BSEF/QUASIMEME INTERLABORATORY STUDY ON BROMINATED FLAME RETARDANTS

Jacob de Boer[1], David E. Wells[2] and Koidu Norén[3]

[1]Netherlands Institute for Fisheries Research, P.O. Box 68, 1970 AB IJmuiden, The Netherlands
[2]FRS Marine Laboratory, P.O. Box 101, AB11 9DB Aberdeen, UK
[3]Karolinska Institutet, Stockholm, S-17177 Sweden

Introduction

Polybrominated diphenyl ethers (PBDEs) have been produced as flame retardants since the early 1970s. They have been found in the aquatic environment since the late 1970s[1,2]. Following their discovery in sperm whales from deeper Atlantic waters[3] and in human milk[4], many laboratories have started to work on PBDE analysis in the environment. A first international interlaboratory study on the analysis of PBDEs was conducted in 1999-2000[5]. The results showed that the 18 participating laboratories were able to produce comparable results for BDE 47 in various matrices, but there were significant analytical difficulties for other BDEs, in particular for the BDEs 99 and 209. Meanwhile the presence of other brominated flame retardants (BFRs), such as hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A) and the dimethyl derivative of TBBP-A (MeTBBP-A) in the environment have been reported. Therefore, it appeared to be useful to organize a new interlaboratory study to include these new flame retardants, along with a further study on the PBDEs. This study was conducted between 1 November 2001 and 15 March 2002.

Methods and Materials

Seven test materials were prepared. One ampouled tissue, lake trout homogenate, provided by Cambridge Isotope Laboratories (CIL) (coded BT1), which had been certified previously for PCBs. One sterilised canned shellfish sample: mussels (*Mytilus edulis*) from the English south coast, sampled by the Centre of Environment, Fisheries and Agriculture Science (CEFAS), Burnham on Crouch, UK (coded BT2), one human milk test material from Sweden (coded BT3), one freeze-dried sediment from the Western Scheldt, The Netherlands (coded MS3), and one cleaned extract from the same sediment (coded MS4). In addition, two solutions, one containing the BDEs 28(2,4,4'-tri BDE), 47 (2,4,2',4'-tetra BDE), 99 (2,4,5,2',4'-penta BDE), 100 (2,4,6,2',4'-penta BDE), 153 (2,4,5,2',4',5'-hexa BDE), 154 (2,4,5,2',4',6'-hexa BDE), and 183 (2,3,4,6,2',4',5'-heptaBDE) (coded SS1), and one containing BDE209 (decaBDE), HBCD, TBBP-A, and Me-TBBP-A in toluene (coded SS2) in undisclosed concentrations were prepared and ampouled. The standards were a gift from CIL. All biological samples were tested for homogeneity. No significant inhomogeneity was observed, and all materials were suitable for the laboratory studies.

All standards were made from 99.9 % pure crystals, and provided as solutions. The uncertainty of the concentration of each compound was within 10 %. The objective of the study was to determine the between-laboratory variance. Therefore only one result per determinand per sample was requested. The participants were asked to use their own analytical method. Advice was given on avoiding specific errors during the analysis. At least two GC columns of different polarity were recommended to check for co-elution. In each case, the best result, as judged by the participant, was reported. The reported

results were corrected for recovery. In addition participants sent chromatograms (one of each sample, and one of each standard solution from each GC columns used) and their method description to the co-ordinator.

The statistical evaluation of this study was carried out by the QUASIMEME office (FRS Marine Laboratory, Aberdeen, UK). The evaluation was made using the new method of Cofino[5,6] based on quantum statistics. The results were compared with the robust statistical analysis, which has been used before in the QUASIMEME programme[7]. Z-scores were calculated for each contaminant in all matrices.

Results and Discussion

Results of 36 laboratories from 13 different countries were received. An overview of the results of this study is given in Table 1. Only 13 laboratories were able to produce results for HBCD in the solution SS2, whereas only 7 laboratories produced results for TBBP-A. Even fewer values were reported in the other materials: 6 and 3, respectively. Many laboratories are establishing methods for these 'new' flame retardants, and considered that the available methods were not fully optimised to participate in this study. However, the PBDE results show a good improvement since the first interlaboratory study (ILS)[5].

BDE28

Compared with the first ILS[5], a substantial increase is observed in the number of laboratories analysing BDE28, from 8 to 12-29 in this round. The CVs obtained are acceptable for SS1 (16 %), BT1, BT2 and MS1 (28-32 %), particularly for such low concentrations. A lower CV would have been expected for the clean sediment extract, MS2, (CV 51 %.) The BDE28 concentration in human milk was very low, which was probably the major reason for the large CV (115 %).

BDE47

Twenty to 36 laboratories have analysed BDE47. The results compare were well with those from the first study[5]. Most participating laboratories are able to determine BDE 47 with good agreement in both biota and sediments (15-23%). Even in human milk, an acceptable CV of 25 % was obtained.

BDE99

Compared with the first study[5], improvement was obtained for BDE99. In the first study the CV values ranged from 25 to 35 % at a concentration level of 3-101 ng/g in biota and sediment. In the current study the CV values ranged from 22-35 % at a concentration level of 1-13 ng/g. However, the obtained probability factor (p value) in this study was 57 %, while it was 36 % in the first study[5]. This shows that a larger number of laboratories were in agreement. The CV in the human milk was larger (69 %, n=20), and was most likely caused by the low concentration (0.02 ng/g).

BDE100

Good results were also obtained for BDE100. The range of CV values for biota and sediments (24-37 %, concentrations: 0.4-2.7 ng/g) is comparable with the range found in the first ILS (17-27 %, concentrations 0.15-98 ng/g). Again, the low concentration BDE100 of human milk resulted in a CV of 53 % (n=12).

BDEs 153 and 154

The BDE 153 and 154 results are comparable with those of the first study (CVs: 31-55 % for biota and sediments). Slightly higher CV values were obtained (48-76 %) for the human milk.

BDE183

BDE183 was not included in the first ILS. The results obtained show that laboratories are still developing methods for this BDE (CVs 30-82 % for biota and sediments, 98 % for human milk).

Table 1. Summary of results of the BSEF/QUASIMEME interlaboratory study on BFRs

Material	BDE28			BDE47			BDE99		
	Mean	CV%	n	Mean	CV%	n	Mean	CV%	n
SS1	207 (221)	16	29	449 (436)	16	36	552 (581)	26	36
BT1	0.42	32	19	9.1	15	29	2.2	35	30
BT2	0.08	28	19	1.6	22	28	1.0	31	27
BT3	0..01	115	12	0.06	25	20	0.02	69	18
MS1	0.54	31	18	9.1	23	23	13	22	23
MS2	0.19	51	19	3.5	25	27	20	23	27
Material	BDE100			BDE153			BDE154		
	Mean	CV%	n	Mean	CV%	n	Mean	CV%	n
SS1	142 (146)	19	35	152 (146)	33	36	181 (182)	22	34
BT1	1.6	31	28	2.2	31	30	2.7	41	29
BT2	0.37	24	26	0.06	55	24	0.06	38	22
BT3	0.01	53	12	0.02	48	13	0.003	76	10
MS1	2.7	37	23	1.8	31	23	1.5	32	23
MS2	4.3	35	27	2.8	53	27	2.2	46	25
Material	BDE183			BDE209			HBCD		
	Mean	CV%	n	Mean	CV%	n	Mean	CV%	n
SS1	97 (109)	17	30						
SS2				828 (780)	40	16	358 (384)	29	13
BT1	0.16	30	19	0.31	165	8	2.2	26	6
BT2	0.03	61	13	0.56	256	6	-	-	2
BT3	0.01	98	7	0.35	120	5	-	-	2
MS1	0.47	82	20	923	65	13	76	123	6
MS2	0.79	56	14	1871	27	15	141	15	9
Material	TBBP-A			MeTBBP-A					
	Mean	CV%	n	Mean	CV%	n			
SS2	569 (465)	47	7	396 (214)	12	6			
BT1	-	-	0	-	-	2			
BT2	0.90	190	3	-	-	0			
BT3	-	-	1	-	-	1			
MS1	0.65	173	3	-	-	1			
MS2	5.7	104	3	-	-	0			

Mean in ng/g (target values in brackets), calculated with Cofino statistics; CV%: coefficient of variation according to Cofino statistics in %; n: number of observations.

The result of the clean sediment extract (CV 56 % compared to 82 % for MS1) indicates that some of the analytical problems may occur during extraction and clean-up.

BDE209

The laboratories still clearly disagree on the BDE209 determination in biota. The concentrations of BDE209 in fish and shellfish, and in human milk are low, but the critical question; "is BDE209 present in biota or not", cannot be answered at present. The performance of the laboratories for the sediment sample MS1 (CV 65 %) was even less good than that in the first study (CVs 51-54 %), even though the concentration in MS1 was considerably higher (923 ng/g, and 2.9-64.5 in the first ILS). The clean sediment extract result (CV 27 %) shows that most problems appear to occur during extraction and clean-up (e.g. use of suitable solvents, exposure to light). The GC conditions (e.g. use of short columns, limited exposure to high temperatures) are apparently under control.

HBCD

Six laboratories obtained an acceptable result for BT1 (CV 26 %), and 9 laboratories produced good results for MS2 (CV 15 %). The solution SS1 did not cause excessive difficulties for the 13 laboratories (CV 29 %). The clean sediment extract results shows that the problems with HBCD occurred during extraction and clean-up procedures. Although isomerization of the three HBCD isomers occurs in the GC, the main sources of error appear to be in the extraction and clean-up.

TBBP-A and MeTBBP-A

Obviously, this interlaboratory study was premature for TBBP-A and MeTBBP-A. The comparability of the few results for TBBP-A, is poor, even for the unknown solution. Also, the means deviate from the target values. The problem of the lack a commercially available MeTBBP-A standard has now been resolved. However, that may have prevented laboratories from submitting results.

Summarizing, progress has been made for BDE99 and some other BDEs. The determination of the BDEs 183 and 209 is still not under control in most laboratories. Human milk is a difficult material for many laboratories due to the low BDE concentrations. A few laboratories could produce comparable results for HBCD in lake trout, but most participants require more time to optimise their methods for HBCD, TBBP-A and Me-TBBP-A.

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