COMPARISON OF PBDD/Fs AND PCDD/Fs IN FLUE GASES AND FLY ASH FROM A MSW INCINERATOR

Löthgren C-J[1], Hagberg J[2], van Bavel B[2], Lindström G[2]

[1]SAKAB AB, Norrtorp, S-692 85 Kumla, Sweden
[2]MTM Research Centre, Department of Natural Sciences, Örebro University, S-701 82 Örebro, Sweden

Introduction
Incineration of chlorine containing waste is known to 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.

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.[1] Toxicologically they show nearly the same dioxin like toxicity as their chlorinated homologues as recently reviewed by Birnbaum.[2] Studies at Örebro University imply that some of the brominated/chlorinated dioxins are more toxic than 2,3,7,8-TCDD.[3]

Formation of brominated dioxins and furans (PBDD/Fs) during thermal treatment of BFRs or BFR containing waste has been shown in both laboratory and pilot scale experiments.[4,5] PBDD/Fs are also found in fly ash from municipal solid waste incinerators (MSWIs).[6] Analyses of fly ashes from two incineration lines in Sweden, one hazardous waste incinerator and one MSWI co-incinerating electronic waste, showed ten times higher levels of PBDD/Fs in the fly ash from the MSWI.[7] With the knowledge of that result, it was decided to investigate also the flue gas concentrations at the MSWI and to which extent the PBDD/Fs are removed in the fabric filter of the plant.
In this paper the flue gas and fly ash concentrations of tetra- and penta substituted PCDD/Fs and PBDD/Fs from a sampling campaign in the autumn 2005 are presented.

Materials and Methods
Sampling
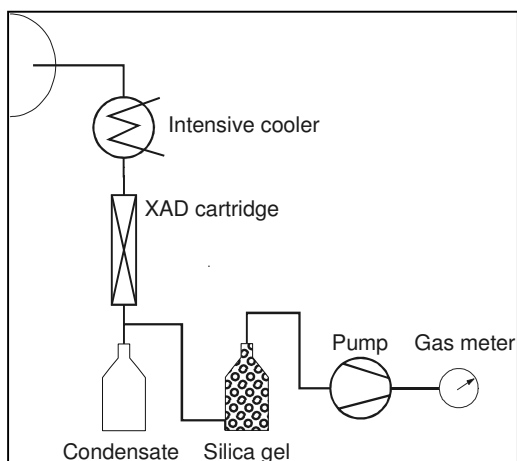Flue gases were sampled for gaseous PCDD/Fs and PBDD/Fs before and after the fabric filter of the incinerator in four consecutive one week campaigns. The sampling periods were arranged so that the first period started just after a maintenance stop and included the start up period of the plant.
Flue gases were pumped out from the flue gas channel through a glass probe and an intensive cooler, tempered at +4 ℃, into a XAD-II cartridge spiked with 13C-labelled 1,2,3,7,8-PeCDF, 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF. Recoveries for the sample spikes varied between 40-99%. Both the condensate and the cooled flue gas were pumped through the cartridge. After the cartridge the condensate was separated and the flue gas was dried further in silica gel before the flue gas volume was determined with a gas meter. A simplified sketch of the sampling set up is shown in fig. 1. In a pilot experiment, performed prior to the main sampling campaign, less than 2 percent of the total levels of PCDD/Fs and PBDD/Fs absorbed onto the XAD-II resin were detected in the collected condensate. Therefore analyses of condensates were excluded in the main study. Daily samples of fly

Figure 1: Overview of sampling set-up for flue gases

ash from the fabric filter were taken and put together in one collective sample per flue gas sample, i.e. one sample per week.

Sample preparation and analysis
The XAD-II resin was transferred to a soxhlet glass container and spiked with internal standards (IS). Samples were refluxed for 24 hrs in toluene. 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 and then 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-TCDD, 1,2,3,7,8,9-HxCDD and 2,3,7,8-TBDD) 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. Throughout the whole sampling and sample preparation the samples was kept shielded from UV light to avoid photo degradation.

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.

Criteria for determination of PBDFs
Tetra- to pentaPBDD/Fs were analysed in all samples. Peaks were identified against ion ratio and the retention times of the following congeners: 1,2,7,8-TBDF, 1,3,6,8-, 1,3,7,9-, 1,3,7,8-, 2,3,7,8-, 1,2,3,4-TBDD , 1,2,3,7,8-PeBDF, 1,3,4,7,8-PeBDF and 1,2,3,7,8-PeBDD (Wellington Laboratories Inc., Guelph, Canada) and ^{13}C labelled: 2,3,7,8-TBDF, 2,3,7,8-TBDD, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF and 1,2,3,7,8-PeBDD (Cambridge Isotope Laboratories Inc., Andover, MA, USA). In those cases where sample peaks did not have a match in the standards the identity was primarily based on ion ratios. To fully manifest the PBDF identity of peaks with correct ion ration but lacking a standard match, the following signals were monitored; [PBDF-COBr], [PBDE + 1Br] and [PBDE+2Br]. The fragment obtained when the COBr group leaves the PBDF molecules is formed by EI ionization of PBDFs but not for PBDEs. The other two signals are to make sure that the observed PBDFs are not resulting from thermal degradation of PBDEs (of higher substitution levels of bromine) at the injector or in the column.

Results and Discussion
Occurrence of PBDD/Fs
In all samples several (>10) TBDF and TBDD congeners were detected and among them were 2,3,7,8-TBDF and 2,3,7,8-TBDD identified. The penta substituted homologue groups were dominated by 1-2 congeners that were not 2,3,7,8-substituted.

Relative levels
For tetra and penta substituted homologues, the quotient of brominated to chlorinated isomers have been plotted for raw gas, clean gas and fly ash in fig. 2. Generally the PeBDF/PeCDF ratio has the largest value in most of the samples. In sampling week no 2, 3, and 4 no PeBDD was detected in clean gas and the amount of a brominated homologue exceeds the amount of the corresponding chlorinated homologue at four occasions, all in the clean gas.

It can further bee seen that the fraction of brominated homologues are lowest in the fly ash, increases in the raw gas and are highest in clean gas. This result indicates that the removal efficiency in the fabric filter is less efficient for PBDD/Fs. Therefore, the removal efficiency for gaseous homologues was plotted and the result is shown fig. 3.
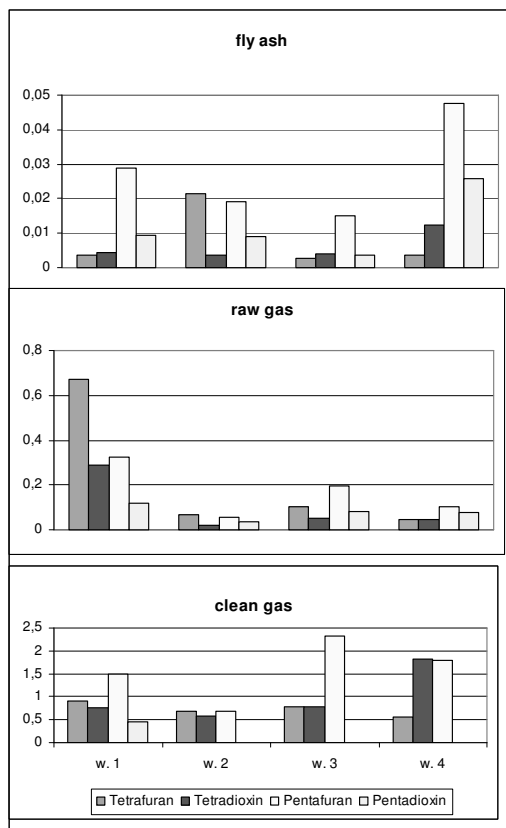

Figure 2: Presentation of the Br/Cl ratio for fly ash, raw gas and clean gas during the four sampling weeks

Figure 3 further supports the idea of a less efficient removal of PBDD/Fs in the fabric filter, though the variation is large. For example no PeBDD was found in the flue gases after the fabric filter in sampling week no 2, 3 and 4, whereas the removal efficiency for PeBDF in the third sampling week was as low as 40%. The low results in the first week can partly be explained by the start up period.
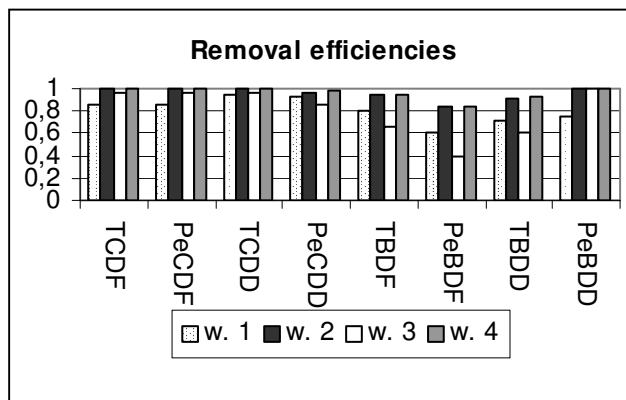

Figure 3: Removal efficiency for tetra and penta substituted chlorinated and brominated homologue groups

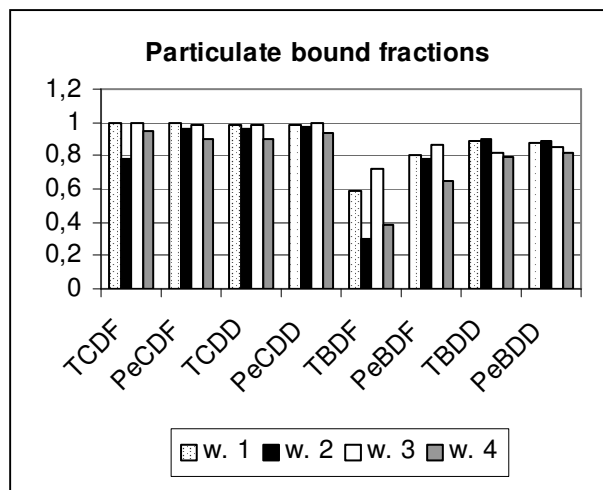**Figure 4:** Comparison of particulate bound tetra and penta substituted chlorinated and brominated homologue groups

In an attempt to estimate the particulate fraction in the raw gas, the total amount of the four different homologue groups was calculated for each sampling week (Σi), for raw gas, clean gas and fly ash. The particulate fraction was then calculated using the following formula:

$$\text{particulate fraction} = \frac{\sum \text{clean gas} + \sum \text{fly ash} - \sum \text{raw gas}}{\sum \text{clean gas} + \sum \text{fly ash}}$$

The result for each homologue group is shown in fig. 4. The particulate fractions for PBDD/Fs were found to be lower compared to PCDD/Fs. For the PBDD/Fs the fraction varied between 30% for TBDF in the second sampling week to 89% for TBDD and PeBDD, also in the second sampling week. For the PCDD/Fs the particulate fraction varied between 77% for TCDF in the second sampling week to >99% for TCDF and PeCDF in the first sampling week. This level is higher than results reported from direct measurements.[8] The calculation method used here is sensitive to the estimation of flue gas volumes and ash production. Small errors may shift the result considerably. On the other hand, the possibility of a PCDD/F rearrangement between particulate filters and gas phase adsorbents in sampling equipments has been discussed.[8] Such rearrangements will also shift the particulate bound fraction and cause errors in the results.

Concluding remarks
This study indicates that the behaviour of PBDD/Fs and PCDD/Fs differs in the flue gas cleaning equipment of MSWIs. The overall removal efficiency for brominated dioxins and furans are lower than for the chlorinated homologues. This can partly be explained by the finding that a lower fraction of PBDD/Fs are particulate bound compared to PCDD/Fs. In addition, the clean gas has ha higher fraction of PBDD/Fs, which call attention to the importance of control, regulation and implementation of PBDD/F emission limits.

Acknowledgements

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