RELEASE OF ORGANIC POLLUTANTS DURING ACCIDENTAL FIRES

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Introduction

Accidental fires can damage people not only by heat, but in many cases hazardous gases released during burning poses the main risk. In addition to classical toxic gases like carbon monoxide and hydrogene cyanide, a broad range of organic compounds with different toxicities can be released. In case of organic material burning in the presence of chlorine, the generation of organochlorine compounds can be expected. Focussing on PCDD and PCDF, especially those burning events have been examined where a generation of these compounds had to be expected because of the special constitution of the burning or smouldering material, like industrial fires, transformer, condenser (1, 2, 3, 4) and PVC burning (5, 6, 7).

PVC is known to form PCDD/PCDFs in case of thermal treatment under special conditions. Because of its technological qualities, PVC is used e.g. for pipe lines, floor coverings, furniture and apparatus boxes and can be found in nearly every household. In case of residential fires, the release of PCDD/PCDF therefore has always to be taken into account as a possible risk.

Recently, it was found that burning of brominated compounds (e.g. polybrominated biphenyls and diphenyl ethers) resulted in the generation of polybrominated dioxins and furans (PBDD/ PBDF) (8, 9, 10). Such organobromine compounds were used e.g. as flame retardants especially in some plastics. Burning of these substances and materials can lead to the formation of PBDD/PBDF (9, 11, 12, 13). Such flame protected products are still in use, the release of PBDD/PBDF has to be concerned in case of residential fires.

Experimentals

During and after residential fire damages several samples (gases, ashes) were analyzed in regard to their content of PCDD/PCDF and PBDD /PBDF. In order to assess the exposition of residents and employees, the following examinations were performed:

* Samples of gas and ashes were taken directly after five fire accidents.
* Fire man's trousers were analyzed after fighting a fire.

In order to achieve an impression of the release of PBDD/PBDF by a suspected source, a fire simulation was performed, using TVs with flame protected conductive plates.

Ashes and trouser samples were analyzed without preparation. Gas sampling was conducted by a low volume sampler using purified XAD-2 resin. Sampling duration was dependent on local circumstances (e.g. hindering of the fire brigade) and ranged from 19 to 45 minutes.

Fire simulation was performed with two TVs. Their conductor plates were substituted by PBDPE-protec-

ted plates (4,8 % (weight) Penta-BDPE). They were burnt in a barrel where the bottom was substituted by a grate. At the top, exhaust gas was taken following VDI 3499 (Blatt 2).

Samples were spiked and then extracted with toluene in a Soxhlet. After clean-up of the extract (columns packed with silica-gel- and aluminiumoxide) and concentration, the different fractions were analyzed by GC/MS. Analytical screening and high-chlorinated and high-brominated compounds were analyzed using a non-polar capillary column (Ultra 2). Identification of other isomers was performed on a polar capillary column (CP Sil 88), detection of PCDD/PCDF, PBDD/PBDF and PBDPE by MS within MID-mode, detection of PCB and chlorinated benzenes by ECD. Quantification was based on the internal standards, with a minimum recovery of 70 %. Higher brominated isomers were quantified by externally calibration.

Internal standards:
PCDD/PCDF: mixture of a ^{13}C-marked PCDD- and PCDF-standard for each chlorination grade
PBDD/PBDF and PBDPE: ^{13}C-marked 2,3,7,8-TBDD and -TBDF
PCB: Mirex
Chlorinated Benzenes: 1,3,5-Tribromobenzene.

Results

The analysis of gaseous emissions directly after fire events gave the following results: In addition to PCB, chlorinated benzenes and polybrominated biphenyl ethers (PBDPE), up to 11,98 ng/m^3 of PCDD/PCDF (sum) resp. 0,14 ng/m^3 (TE, BGA) and up to 3,8 ng/m^3 PBDD/PBDF have been found. Maximum contamination of ashes from household burning were 0,218 ug/kg PCDD/PCDF (TE) in one and 27,28 ug/kg PBDD/PBDF in another sample. PBDD were found in small amounts and only in one third of the samples. Table 1 gives the details.
The fire man's trousers showed a PCDD/PCDF - contamination of 46,93 ug/kg PCDD/PCDF resp. 203 ng TE (BGA) per kilogram. PBDF-contamination amounted to 2,01 ug/kg, PBDD were not found.
The fire simulation resulted in 825 ug/m^3 PBDD/PBDF in the exhaust gas and 79.3 mg/kg PBDD/PBDF in the ashes. Details are shown in table 2.

Discussion

The results of the fire simulation and of the fire man's trousers indicate a severe health threat to people who are occupationally or privately exposed to household fires, not only by chlorinated, but additionally by brominated dioxins and furans. The limit for the sum of eight isomers of PCDD/PCDF in the Gefahrstoffverordnung in products is set to 5 ug/kg. With 0,71 ug/kg, referring to the eight isomers mentioned above, the contamination of the fire man's trousers lies less than 10-fold under this limit and can therefore be removed without special demands.
Following the Gefahrstoffverordnung, fire events with probable release of PCDD/PCDF have to be registered [Appendix III, Point 3.2]. In addition, personel protection equipment is demanded in cases, where the 5 ppb-limit (eight isomers) is exceeded [Point 3.1 and 3.3]. Following our analyses, ashes of residential fires can lie in the same range as the 5 ppb-limit. We suppose that further investigations will perhaps show that this limit can even be exceeded.
To the authors' opinion, a checking of residues of residental fires due to their contamination with PCDD/PCDF and PBDD/PBDF seems to be necessary. In addition, fire men's protection suits have to be decontaminated or separately be removed. Experts claim for wrapping them up in foil and store them in special containers (14).
In order to protect man and the environment from the release of PCDD/PCDF and PBDD/PBDF within accidental fires, a technical guide for this problem seems to be necessary. In addition, PBDPE and PBDD/PBDF should be regulated in the Gefahrstoffverordnung in the same way as their chlorinated dioxins and furans.

Tab. 1: PCDD/PCDF, PBDD/PBDF and other organohalogene compounds in emissions of residental fire accidents.

* may include additional substance

	1 gas [ng/m³]	2 gas [ng/m³]	3 gas [ng/m³]	5 gas [ng/m³]	1 ash [ng/g]	2 ash [ng/g]	3 ash [ng/g]	4 ash [ng/g]	5 ash [ng/g]
2378-TetraCDD	< 0,01	< 0,01	< 0,01	< 0,01	< 0,001	< 0,001	< 0,001	< 0,001	< 0,001
2378-TetraCDF	< 0,01	0,09	0,02	0,20	0,014	0,007	0,025	0,014	0,014
Sum TetraCDD	0,10	0,12	0,22	0,21	0,058	0,006	0,007	0,082	0,013
Sum PentaCDD	0,11	0,16	< 0,01	0,33	0,130	0,009	0,055	0,279	0,030
Sum HexaCDD	0,19	0,54	0,04	0,83	0,204	0,074	0,058	2,140	0,246
Sum HeptaCDD	0,57	0,71	0,06	0,71	0,366	0,178	0,053	12,944	0,043
OctaCDD	24,07	0,70	0,10	0,73	0,830	0,594	0,074	37,292	0,062
Sum PCDD	25,05	2,25	0,41	2,81	1,588	0,861	0,247	52,746	0,394
Sum TetraCDF	0,09	0,99	0,20	2,79	0,014	0,026	0,140	0,167	0,096
Sum PentaCDF	0,42	0,81	0,27	2,70	0,193	0,059	0,131	0,292	0,066
Sum HexaCDF	1,72	0,66	0,03	1,47	0,285	0,014	0,092	0,354	0,029
Sum HeptaCDF	0,37	0,59	0,18	1,39	0,327	0,011	0,052	0,498	0,014
OctaCDF	1,13	0,48	0,05	0,82	0,152	0,024	0,020	0,361	0,007
Sum PCDF	3,72	3,53	0,73	9,17	1,149	0,134	0,435	1,672	0,212
Sum PCDD+PCDF	28,77	5,78	1,14	11,98	2,737	0,995	0,682	54,418	0,606
tox.equivalents (BGA)	0,08	0,04	0,02	0,14	0,028	0,006	0,008	0,218	0,008
2378-TetraBDD*	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
2378-TetraBDF *	< 0,1	< 0,1	< 0,1	0,1	< 0,05	0,81	< 0,05	< 0,05	< 0,05
Sum DiBDD	< 0,1	< 0,1	< 0,1	0,3	< 0,05	< 0,05	< 0,05	0,08	< 0,05
Sum TriBDD	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Sum TetraBDD	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	0,16	< 0,05	< 0,05	< 0,05
Sum PentaBDD	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Sum HexaBDD	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Sum HeptaBDD	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
OctaBDD	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Sum PBDD	< 0,1	< 0,1	< 0,1	0,3	< 0,05	0,16	< 0,05	0,08	< 0,05
Sum DiBDF	< 0,1	< 0,1	< 0,1	< 0,1	0,11	2,30	0,17	0,10	0,44
Sum TriBDF	< 0,1	< 0,1	< 0,1	2,0	0,06	7,31	0,12	0,13	0,27
Sum TetraBDF	< 0,1	< 0,1	< 0,1	1,5	0,14	8,59	0,23	0,12	0,15
Sum PentaBDF	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	5,71	< 0,05	0,06	0,06
Sum HexaBDF	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	2,34	< 0,05	< 0,05	< 0,05
Sum HeptaBDF	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	0,87	< 0,05	< 0,05	< 0,05
OctaBDF	< 0,1	< 0,1	< 0,1	< 0,1	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Sum PBDF	< 0,1	< 0,1	< 0,1	3,4	0,30	27,28	0,53	0,42	0,92
Sum PBDD+PBDF	< 0,1	< 0,1	< 0,1	3,8	0,30	27,28	0,53	0,49	0,92
Sum PBOPC	0,88	2,37	23,56	49,28	0,13	1,48	0,12	< 0,05	0,14
Sum PCB	12,36	79,48	11,49	466,6	17,25	4,12	57,52	11,71	7,71
Sum chlorinated benzenes	17,53	40,71	11,95	26,33	2,13	1,55	2,52	5,23	2,78

Tab. 2: PCDD/PCDF, PBDD/PBDF and other organohalogene compounds in a fire brigadier's trousers a fire simulation

* *may include additional substance* *n.a. = not analyzed*

	trousers	fire simulation	
		gas	ash
	[ng/g]	[mg/m³]	ug/g]
2378-TetraCDD	0,005	n.a.	n.a.
2378-TetraCDF	0,084	n.a.	n.a.
Sum TetraCDD	0,047	n.a.	n.a.
Sum PentaCDD	0,006	n.a.	n.a.
Sum HexaCDD	0,335	n.a.	n.a.
Sum HeptaCDD	3,600	n.a.	n.a.
OctaCDD	35,860	n.a.	n.a.
Sum PCDD	40,048	n.a.	n.a.
Sum TetraCDF	1,361	n.a.	n.a.
Sum PentaCDF	1,660	n.a.	n.a.
Sum HexaCDF	0,883	n.a.	n.a.
Sum HeptaCDF	1,406	n.a.	n.a.
OctaCDF	1,372	n.a.	n.a.
Sum PCDF	6,882	n.a.	n.a.
Sum PCDD+PCDF	46,930	n.a.	n.a.
tox.equivalents (BGA)	0,203	n.a.	n.a.
2378-TetraBDD*	< 0,05	n.a.	n.a.
2378-TetraBDF*	0,06	n.a.	n.a.
Sum DiBDD	< 0,05	n.a.	n.a.
Sum TriBDD	< 0,05	0,015	1,50
Sum TetraBDD	< 0,05	0,005	0,40
Sum PentaBDD	< 0,05	< 0,005	0,10
Sum HexaBDD	< 0,05	< 0,005	< 0,05
Sum HeptaBDD	< 0,05	< 0,005	< 0,05
OctaBDD	< 0,05	< 0,005	< 0,05
Sum PBDD	< 0,05	0,020	2,00
Sum DiBDF	0,32	n.a.	n.a.
Sum TriBDF	0,26	0,445	45,70
Sum TetraBDF	0,82	0,320	29,60
Sum PentaBDF	0,50	0,035	1,90
Sum HexaBDF	0,12	0,005	0,07
Sum HeptaBDF	< 0,05	< 0,005	< 0,05
OctaBDF	< 0,05	< 0,005	< 0,05
Sum PBDF	2,01	0,805	77,27
Sum PBDD+PBDF	2,01	0,825	79,27
Sum PBDPE	90,92	0,730	13,80
Sum PCB	16412	n.a.	n.a.
Sum chlorinated benzenes	91,71	n.a.	n.a.

References

1) Weiß, A.: Der Maschinenschaden 56, 9 - 13 (1983)
2) Schecter, A.: Chemosphere 16, 2155 - 2160 (1987)
3) des Rosiers, P.E.: Chemosphere 16, 1881 - 1888 (1987)
4) Draper, W. M., Phillips, J.: Chemosphere 17, 1831 - 1850 (1988)
5) Marklund, S., Andersson, R., Tysklind, M., Rappe, C.: Chemosphere 18, 1031 - 1038 (1989)
6) Funcke, W., Theisen, J., Balfanz, E., König, J.: Staub - Reinhaltung der Luft 48, 393 - 396 (1988)
7) Theisen, J., Funcke, W., Balfanz, E., König, J.: Chemosphere 19, 423 - 428 (1989)
8) Thoma, H., Rist, S., Hauschulz, G., Hutzinger O.: Chemosphere 15, 649 - 652 (1986)
9) Hutzinger, O., Dumler, R., Lenoir, D., Teufl, C., Thoma, H.: Chemosphere 18, 1235 - 1242 (1989)
10) Thoma, H., Hauschulz, G., Knorr, E., Hutzinger O.: Chemosphere 16, 277 - 285 (1987)
11) Buser, H.-R.: Environ. Sci. Technol. 20, 404 - 408 (1986)
12) Pinkerton, M. N., Kociba, R. J., Petrella, R. V., McAllister, D. L., Willis, M. L., Fulfs, J. C., Thoma, H., Hutzinger, O.: Chemosphere 18, 1243 - 1249 (1989)
13) Clausen, E., Lahaniatis, E.S., Bahadir, M., Bieniek, D.: Fresenius Z. Anal. Chem. 327, 297 - 300 (1987)
14) Schuering, K.-H.: brandschutz/Deutsche Feuerwehr-Zeitung 9, 534 - 540, 1988