

OCCURRENCE AND LEVELS OF PCDD/Fs AND PBDD/Fs IN TWO SWEDISH LAKE SEDIMENTS

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Introduction

During the last two decades there has been a large increase in the usage of brominated flame retardants (BFRs). Undoubtedly, increasing quantities of bromine containing waste will be introduced in the incineration processes. Formation of PBDD/Fs during thermal treatment of BFRs or BFR containing waste has been shown both in laboratory and pilot scale experiments^{1,2}. PBDD/Fs exhibit similar properties as their chlorinated homologues and are expected to bio accumulate in a similar way. However, PBDD/Fs have larger molecular weight, lower vapour pressure, slightly lower water solubility and are more lipophilic. PBDD/Fs are more sensitive towards photo degradation which might result in a lower persistence than PCDD/Fs³. Toxicologically PBDD/Fs show nearly the same dioxin like toxicity as their chlorinated homologues as recently reviewed by Birnbaum⁴. Several studies have also shown that polybrominated dibenzofurans (PBDFs) originate from photolytic degradation of BFRs such as brominated diphenyl ethers (PBDEs)^{5,6}.

Considering this information and the potential large emission sources, it is very likely that the levels of PBDD/Fs are rising in the environment. Today, there is only limited information on levels of these compounds in the environment probably due to analytical difficulties as well as historically low levels. Here we present a screening of two different lake sediments. One lake is situated in an urban area, near a landfill (Lake Djulösjön) and the other lake is located in rural woodland protected under the Swedish EPA directive (Lake Stensjön).

Materials and Methods

Frozen lake sediments were thawed and placed in petri dishes. The wet samples were dried during two days in a dark fume cupboard. The sediments were weighed and placed in cellulose extraction timbles. Internal standards (¹³C-labelled PCDD/Fs, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,7,8-PeBDD and 1,2,3,4,7,8-HxBDF) were added to the samples and the timbles were then placed in a Dean-Stark extraction device. Toluene (400 ml) was used as extraction medium and the samples were refluxed for 24 hrs in darkness. A laboratory blank was run parallel with the sediment samples.

Sample clean-up

Sample clean-up was done on three open columns (multilayer silica, AlOx and active carbon). The multilayer silica columns contained KOH silica, neutral activated silica, 40% H₂SO₄ silica gel, 20% H₂SO₄ silica gel, neutral activated silica gel and activated Na₂SO₄ and was eluted with hexane. This column was followed by an AlOx column eluted with hexane/dichloromethane. The dioxin fraction was evaporated to approximately 1 ml and added to a 25 ml glass column containing Carboxen 101 dispersed on Celite 545, which was eluted with 10 ml of hexane followed by 80 ml of toluene to elute the planar fraction containing PCDD/Fs and PBDD/Fs. After the addition of a recovery standard (¹³C labelled 1,2,3,4-TeCDD, 1,2,3,7,8,9-HxCDD and 2,3,7,8-TeBDD) the samples were evaporated and transferred to amber glass auto sampler vials in 25 µl of tetradecane. The extracts and standards were stored in -18° C until HRGC-HRMS analysis.

Analysis

HRGC/HRMS analysis was performed on a Micromass Ultima operating at >10 000 – 12 000 resolution using EI ionization at 35 eV. All measurements were achieved in selective ion recording (SIR) mode, monitoring the two most abundant ions in the chlorine cluster. For confirmation of the PBDD/F measurements the three most abundant ions of

the molecular bromine cluster were measured. Splitless injection of 1 µl of the final extract was used on a 30 m DB5-MS (0.25 mm i.d., 25µm) column for PBDD/F analysis, and a 60 m Rtx DIOXIN 2 (0.25 mm i.d., 25 µm) for PCDD/F analysis. Throughout the whole sample preparation the samples was kept shielded from UV light to avoid photo degradation.

Results and Discussion

Levels of PCDD/F

The levels from the PCDD/F analysis are presented in Table 1. The PCDD/F pattern in sediments from both lakes is due to air deposited contamination of PCDD/Fs which have been further subjected to biological accumulation for a longer time period. The differences in concentrations are somewhat unexpected. Lake Stensjön, which is situated in the woodlands relatively far from known PCDD/F sources, has two- to ten-times higher concentrations as Lake Djulösjön. The difference can be explained by the fact that the water residence time was shorter than expected in Lake Djulösjön. Comparing the two sediments from Lake Djulösjön, there are slightly lower concentrations in the surface layer. Despite the fact that only two sediment samples are analysed from this lake the results points towards decreasing PCDD/F content in the upper sediments in Lake Djulösjön.

Table 1. Levels of PCDD/Fs in lake sediments. All levels in pg g⁻¹ dry weight.

Sample	Lake Stensjön	Lake Djulösjön	Lake Djulösjön
	0-1 cm	0-2 cm	2-3 cm
2378-TCDF	18.4	4.6	5.9
12378-PeCDF	19.7	2.6	3.4
23478-PeCDF	25.9	4.3	5.9
123478-HxCDF	34.3	4.7	4.9
123678-HxCDF	31.3	3.6	3.8
234678-HxCDF	30	4.8	5.1
123789-HxCDF	11.9	1.2	1.1
1234678-HpCDF	193	44.7	47.1
1234789-HpCDF	21.9	4.0	3.3
OCDF	467	122	140
2378-TCDD	1.2	0.23	0.27
12378-PeCDD	8.5	1.0	0.76
123478-HxCDD	9.2	1.6	1.2
123678-HxCDD	24.6	3.2	3.2
123789-HxCDD	24.6	3.1	4.0
1234678-HpCDD	180	60.0	59.5
OCDD	1295	703	807
Sum (pg g⁻¹)	2395	970	1097
Sum (pg TEQ g⁻¹)	45	7.3	8.3

Occurrence of PBDD/F

In the sediments only a few PBDD/F congeners have been identified by both retention time (match to C¹²- and C¹³-standards) and ion ratio (within 15% of the theoretical Br ratio). These are; 2,7-DiBDF, 2,8-DiBDF, 2,7-&-2,8-DiBDD (co-eluting), 2,3,8-TriBDF, 2,3,7-TriBDD, 1,2,7,8-TeBDF, 1,3,6,8-TeBDD, 1,3,7,9-TeBDD and 2,3,4,7,8-PeBDF. In addition, seventeen compounds have been identified as PBDD/Fs by ion ratio (<15%), only including non-2,3,7,8-substituted congeners. The sediments are dominated by the presence of mono- to hexa-substituted furans, where the tri- and tetra-substituted congeners are prevailing. Watanabe and co-workers also reported findings of PBDFs in the same range in Japanese sediments as well as the occurrence of tetra- to hexa-substituted PBDF in airborne dust⁷.

Tentatively, we have estimated the total concentration of the identified compounds. The surface sediment samples from both Lake Stensjön and Lake Djulösjön show the same levels of PBDD/Fs (540 pg/g dry weight). The sediment taken at the lower depth in Lake Djulösjön has a lower concentration (440 pg/g dry weight). Possibly, this could point towards a slight increase of PBDD/Fs in the upper sediment. With only two exceptions, the same congener pattern was found in the sediment discs from lake Djulösjön.

The PBDD/F patterns in the both lakes are very similar, but in Lake Stensjön the tri-brominated furans are present at higher concentrations in Lake Djulösjön. In addition, 1,3,6,8- and 1,3,7,9-TeBDD were found only in lake Djulösjön and the levels decreased with sediment depth. In all three sediments, only traces of 2,3,7,8-TeBDF were found (below limit of quantification) but significant amounts of 2,3,4,7,8-PeBDF. These results resemble the findings of PBDD/Fs in sediments from industrialized sites in Japan⁸. In relation to the Japanese sediments, the levels presented here are lower.

In both lake sediments both the penta- and the hexa PBDF patterns were dominated by one isomer. Interestingly, these two compounds were also the most abundant in a study where decabromodiphenyl ether (decaBDE) was subjected to photolytic degradation in toluene⁹. In addition, the PBDD/F pattern in the sediments did not resemble the pattern obtained from fly ash samples. This might imply that the PBDD/Fs encountered in the sediments are biologically altered photolytically induced degradation products from airborne PBDEs.

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