

POTENTIAL RISK OF OCCUPATIONAL EXPOSURE TO HIGH LEVELS OF PBDD/Fs DURING RESTORATION OF ELECTRICITY SUBSTATIONS AFTER SPONTANEOUS COMBUSTION

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Introduction

Incomplete combustion of materials containing brominated flame retardants, for example polybrominated diphenyl ethers, may result in substantial amounts of polybrominated dibenzo-*p* dioxins and furans, PBDD/Fs¹⁻³. Since the PBDD/Fs are pollutants with similar qualities as their chlorinated homologues, i.e. polychlorinated dibenzo-*p* dioxins and furans (PCDD/Fs), they are persistent, bio accumulative and toxic. In this study, different soot samples were collected from an electricity substation after a spontaneous combustion and were analysed for tetra- to octa substituted PBDD/Fs. By using a wipe testing procedure three soot samples were collected from the surfaces on the outside of the stainless steel cover, and three samples were taken from surfaces inside the substation where the different electric cables are connected and where the fire started. The electricity substation was approximately 20 years old and all cables were isolated by plastics potentially containing flame retardants. In this study we can reveal high levels PBDD/Fs in the different soot samples which may constitute a potential risk to electricians working with restoring the function of the electricity substation and other persons handling the waste material originating from the spontaneous combustions.

Materials and methods

Soot samples

Samples of soot were collected by using a wipe test procedure. The samples were taken approximately 2-3 hours after the fire had gone out and no attempts had been made to put out the fire. Two Kleenex tissues were folded together by using a tweezers. A surface of approximately 10 x 20 cm were wiped with the folded tissue and then placed in an amber glass bottle. This procedure was repeated three times on three different surfaces containing soot on the outside of the stainless steel cover of the burnt substation. Three samples were taken in a similar fashion from within the destroyed substation, close to the electric cables and from where the fire had started. Since there were ash residues inside the substation the samples were collected with the ambition to only sample soot and not ash. At the same time two blank samples were prepared by folding two Kleenex tissues and placing them in amber glass bottles. All samples were stored in dark and at room temperature before sample extraction.

Chemicals

Samples were spiked with a ¹³C-labelled internal standard mixture EDF-5408 (CIL, Andover, USA), including ¹³C-labelled 2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD, 1,2,3,4,6,7,8-HpBDD, OBDD, 2,3,7,8-TeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and OBDF before extraction. As recovery standard the EDF-5409 mixture from CIL, Andover, USA including 1,2,3,7,8-PeBDF and 1,2,3,7,8,9-HxBDD was used. The same congeners were also present in the native standard mixture.

Organic solvents used were of pesticide grade and purchased from Fluka (methanol, *n*-hexane, dichloromethane, and toluene). Ethanol was purchased from Sharlau.

Sample preparation

The Kleenex tissues containing the soot were extracted in toluene for 24 hours by using Soxhlet extraction. Before extraction, the samples were spiked with ¹³C-labelled internal standards. The extracts were treated with a serial clean up using three different 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 Na₂SO₄ and was eluted with *n*-hexane. This column was followed by an AlOx column eluted with *n*-hexane/ dichloromethane. Additional clean up and fractionation was done on an active carbon column, containing Carboxack C dispersed on Celite 545, which was eluted with 7 ml of *n*-hexane for

non-planar compounds and then 90 ml of toluene to extract the planar fraction containing PBDD/Fs. Addition of ^{13}C -labelled recovery standards was done prior to instrumental analysis. Throughout the sample preparation the samples were kept shielded from UV light to avoid photo degradation. Toxic equivalents (TEQs) were calculated using congener-specific relative potencies for PBDD/Fs and World Health Organization toxic equivalency factors (TEFs) for PCDD/Fs ^{4,5}.

Instrumental analysis

HRGC/HRMS analysis was performed on a Micromass Autospec Ultima operating at >10 000 resolution using EI ionization at 35 eV. All measurements were performed in the selective ion recording mode (SIR), monitoring the two most abundant ions of the molecular bromine cluster. Quantification was performed using the internal standard method. A 30 m BPX5 column was used to separate the PBDD/Fs (SGE; 30m x 250 μm i.d. x 0.10 μm film thickness) and programmable temperature vaporizing (PTV) injection was applied to inject 10 μl of the final extract (kept in toluene) on the GC column. A GC temperature program was used to optimize the response (and minimize the degradation in the injector and on the column) depending on column length and GC performance. Detection levels were calculated at a S/N ratio of 3, corrected for recovery of the internal standard. The criteria for positive peak identification were isotope ratio within $\pm 15\%$ of the theoretical value and retention time match with that of the corresponding labelled compound.

Results and discussion

All PBDD/F congeners were detected in the soot samples except OBDF, see table 1. OBDF could not be determined by using the relatively long column used in this study possibly due to substantial degradation during the analytical separation. The recoveries varied between 49 to 140 % for all congeners except OBDD and the hexa substituted congeners in sample 5. The recoveries for the hexa substituted congeners were approximately 30 % as a result of co-eluting compounds disturbing the chromatography. The recovery for OBDD was between 20 to 30 % and the low recovery was possibly related to the same issues that prevented the detection of OBDF.

Table 1. Amounts of PBDD/Fs detected in soot samples obtained from wipe tests of different surfaces of an electricity substation after self-ignition, presented as pg per wipe test.

	Concentrations in soot from surfaces within the substation (pg)			Concentrations in soot from surfaces on the outside of the substation (pg)		
	1	2	3	4	5	6
<i>Furans</i>						
2,3,7,8-TeBDF	160	870	210	860	80	240
1,2,3,7,8-PeBDF	67	510	110	480	13	87
2,3,4,7,8-PeBDF	62	580	110	350	8,9	150
1,2,3,4,7,8-HxBDF	34	270	50	460	30	66
1,2,3,4,6,7,8-HpBDF	49	370	96	480	44	54
OBDF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
<i>Dioxins</i>						
2,3,7,8-TeBDD	13	69	19	140	3,7	44
1,2,3,7,8-PeBDD	13	66	20	190	4,2	34
1,2,3,4,7,8-HxBDD/ 1,2,3,6,7,8-HxBDD	27	155	45	270	1,5	42
1,2,3,7,8,9-HxBDD	28	200	52	360	2,1	51
1,2,3,4,6,7,8-HpBDD	130	820	250	830	10	140
OBDD	66	630	170	140	<30	36
Sum (pg)	650	4550	1130	4560	200	950
Benisch ^a pg TEQ	180	1040	245	1090	78	300
Benisch ^b pg TEQ	130	760	180	810	56	220
WHO ^c pg TEQ	90	630	140	760	25	200

^{a, b}TEQ derived by using REP values from Behnisch et al. (2003) applying EC20 and EC50 respectively⁴.

^cTEQ derived by using WHO₁₉₉₇ toxic equivalent factors (TEFs) for PCDD/Fs⁵.

n.a.= not analysed.

Considerable amounts of PBDD/Fs could be detected in the different soot samples, see table 1. The amounts varied substantially even if the soot samples were collected from approximately the same areas possibly reflecting the occurrence of different temperature zones at which the soot particles and the flue gas have had different possibilities to cool and adsorb. The contribution of low brominated furans were substantial with 2,3,7,8-TeBDF being the most dominating congener in most of the samples. Among the dioxin congeners the higher brominated compounds had the largest contribution. Duan and co-workers also detected extremely high concentrations of primarily the lower brominated furans when they studied the formation of PBDD/Fs during incineration of waste printed circuit boards during different temperature conditions¹. At different temperatures between 250 and 400°C the formation of PBDD/Fs were significant and at temperatures above 325°C the sum of 2,3,7,8-TeBDF, 1,2,3,7,8- and 2,3,4,7,8-PeBDF constituted more than 50% of the formed PBDD/Fs. However, at temperatures above 625°C the concentration of PBDD/Fs decreased significantly and the compounds were almost destroyed. The high levels of tetra- and pentabrominated furans found in this study are most possibly due to incomplete combustion at relatively low temperatures since the surface of the electric substation was well ventilated as it was placed outdoors.

Two of the soot samples, one from surfaces within the substation and one from surfaces on the outside of the substation, had significantly higher levels than the other samples. Possibly the two samples were taken from the same side of the substation where the formation and adsorption of PBDD/Fs had been stronger. When comparing the congener profile of the samples (Fig.1) there was no shift in the pattern when comparing the high level samples (i.e. sample 2 and 4) with the remaining samples showing that the distribution and thereby the formation of different PBDD/F congeners were similar in all samples. However, sample 5 had a somewhat different congener profile possibly affected by the poor recovery of the hexa substituted congeners.

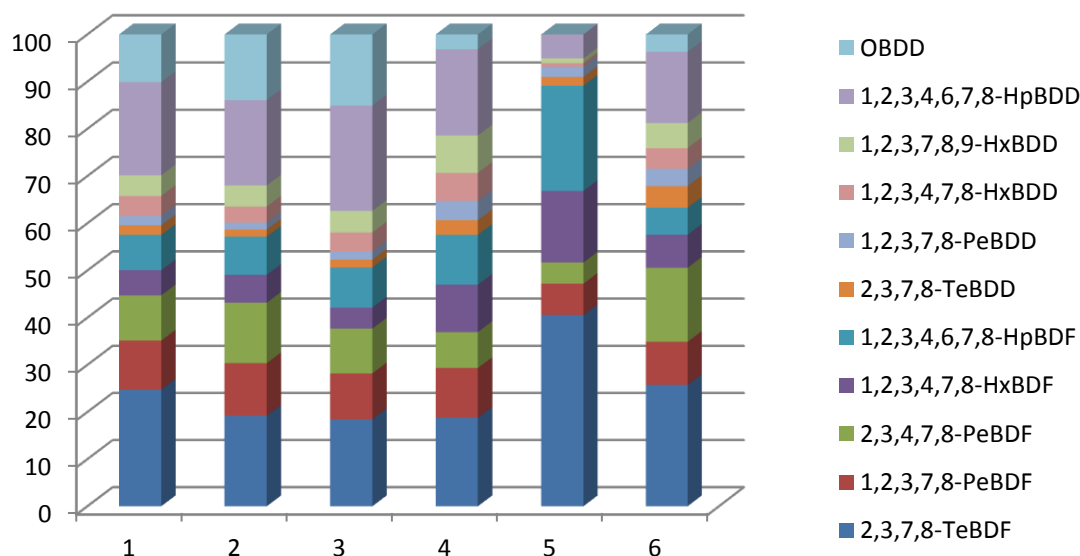


Figure 1. Distribution of PBDD/F congeners, expressed as a percentage, detected in the different soot samples (1-6). Note that OBDF were not included in the determination.

An attempt was done to establish TEQ based amounts (pg TEQ) by using congener specific relative potencies (REPs) as well as toxic equivalent factors for PCDD/Fs since not all PBDD/F congeners have individual REP values, see table 1. REP values for all congeners except 1,2,3,4,7,8-HxBDD, 1,2,3,4,6,7,8-HpBDD and OBDD were taken from Behnisch et al (2003)⁴. For the HxBDD congener, the congener specific REP value for 1,2,3,6,7,8-HxBDD was used since they ought to be similar and for the hepta and octa PBDDs the TEF values for the chlorinated homologues were applied. The high amounts of the lower brominated congeners resulted in very high pg TEQ levels. When using the congener specific REPs the calculated TEQ amounts present in the soot samples were somewhat higher since the REP value for 2,3,7,8-TeBDF is significantly higher than the assigned TEF-value for 2,3,7,8-TeCDF. Since these results are expressed as pg per wipe they are not comparable with other studies. Nonetheless, the detected amounts are considerable and pose a potential risk for workers to be

occupationally exposed to very high levels of PBDD/Fs when restoring and handling the waste originated from electricity substations that have been destroyed by spontaneous combustion.

Concluding remarks and further perspectives

Relatively small amounts of soot from both the inside and the outside of an electricity substation destroyed after spontaneous combustion contained very high levels of PBDD/Fs. These high levels may pose a risk of occupational exposure to these harmful substances to electricians restoring substations that have been destroyed by spontaneous combustion and other workers handling the waste generated after the restoration.

In a future perspective the amounts of the PBDD/Fs are to be verified by performing analysis on a shorter column. Another ambition is to determine the concentrations of PCDD/Fs so that the relationship between PBDD/Fs and PCDD/Fs formation during spontaneous combustion of electricity substations may be investigated.

Acknowledgements

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