High Levels of Potentially Biogenic Dibromo and Tribromo Dibenzo-p-dioxins in Swedish Fish

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Introduction

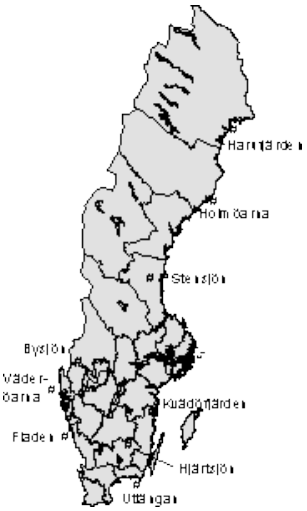
The occurrence of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in biota has been extensively studied during the last decades. Their brominated analogues PBDD/Fs and mixed bromo/chloro-DD/Fs (PXDD/Fs) have been much less studied, although it is known that PBDD/Fs are formed during pyrolysis of brominated flame retardants and PBDD/Fs and PXDD/Fs are emitted from incineration sources.

During the early 90's Wiberg *et al.*[1,2] analyzed samples of salmon, osprey and human milk for PCDD/Fs, PBDD/Fs and PXDD/Fs. Only PCDD/Fs were detected, despite low limits of detection (LODs), < 1 ppt in most cases, for PBDD/Fs and PXDD/Fs. Likewise, Loganathan *et al.*[3] analyzed carp for PBDD/Fs, but did not find any. Their LODs ranged from 2 to 8 ppt. However, given the increasing levels of other brominated compounds, e.g. polybrominated diphenyl ethers, in recent years, it is not unreasonable to expect that levels of PBDD/Fs and PXDD/Fs may have also increased. Swedish EPA therefore initiated a study on the levels of organohalogen compounds in Swedish fish. In this paper we present the results obtained for the PCDD/Fs, PBDD/Fs and PXDD/Fs.

Materials and Methods

Fish were sampled in three regions, North-East, South-East and South-West. In each region, three sampling sites were selected (Figure 1), representing, limnic, littoral and pelagial environments, respectively. When possible, stationary species, like perch (*Perca fluviatilis*) and viviparous benny (*Zoarces viviparus*), were selected. However, these are normally not found in the pelagial zone. Herring was therefore collected at the pelagial locations, although it is known that herring populations move over somewhat larger areas. The samples and sample descriptions are given in Table 1.

Table 1. Samples and sample characteristics.



Sample location	Number of samples	Species	% female	Sample size (g)	% lipids
NE Sweden					
1. Stensjön	8	Perch	83	100	0.53
2. Holmöarna	8	Perch	100	100	0.76
3. Harufjärden	16	Herring	100	30	2.2
SE Sweden					
4. Hjärtsjön	8	Perch	65	100	0.55
5. Kvädöfjärden	8	Perch	62	100	0.66
6. Utlängan	16	Herring	100	30	2.2
SW Sweden					
7. Bysjön	8	Perch	77	100	0.63
8. Väderöarna	8	V. benny	77	100	0.59
9. Fladen	16	Herring	100	30	5.3

Figure 1. Sample locations.

The samples were analyzed using a traditional PCDD/F method, which had been validated for PBDD/Fs and PXDD/Fs. In short, the samples were ground with sodium sulfate and column extracted with bipolar solvent mixtures. The lipid weights were determined gravimetrically, the residues were reconstituted, and the lipids were removed using multi-layer columns packed with KOH-silica, silica, 40% sulfuric acid silica, 20% sulfuric acid silica, silica and sodium sulfate. The PCDD/F, PBDD/Fs, PXDD/Fs and non-*ortho* PCBs were then isolated using carbon column fractionation. Finally, the purified extracts were analyzed by gas chromatography - high-resolution mass spectrometry (GC-HRMS).

Results and Discussion

The results of the PBDD/F and PXDD/F analyzes are given in Table 2. In most of the samples, no target analytes could be detected. The LODs for the low molecular weight analytes were all comparable to those obtained for PCDD/Fs, and ranged between 0.03 and 0.4 pg/g wet weight (ww), while the penta- through hepta-BDD/Fs had higher LODs, 0.3 to 6 pg/g ww. The latter gave higher LODs due to lower relative response factors and wider peak profiles.

However, di- and tri-BDDs were detected in all perch samples from Kvädöfjärden at average concentrations of 0.48 and 2.4 pg/g ww. At first, these levels do not seem that high, but considering the low lipid percentages of perch, the levels are rather high. The average di- and tri-BDD concentrations were 72 and 360 pg/g, on a lipid weight (lw) basis. It is worth mentioning that the average concentration of 2,3,7,8-TCDF, the most abundant PCDD/F, was only 16 pg/g lipids. Thus, the DBDD and TrBDD levels were 5-fold and 22-fold higher than TCDF.

Table 2. Levels (pg/g fresh weight) of PBDD/Fs and PXDD/Fs in Swedish fish samples. For sample locations and descriptions, see Table 1 and Figure 1.

Location number	1	2	3	4	5	6	7	8	9
Location	Stensjön	Holm-öarna	Haru-fjärden	Hjärt-sjön	Kvädö-fjärden	Utlängan	Bysjön	Munsö	Fladen
Br2DF	<0.03	<0.03	<0.1	< 0.03	< 0.03	<0.1	< 0.03	< 0.03	<0.1
Br2DD	<0.03	<0.03	<0.2	< 0.03	**0.48**	<0.2	< 0.03	< 0.03	<0.2
3Br-278ClDF	<0.03	<0.03	<0.2	< 0.03	< 0.05	<0.2	< 0.04	< 0.03	<0.2
2Br-378ClDD	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2
1Br-2378ClDF	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2
1Br-2378ClDD	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2
Br3DF	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2
Br3DD	<0.03	<0.03	<0.3	<0.03	**2.4**	<0.3	<0.03	<0.03	<0.3
BrCl5DF	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2	<0.03	<0.03	<0.2
BrCl5DD	<0.03	<0.03	<0.3	<0.03	<0.03	<0.3	<0.03	<0.03	<0.3
2378-TeBDF	<0.1	<0.1	<0.2	<0.1	<0.1	<0.2	<0.1	<0.1	<0.2
2378-TeBDD	<0.1	<0.1	<0.4	<0.1	<0.1	<0.4	<0.1	<0.1	<0.4
12378-PeBDF	<0.3	<0.3	<2	<0.3	<0.3	<2	<0.3	<0.3	<2
23478-PeBDF	<0.3	<0.3	<2	<0.3	<0.3	<2	<0.3	<0.3	<2
12378-PeBDD	<0.3	<0.3	<2	<0.3	<0.3	<2	<0.3	<0.3	<2
123478/123678-HxBDF	<0.3	<0.3	<2	<0.3	<0.6	<2	<0.7	<0.3	<2
234678-HxBDF	<0.3	<0.3	<2	<0.3	<0.3	<2	<0.3	<0.3	<2
123789-HxBDF	<0.3	<0.3	<2	<0.3	<0.3	<2	<0.3	<0.3	<2
123478/123678-HxBDD	<1.0	<1.0	<4	<1.0	<1.0	<4	<1.0	<1.0	<4
123789-HxBDD	<1.0	<1.0	<4	<1.0	<1.0	<4	<1.0	<1.0	<4
1234678-HpBDF	<1.5	<1.5	<6	<1.5	<1.5	<6	<1.5	<1.5	<6
1234789-HpBDF	<1.5	<1.5	<6	<1.5	<1.5	<6	<1.5	<1.5	<6
1234678-HpBDD	<1.5	<1.5	<6	<1.5	<1.5	<6	<1.5	<1.5	<6

Since the substitution patterns are unknown for the PBDDs detected, it is impossible to calculate TCDD equivalents (TEQs). In fact, only two components, 2,7/2,8-DBDD and 2,3,7-tri-BDD have, to our knowledge, been investigate. Mason *et al.*[4] reported high binding affinites for both components to the rat hepatoma Ah-receptor. The affinity of 2,3,7-tri-BDD (EC50, 1.2 nM) were almost as strong as TCDD (EC50, 1.0 nM), while 2,7/2,8-DBDD was an order of magnitude less potent (EC50, 0.16 nM). However, they induced aryl hydrocarobon hydroxylase (AHH) and ethoxyresorufin deethylase (EROD) less. The relative induction potencies were 0.03 and 0.002 for 2,3,7-tri-BDD and 2,7/2,8-DBDD, respectively, as compared to TCDD.

If the relative potencies of the PBDD congeners found in perch from Kvädöfjärden were of the same magnitude as 2,7/2,8-DBDD and 2,3,7-tri-BDD; the overall contribution to the total TEQ from the PBDDs would be similar to that of the PCDD/Fs (Table 3). It is therefore important to identify the DBDD and TrBDD congeners and estimate their TEFs.

Table 3. Levels (pg/g lipids) of PCDD/F, non-*ortho* PCB, DBDD and TrBDD in fish.

Lokal	PCDD/F pg TEQ/g	non-*ortho* PCB pg TEQ/g	DBDD pg/g	TrBDD pg/g
1. Stensjön	19 ± 6.3	22 ± 7	< 6	< 8
2. Holmöarna	32 ± 4.4	38 ± 6	< 6	< 8
3. Harufjärden	47 ± 16	22 ± 6	< 8	< 10
4. Hjärtsjön	25 ± 6	56 ± 12	< 4	< 5
5. Kvädöfjärden	14 ± 2.3	19 ± 4	72 ± 10	360 ± 47
6. Utlängan	40 ± 13	33 ± 13	< 12	< 16
7. Bysjön	28 ± 5	21 ± 5	< 5	< 5
8. Väderöarna	28 ± 5	67 ± 27	< 10	< 13
9. Fladen	8.5 ± 2	8.6 ± 2	< 7	< 9

The fact that PBDDs only were detected at one location indicates a local, rather than general, source of pollution. Our hypothesis is that the DBDDs and TrBDDs are of natural origin, since a TrBDD was recently detected in blue mussel (*Mytilus edulis*) tissue[5] and red macroalga *Ceramium tenuicorne.*[6] The levels were similar to, or even greater than, those of hydroxy-polybromodipheyl ethers (HO-PBDEs) and methoxy-polybromodipheyl ethers (MeO-PBDEs). Furthermore, several hydroxy-PBDDs (HO-PBDDs) and methoxy-PBDEs (MeO-PBDDs) metabolites were found in the Australian marine sponge *Dysidea dendyi.*[7,8] Thus, it seems plausible that Baltic marine algae or sponge, under certain environmental conditions, may produce significant quantities of PBDDs .

If that is the case, large spatial and temporal variations in the DBDD and TrBDD levels are to be expected, which is consistent with our findings, and it cannot be excluded that the PBDDs sometimes reaches such high levels that they pose a risk to organisms in the marine environment, or even to humans consuming the fish.

Acknowledgements

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