	11.1	2.5	1.49	0.42	0.29	1.1
FF20020008	Mussels	Skagerack				2.2	0.12	0.069	0.02	0.02	0.21
FF20020356	Salmon	Baltic Sea*	10	1.9	4000	4.5	2.2	1.4	0.31	0.28	1.5
FF20020369	Salmon	Baltic Sea*	10	2	3900	5.7	2.6	1.7	0.36	0.31	1.7
FF20020380	Salmon	Baltic Sea*	9	2	6400	6.4	2.9	1.9	0.37	0.35	1.9
FF20020390	Salmon	Baltic Sea*	9	2	6500	8.7	4.4	2.9	0.61	0.55	2.9
FF20020400	Salmon	Baltic Sea*	6	2.5	10100	9.1	4.5	2.9	0.60	0.52	3.1

No	Species	Location caught	No of indiv.	Age (years)	Mean weight (g)	Fat (%)	Sum PBDEs	BDE-47	BDE-99	BDE-100	HBCD
FF20020407	Salmon	Baltic Sea*	8	1.9	2500	8.9	5.2	3.5	0.68	0.62	3.6
FF20010004	Salmon	Gotland*	1	1	4259	10.1	3.1	2.2	0.40	0.34	2.4
FF20010005	Salmon	Gotland*	1	1	4960	3.8	1.8	1.2	0.25	0.20	1.5
FF20010006	Salmon	Gotland*	1	1	3609	9.2	2.8	2.0	0.31	0.32	1.9
FF20010007	Salmon	Gotland*	1	1	4397	8.3	1.7	1.2	0.20	0.20	1.5
FF20010008	Salmon	Gotland*	1	1	3282	5.4	1.8	1.2	0.18	0.28	1.1
FF20010009	Salmon	Gotland*	1	1	4079	7.8	2.7	1.8	0.38	0.30	1.7
FF20010010	Salmon	Gotland*	1	1	4141	8.4	2.4	1.7	0.26	0.27	1.3
FF20010011	Salmon	Gotland*	1	1	4561	6.7	1.7	1.2	0.20	0.19	1.3
FF20010012	Salmon	Gotland*	1	1	3410	9.8	3.5	2.4	0.47	0.39	2.6
FF20010013	Salmon	Gotland*	1	1	4415	9.7	2.7	1.9	0.33	0.31	1.5
FF20020417	Salmon	Gävle Bay*	9	2	5280	8.7	3.7	2.5	0.42	0.51	2.2
FF20020428	Salmon	Gävle Bay*	10	1.4	5180	8.2	3.7	2.4	0.42	0.52	2.1
FF20020436	Salmon	Gävle Bay*	7	2.9	10800	7.1	4.8	3.1	0.58	0.68	3.2
FF20020443	Salmon	Gävle Bay*	6	2.8	10580	7.7	5.0	3.3	0.60	0.68	3.3
FF20020332	Salmon	Luleå arch.*	9	2	6910	5.7	4.3	2.8	0.58	0.53	4.4
FF20020333	Salmon	Luleå arch.*	11	1.9	5800	7.6	4.5	2.9	0.56	0.61	3.2
FF20020334	Salmon	Luleå arch.*	10	2.6	10450	8.0	5.1	3.2	0.69	0.68	3.3
FF20020335	Salmon	Luleå arch.*	10	2.8	9560	7.3	4.7	3.0	0.64	0.61	3.4
FF20020117	Salmon	Vänern	7	1.4	3215	4.6	3.5	1.9	0.40	0.65	1.6
FF20030011	Salmon	Vänern	9	3	3280	6.4	2.5	1.4	0.28	0.43	1.7
FF20030022	Salmon	Vänern	10	3.1	4540	6.7	2.6	1.4	0.29	0.46	1.8
FF20030069	Salmon	Vänern	10	2.6	3250	6.0	3.2	1.7	0.41	0.60	2.0
FF20030077	Salmon	Vänern	7	3.3	4610	7.9	5.0	2.5	0.68	0.93	2.8
FF20020106	Salmon	N Vänern	10	1.6	3516	5.7	4.1	2.2	0.55	0.66	3.4
FF20020035	Salmon	N Vättern	10	1.4	2955	3.5	3.8	1.6	0.71	0.82	1.6
FF20010238	Salmon	S.Vättern	10	1.4	3574	3.9	5.5	2.2	1.2	1.12	3.8
FF20030030	Salmon	Vättern	7	3.3	4860	9.2	4.9	1.8	1.3	0.78	2.4
FF20030038	Salmon	Vättern	7	3.9	7630	10.2	6.9	2.8	1.4	1.4	3.9
FF20030086	Salmon	Vättern	8	3.1	6170	4.3	7.7	3.0	1.5	1.7	4.0
FF20020007	Shrimps	Skagerack				1.5	0.21	0.147	0.01	0.03	0.03
FF20020210	Sprat	Baltic Sea*	50	3.6	20.3	9.6	2.4	1.6	0.33	0.24	1.7
FF20020250	Sprat	Baltic Sea*	22	5.0	9.2	9.2	2.0	1.4	0.21	0.22	1.7
FF20020342	Sprat	Baltic Sea*	106	4.1	9.3	11.7	1.6	1.1	0.21	0.16	1.3
FF20020343	Sprat	Baltic Sea*	105	4.2	9.6	9.6	1.5	1.0	0.16	0.15	1.3
FF20020346	Sprat	Baltic Sea*	96	4.2	9.7	10.3	1.8	1.2	0.22	0.18	1.3
FF20020347	Sprat	Baltic Sea*	104	3.9	9.4	10.3	1.5	1.0	0.17	0.15	1.3
FF20020357	Sprat	Baltic Sea*	100	5	9.1	6.2	1.5	1.0	0.14	0.16	1.3
FF20020358	Sprat	Baltic Sea*	102	4.1	8.9	6.9	1.4	0.98	0.17	0.14	1.3
FF20020454	Turbot	Gotland*	10	7.5	704	1.0	0.39	0.25	0.04	0.05	0.06
FF20020465	Turbot	Gotland*	10	8.5	1116	0.9	0.44	0.28	0.04	0.06	0.08
FF20020476	Turbot	Gotland*	10	5.4	649	0.8	0.26	0.18	<0.025	<0.05	0.05
FF20020509	Turbot	NE Gotland*	10	9	903	0.8	0.50	0.35	0.04	0.07	0.06
FF20020487	Turbot	S Marsö*	9	7.4	724	0.7	0.29	0.19	0.03	0.04	0.06
FF20020516	Vendace roe	Luleå*	69			10.9	1.9	1.02	0.47	0.21	0.32
FF20020288	Vendace roe	Vänern				9.7	5.1	2.35	1.3	0.77	2.6
FF20020517	Vendace roe	Vänern	88			13.9	7.0	3.33	1.7	1.1	2.9