Occurrence and levels of PCDD/Fs and PBDD/Fs in fly ash from two different incinerators at a hazardous waste treatment plant

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Introduction

Incineration of chlorine containing waste can result in formation of chlorinated dibenzo dioxins and furans (PCDD/Fs). The increased usage of brominated flame retardants (BFRs) undoubtedly contributes to increasing quantities of bromine containing waste. This might eventually result in an elevated formation of brominated (PBDD/F) and brominated/chlorinated dioxins (PXDD/F) during waste incineration. Formation of PBDD/Fs during thermal treatment of BFRs or BFR containing waste has been shown in both laboratory and pilot scale experiments[1,2]. PBDD/Fs are also found in fly ash from incinerated municipal solid waste[3]. PBDD/Fs exhibit similar properties as their chlorinated homologues and are expected to bio accumulate in a similar way. PBDD/Fs are more sensitive towards photo degradation which might result in a lower persistence than the PCDD/Fs[4]. Toxicologically they show nearly the same dioxin like toxicity as their chlorinated homologues as recently reviewed by Birnbaum[5]. Studies at Örebro University imply that some of the brominated/chlorinated dioxins are more toxic than 2,3,7,8-TeCDD[6].

In the here presented study PCDD/Fs and PBDD/Fs were analysed in fly ash from two separate waste incineration lines at a hazardous waste incineration plant in Sweden. In line 1 (WTE 1) hazardous waste including PCB oil and other chlorinated organic solvents are incinerated in a rotary kiln furnace at high temperatures. In line 2 (WTE 2) domestic refuse mixed with less hazardous waste and waste of electronical and electronic equipment are incinerated in a grate furnace.

Materials and Methods

Approximately 10 g of fly ash was treated with a HCl solution. The wet fly ash was rinsed and dried through vacuum filtration. Fly ash and filter paper was kept in dark in a fume cupboard over night to dry further. The following day the ash was weighed and placed in a cellulose extraction timble. Internal standards (C[13]-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 soxhlet. Toluene (400 ml) was used as extraction medium and the samples were refluxed for 24 hrs in darkness.

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% H_2SO_4 silica gel, 20% H_2SO_4 silica gel, neutral activated silica gel and activated Na_2SO_4 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 Carbopack C dispersed on Celite 545, which was eluted with 10 ml of hexane followed with 80 ml of toluene to elute the planar fraction containing PCDD/Fs and PBDD/Fs. After the addition of a recovery standard (^{13}C-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.

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

2200

degradation.

Results and Discussion

Levels of PCDD/Fs

The PCDD/F concentrations in the two fly ash samples are presented in Table 1. The PCDD/F content is almost 50 percent higher in WTE 1 than in WTE 2. The homologue pattern is somewhat different between the two incineration lines, due to differences in the waste incinerated as well as differences in incinerators. The penta chlorinated congeners as well as hexa substituted furans constitute the major part of the total TEQ in WTE 1. However, the WTE 2 fly ash has dominating contribution of 2,3,7,8-TeCDF, 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD.

Table 1. Levels of PCDD/Fs in fly ash samples. All levels in pg g^{-1}.

Sample	WTE 1	WTE 2
2378-TCDF	62	95
2378-TCDD	5.5	12
12378-PeCDF	126	85
23478-PeCDF	134	73
12378-PeCDD	49	34
123478-HxCDF	194	77
123678-HxCDF	211	85
234678-HxCDF	285	75
123789-HxCDF	42	23
123478-HxCDD	39	19
123678-HxCDD	71	40
123789-HxCDD	36	19
1234678-HpCDF	867	215
1234789-HpCDF	67	27
1234678-HpCDD	442	252
OCDF	430	129
OCDD	1700	1003
Sum (pg TEQ g^{-1})	**236**	**136**

Occurrence of PBDD/Fs

In the PBDD/F analysis the following congeners were identified by retention time (match to C^{12} and C^{13} standards) and by ion ratio (within 15% of the theoretical Br ratio); 2,7-DiBDF, 2,8-DiBDF, 2,3,8-TriBDF, 2,3,7,8-TeBDF, 1,2,7,8-TeBDF, 1,3,6,8-TeBDD, 1,3,7,9-TeBDD and 1,2,3,7,8-PeBDF. Moreover, eighteen other compounds have been identified as possible PBDD/Fs through ion ratio, representing mono- trough penta-substituted BDD/Fs. Every PBDD/F congener found in WTE 1 was identified at higher levels in WTE 2, and additional congeners were found in WTE 2. The majority of compounds identified by ion ratio were mono- to tri BDFs in both fly ash samples. In WTE 1 the major individual isomers were 2,7-DiBDF, 2,8-DiBDF, 1,3,6,8-TeBDD and 1,3,7,9-TeBDD. The WTE 2 fly ash showed the same congeners together with two unidentified PeBDDs. No hexa-substituted congeners were found.
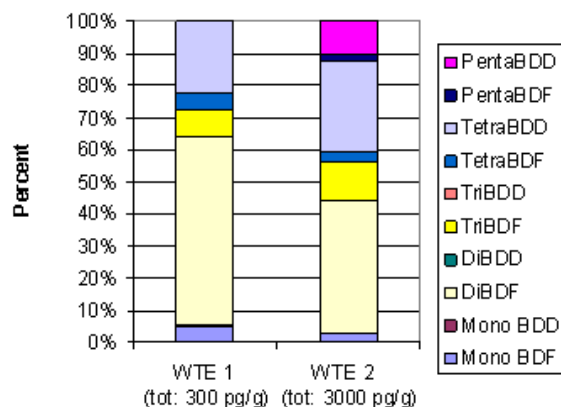
Figure 1. Distribution of the different PBDD/DF homologues (%).

In Figure 1, the contribution of the different homologue groups in relation to the total amount PBDD/F is plotted. Differences in distribution can be seen between the two ash samples in homologue pattern. Co- incineration of electronic waste resulted in higher total levels of PBDD/Fs and relatively more tetra- to penta- brominated dioxins and furans in the fly ash from WTE 2.The total concentration of PBDD/Fs in the fly ash from WTE 2 (3 000 pg/g) was estimated around ten times higher than in WTE 1 (300 pg/g). All concentrations were significantly lower than reported by Sakai and co-workers in incineration residues in a study on combustion of brominated flame retardants[7]. The lower levels in our study are probably explained by the co-combustion with municipal solid waste as compared to single incineration of electronic waste.

Concluding remarks

Incineration of hazardous waste in a high temperature rotary kiln furnace resulted in somewhat higher levels of chlorinated dioxins and furans than co-combustion of electronic waste and municipal solid waste (0.24 ng TEQ/g and 0.14 ng TEQ/g) in a conventional grate furnace. A screening of the samples for brominated dioxins and furans indicated higher levels of mono- through penta PBDD/Fs in the line where municipal and electronic wastes were co-combusted. Also the relative distribution of the homologue groups of the ash samples differed between the two incineration lines. The levels on the ashes were lower than reported levels from single incineration of electronic waste. Possibly, co-combustion of PBDE containing waste with hazardous waste could lead to a fly ash with high levels of both PCDD/Fs and PBDD/Fs.

The elevated levels of PBDD/Fs can also be problematic in municipal solid waste (MSW) incineration plants since many items containing electronics (containing brominated flame retardant) with short consumer life are expected to be found in domestic refuse.

Acknowledgements

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