Results from the 1st round of the international intercalibration study for PBDD/DF and mixed PC/BDD/DF in standard solutions and incineration samples

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Introduction

Already in 1986 the formation of PBDD/DF from technical brominated diphenyl ethers (BDEs) was shown by Buser et al.[i] Further evidence of the formation of PBDD/DFs from BDEs was presented by Thoma[ii] and Luijk[iii] and from Tetrabromobisphenol-A (TBBP-A) by Thoma[iv] and Dumler[v]. These small scale laboratory experiments, often performed in quartz vials or tubes at elevated temperatures (600-900 ºC), show that formation of PBDD/DF is favoured from the Penta BDE formulation. Also the technical Deca BDE formulation generates considerable amounts of PBDD/DFs while formation from TBBP-A is somewhat lower as recently reviewed by Weber[vi]. In pilot scale incineration of BFRs alone or together with municipal solid waste, formation of PBDD/DFs and mixed PC/BDD/DFs has been shown[vii,viii]. Under normal operating conditions the formation of the mixed PC/BDD/DFs is favoured through 'De Novo' synthesis in the cooling zone of the incinerator as with chlorinated PCDD/DFs. Other thermal processes during production (extrusion, moulding)[ix,x] might result in PBDD/DF formation. In addition products with BFRs, such as rear covers of TV sets, can contain relatively high levels of PBDD/DFs as was recently shown in a Japanese study[xi]. Although only limited data are available and no Toxic Equivalent Factors (TEF) have been assigned, there is strong proof for dioxin-like toxicity of both PBDD/DF and the mixed Cl/Br dioxins and furans as recently reviewed by Birnbaum[xii] et al. Several methods for brominated dioxins, adapted from the analysis of chlorinated dioxins, have been published in the past[xiii,xiv,xv]. But recently there seem to be a new interest for the analysis of PBDD/DF[xvi,xvii]. Problems with interferences of BDEs during clean up and extraction or high resolution GC/MS analysis are known. In addition to thermal breakdown of higher brominated PBDD/DFs or decomposition of Deca BDE to PBDFs. While new data is expected to come out, intercalibration of the methods used by different laboratories is of course an important QA/QC feature. Here we present the first results of an international intercalibration on the analysis of PBDD/DFs and mixed Cl/Br containing dioxins and furans.

Methods and materials

Two fly ash samples and two standard solutions were sent to 25 laboratories for the analysis of both PBDD/DF and mixed Cl/Br dioxins and furans. The laboratories were asked to analyse the compounds listed in Table 1 using their own extraction and clean up procedures and use their own standard solutions for quantification. Sample A consisted of a pooled cyclone ash made available

by Dr. Gunilla Söderström containing both PBDD/DFs and mixed Br/Cl dioxins and furans after incineration of BFRs in a pilot incinerator. Sample B consisted of a fly ash made available by Dr. Roland Weber containing low levels of PBDD/DFs but somewhat higher levels of mixed Cl/Br compounds. Standard solution A was a dilution of mix DF-2046A made available by Cambridge Isotope Laboratories and contained a mixture of 9 Tetra- through Hexa PBDD/DFs at a concentration of 10-1000 pg/ul. The other solution was a mixture of mixed Cl/Br dioxins and furans at a concentration of 10-50 pg/ul donated by Wellington Laboratories.

Results

Of the total of 25 participants 12 were able to report results before the set deadline. The report frequency of 48% is significantly lower than similar studies on the chlorinated homologues were report frequencies are normally over 80%. Also the variation in the data of a standard solution is larger up to 115%. However good results were obtained for several compounds resulting in RSDs between 16 and 39% for the brominated dioxins and furans. Two of the HxBDD were co-eluting on the column used by most of the participants and results were reported for the sum of the two isomers. From the results for the 6 mixed Cl/Br dioxins and furans standard solutions it showed that this analysis was somewhat more difficult and a lower number of participants (8) were able to report levels. In addition a larger RSD was seen for the 5 compounds. All values were in reasonable agreement with the designed values.

Table 1. Results from the 2 standard solutions A and B. All levels in pg/ul.

	1	2	3	4	5	6	7	8	9	10	11	12	Mean	RSD	%RSD
2,3,7-TrBrDD	NA	NA	NA	NA	NA	ND	< 0.06	< 0.2	NA	NA	< 0.6	NA	**ND**	ND	ND
2,3,7,8-TeBrDD	36	15	10	10	14	10	14	10	9	9	9	10	**13**	8	59%
1,2,3,7,8-PeBrDD	234	51	50	78	84	51	61	50	50	62	29	55	**71**	53	74%
*1,2,3,4,7,8-HxBrDD***	NA	*485*	*510*	*334*	*989*	500	505	*490*	*513*	*382*	*540*	710	**542**	175	32%
*1,2,3,6,7,8-HxBrDD***	NA	*485*	*510*	*334*	*989*			*490*	*513*	*382*	*540*	710	**550**	195	35%
1,2,3,7,8,9-HxBrDD	NA	164	240	248	337	240	224	280	263	279	470	270	**274**	78	28%
2,3,7,8-TeBrDF	263	141	110	118	142	120	167	100	79	120	68	120	**129**	50	39%
1,2,3,7,8-PeBrDF	2105	533	510	558	548	470	531	530	528	567	540	550	**664**	455	68%
2,3,4,7,8-PeBrDF	2391	502	510	487	527	470	624	490	504	560	490	530	**674**	542	81%
1,2,3,4,7,8-HxBrDF	NA	353	400	NA	485	420	584	400	403	420	885	480	**483**	155	32%
1,2,3,4,6,7,8-HpBrDF	NA	NA	1000	NA	1423	930	1004	970	1050	1236	NA	NA	**1088**	178	16%
2-Br-7,8-ClDD	NA	9	NA	NA	36	9	15	9	NA	NA	8	NA	**14**	11	75%
2-Br-3,7,8-ClDD	4	9	10	NA	23	11	25	9	NA	NA	11	NA	**13**	7	57%
2,3-Br-7,8-ClDD	8	9	11	NA	89	52	11	9	NA	NA	15	NA	**26**	29	115%
2-Br-1,3,7,8-ClDD	41	52	NA	NA	21	10	68	53	NA	NA	36	NA	**40**	20	50%
2-Br-7,8-ClDF	NA	10	NA	NA	46	10	9	10	NA	NA	9	NA	**16**	15	98%
2-Br-6,7,8-ClDF	10	9	NA	NA	39	10	12	9	NA	NA	21	NA	**16**	11	71%

** Co-eluting isomers on DB-% like columns.

In Table 2 the results from the analysis of fly ash sample A is shown. The sample contained reasonable amounts of PBDD/DFs but relatively low levels of the mixed Br/Cl homologues. The results for both 2,3,7,8- TeBDD and 2,3,7,8-TeBDF are in reasonable agreement, but these results are still not as good as the results achieved with their chlorinated homologues in other studies. The

mixed Cl/Br dioxins and furans were present at a much lower level but were nevertheless detected by 7 of the participants. The agreement of the analysis of both 2-Br-3,7,8-ClDD and 2-Br-6,7,8-ClDF at the low level of 0.01-0.09 ng/g was reasonable good (66-68%). Problems quantifying the totals of the mixed compounds were reported due to large number of congeners and interferences at the different Br/Cl masses monitored. Fly ash B, results not shown here, contained very low levels of PBDD/DFs. The levels of mixed Br/Cl dioxins and furans were in the same low range as fly ash A. To obtain results from the limited amount of fly ash available (3-5g) was a real challenge in this case.

Table 2. Results Fly Ash A, all values in ng/g

	1	2	3	4	5	6	7	8	9	10	11	12	Mean	RSD	%RSD
2,3,7-TrBrDD	NA	NA	NA	NA	NA	0.11	0.069	0.17	NA	NA	0.062	NA	**0.10**	0.05	48%
2,3,7,8-TeBrDD	0.57	ND	0.035	0.14	0.27	0.21	< 0,095	0.13	0.1	0.05	0.30	0.21	**0.20**	0.16	77%
1,2,3,7,8-PeBrDD	1.14	0.98	0.60	0.33	0.34	0.48	0.624	0.58	0.1	0.63	0.19	0.33	**0.53**	0.30	58%
1,2,3,4,7,8-HxBrDD**	NA	1.01	1.8	0.88	0.69	1.1	0.727	1.2	0.71	0.89	1.1	1.9	**1.09**	0.41	38%
1,2,3,6,7,8-HxBrDD**	NA	1.01	1.8	0.88	0.69			1.2	0.71	0.89	1.1	1.9	**1.13**	0.44	39%
1,2,3,7,8,9-HxBrDD	NA	ND	0.49	0.56	0.15	0.69	0.471	0.85	0.46	0.73	1.2	0.52	**0.61**	0.28	46%
2,3,7,8-TeBrDF	7.13	3.40	0.91	2.02	2.39	5.0	1.32	0.8	1.3	0.49	1.9	3.3	**2.50**	1.96	78%
1,2,3,7,8-PeBrDF	12.21	1.27	1.0	1.78	2.11	3.9	1.23	2.8	3.3	1.95	2.1	2.8	**3.04**	3.02	99%
2,3,4,7,8-PeBrDF	22.52	4.35	3.4	4.75	2.01	3.7	3.26	3.3	2.4	4.69	2.6	3.5	**5.04**	5.57	111%
1,2,3,4,7,8-HxBrDF	NA	27.03	15	NA	21.6	30	29.2	29	8.6	33.6	NA	32	**25.1**	8.41	33%
1,2,3,6,7,8-HxBrDF	0.068	NA	NA	NA	NA	NA	NA	NA	4	NA	NA	NA	**2.03**	2.78	137%
1,2,3,7,8,9-HxBrDF	0.054	NA	NA	NA	NA	NA	< 0.10	NA	0.6	NA	NA	NA	**0.33**	0.39	118%
2,3,4,6,7,8-HxBrDF	0.090	NA	NA	NA	NA	NA	0.54	NA	3.5	NA	NA	NA	**1.38**	1.85	135%
1,2,3,4,6,7,8-HpBrDF	NA	NA	220	NA	191.9	150	117	170	84	161	NA	NA	**156**	45.4	29%
Total TriBrDD	NA	NA	NA	NA	NA	0.38	0.28	0.65	NA	NA	0.20	NA	**0.38**	0.20	52%
Total TeBrDD	ND	NA	1.2	NA	NA	1.5	1.39	1.8	1.25	NA	1.4	NA	**1.42**	0.21	15%
Total PeBrDD	10.6	NA	4.5	NA	NA	4.0	4.62	3.6	1.34	NA	1.8	NA	**4.35**	3.05	70%
Total HxBrDD	NA	NA	16	NA	NA	10	7.59	12	8.1	NA	27	NA	**13.4**	7.31	54%
Total TriBrDF	NA	NA	NA	NA	NA	29	23	17	NA	NA	19	NA	**22**	5	24%
Total TeBrDF	NA	NA	47	NA	NA	65	59.2	67	24.4	NA	25	NA	**48**	19	40%
Total PeBrDF	1141	NA	110	NA	NA	130	102	180	123	NA	130	NA	**274**	383	140%
Total HxBrDF	NA	NA	250	NA	NA	250	181	270	109	NA	320	NA	**230**	74	32%
2-Br-7,8-ClDD	NA	ND	NA	NA	0.022	N.D.	< 0.004	0.0061	NA	NA	< 0.002	NA	**0.01**	0.01	80%
2-Br-3,7,8-ClDD	ND	ND	ND	NA	0.018	N.D.	< 0.004	0.0066	NA	NA	< 0.01	NA	**0.01**	0.01	66%
2,3-Br-7,8-ClDD	0.007	ND	0.0036	NA	0.28	N.D.	< 0.004	0.0059	NA	NA	0.017	NA	**0.06**	0.12	194%
2-Br-1,3,7,8-ClDD	0.070	ND	NA	NA	NA	N.D.	< 0.004	<0.0002	NA	NA	< 0.02	NA	**0.07**	NA	NA
2-Br-7,8-ClDF	NA	ND	NA	NA	0.28	0.01	0.033	0.038	NA	NA	0.033	NA	**0.08**	0.11	143%
2-Br-6,7,8-ClDF	0.098	0.114	NA	NA	0.19	0.036	0.028	0.068	NA	NA	< 0.01	NA	**0.09**	0.06	68%
Total TriBrClDD	NA	NA	ND	NA	NA	N.D.	4.79	0.15	NA	NA	< 0.3	NA	**2.47**	3.28	133%
Total TeBrClDD	0.46	NA	ND	NA	NA	0.032	NA	0.096	NA	NA	0.24	NA	**0.21**	0.19	92%
Total PeBrClDD	0.29	NA	0.12	NA	NA	0.091	NA	0.10	NA	NA	0.251	NA	**0.17**	0.09	54%
Total TriBrClDF	NA	NA	0.18	NA	NA	0.34	NA	1.7	NA	NA	3.8	NA	**1.51**	1.68	111%
Total TeBrClDF	2.19	NA	0.32	NA	NA	0.45	NA	3.4	NA	NA	10.3	NA	**3.33**	4.10	123%
Total PeBrClDF	0.16	NA	0.89	NA	NA	0.38	NA	6.6	NA	NA	7.59	NA	**3.12**	3.65	117%

** Co-eluting isomers on DB-% like columns.

Conclusion

Of the participating laboratories 48% were able to report the PBDD/DF or the mixed Br/ClDD/DFs on both the fly ash samples and the two standard solutions. The results for the standard solutions were good for many congeners, the fly ash samples were a bigger challenge due to the limited

amount of material available for analysis. A follow up study with more material or material with higher concentrations of the target compounds would be more feasible.

Acknowledgement

Brock Chittim of Wellington Laboratories is acknowledged for making the mixed Cl/Br dioxins and furans available. Ben Priest, Cambridge Isotope Laboratories is acknowledged for making the PBDD/DF mix available, Dr. Roland Weber is acknowledged for help with fly ash sample B and Dr. Gunilla Söderström, Umeå University is acknowledged for making fly ash A available.

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