Quality assurance and quality control (QA/QC) for PBDD/DF analysis through international interlaboratory comparison studies.

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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.[1] Further evidence of the formation of PBDD/DFs from BDEs was presented by Thoma[2] and Luijk[3] and from Tetrabromobisphenol-A (TBBP-A) by Thoma[4] and Dumler[5]. 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[6]. 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[7,8]. 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)[9,10] 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[11]. 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[12] et al. Several methods for brominated dioxins, adapted from the analysis of chlorinated dioxins, have been published in the past[13,14,15]. But recently there seem to be a new interest for the analysis of PBDD/DF[16,17]. 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 results of two international intercalibration studies on the analysis of PBDD/DFs.

Methods and materials

In 2004 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. 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.

In 2005 one soil sample and four standard solutions were sent to 13 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 2 using their own extraction and clean up procedures and use their own standard solutions for quantification. Soil sample C consisted of a soil sample from open burning of electronic waste and was made available by Dr. Markus Zennegg, EMPA, Dübendorf, Switzerland. Standard solution C contained PBDD/DFs at a concentration of 10 pg/ul, standard solution D contained the same compounds at a concentration pf 100 pg/ul. Both solutions are a dilution of mix EDF-5059 acquired from Cambridge Isotope Laboratories[1]. Solution other solution was a mixture of mixed Cl/Br dioxins and furans at a concentration of 10-50 pg/ul donated by Wellington Laboratories[2].

All 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.

Results

Of the total of 25 participants for the 2004 study 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

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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 form the 2004 study. 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.

Nine of the participants reported results for PBDD/DFs in the soil sample in the 2005 study. The soil sample contained pg/g levels of the target compounds. On an individual congener basis the RSDs taking all entries into account ranged from 18% to 216 %. Total PBDD/DF (tetra to hexa) were reported by 6 participants resulting in a very reasonable RSDs (16%-99%). Standard C and D contained 6 PBDDs and 5 PBDFs at concentrations of 10 pg/ul (Standard C) and 100 pg/ul (Standard D). The mean of the reported values were close to the design value although somewhat lower for the PBDFs for both standard C (7.3-9.3 pg/ul) and Standard D (84-100 pg/ul). The RSDs for the individual isomers were good varying from 13% to 42% for both the high level and the low level standard.

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 in 2004. The report rates for the 2nd round of the PBDD/DF and mixed Br/Cl dioxins and furans study in 2005 were somewhat lower. From the total of 13 participants 9 laboratories were able to report results for the PBDD/DF and 7 for the mixed compounds. For the real life soil sample 10 participants reported data back to us before the deadline.

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