The quality of PBDE analysis in food - Results from an interlaboratory comparison study

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Introduction

In order to ensure consumer protection and reduce human exposure to chlorinated and brominated persistent organic pollutants through food consumption,many countries request frequent monitoring of the presence of these pollutants in food and feed. There is therefore a large demand for chemical laboratories that are able to monitor these contaminants at low levels in food and feed. It is usually required by the authorities that laboratories performing such measurements are accredited according to ISO standards and prove their competence by successful participation in interlaboratory studies[1].

Therefore, the Department of Analytical Chemistry, Division of Environmental Medicine, Norwegian Institute of Public Health in Oslo, Norway, started in 2000 to organise annually world-wide interlaboratory comparison studies on PCDDs/PCDFs in different foodstuffs[2]. The objectives of these exercises were a) to offer a quality assurance instrument for the participating laboratories, b) to assess the between laboratory reproducibility and c) to assess the readiness of expert laboratories world-wide to determine levels of chlorinated organic pollutants in regular foodstuffs.

In the fifth study organised in 2004, the participants were for the first time asked to voluntarily determine the concentrations of polybrominated diphenyl ethers (PBDEs) a new class of persistent organic pollutants. In this paper we present the results of this interlaboratory comparison study with respect to PBDEs in food[3].

Materials and methods

The 2004 study was performed on sample homogenates of chicken meat, trout filet and palm oil. In addition, four standard solutions were provided containing known concentrations of a) PCDDs/ PCDFs, b) non-ortho PCBs, c) mono-ortho PCBs, and d) PBDEs. The testing materials were sent to 77 laboratories in February 2004, and results were returned from 73 laboratories in 24 different countries by the deadline in May. Most laboratories analysed all of the three food items.

As in the previous rounds of this interlaboratory comparison, the test material chosen represented naturally contaminated food samples. The analytes to be determined by each participating laboratory were all seventeen 2,3,7,8-substituted PCDDs and PCDFs, the four non-ortho substituted PCBs #77, 81, 126 and 169, and the eight mono-ortho substituted PCBs #105, 114, 118, 123, 156, 157, 167, 189. In addition, laboratories were asked to determine on a voluntary basis eight polybrominated diphenyl ethers, namely PBDEs #28, #47, #99, #100, #153; #154, #183 and #209. Analysis should be performed using the laboratory's own methods for sample preparation and instrumental analysis, their own standards and quantification procedures, and their own method for lipid determination.

The test materials consisted of three natural products not fortified with standards. Contaminated chicken meat from the “Belgian crisis” obtained from the Chemical and Veterinary Control Agency, Freiburg, Germany, was mixed with background contaminated chicken meat purchased in Oslo. Lake trout from the Norwegian Lake Mjøsa was obtained form the Norwegian Institute of Water Research. Palm oil and the distillate from the deodorizing of palm oil were obtained from FEDIOL, the European Crushers’ and Oil Processors’ Federation. The two oil matrices were mixed 1:1.

The consensus concentration for each analyte in the three food samples was determined as follows: Non-detected congeners were removed from the data set. The median of all reported concentrations for each analyte was calculated. All values above two times the median were then removed from the calculation. The consensus median and consensus mean plus standard deviation were calculated from the remaining data.

Z-scores for were calculated for each laboratory according to the following equation:

$z = (x – X)/s$

where x = reported value; X = assigned value (consensus); s = target value for standard deviation. A s of 20% of the consensus was used, i.e. z-scores between +1 and -1 reflect a deviation of ± 20% from the consensus value.

Results and Discussion

Twenty-one laboratories reported concentrations for the seven tri- to hepta-BDEs. No consensus value was calculated for BDE-209 as too few laboratories had reported this congener. As can be seen in table 1, there is a large difference in the level of the PBDE congeners for the three matrixes. The sum of tri- to penta-BDE were 54 pg/g fresh weight, 92 pg/g fresh weight and 240 ng/g fresh weight for chicken, palm oil and trout, respectively. The RSD for concentrations on fresh weight basis was on average 46% and 40% in chicken and trout, respectively, but much higher in the palm oil (62%).

Figure 1 shows the Z-score for the sum of tri- to hepta-BDEs for chicken, trout and palm oil. As many as 61% of the laboratories obtained Z-scores within ±1 (± 20%) for the heavily contaminated trout, while just one laboratory (5%) achieved results within ± 20% of the consensus value for the low contaminated palm oil. For chicken, five laboratories (24%) ended with Z-score within ±1.

Similar as for the determination of PCDDs/PCDFs, there is a great variation in the methods used for cleanup of samples prior to PBDE analysis. For the gas chromatographic separation the majority of laboratories used splitless injection and a 5% phenyl-dimethylpolysiloxane stationary phase. The column lengths chosen were often shorter than those used for PCDDs/PCDFs, especially for the low volatile BDE-209. Two-thirds of the laboratories used high-resolution MS for detection and only two laboratories used low-resolution MS in the electron capture negative ion mode.

To summarise briefly: for the highly contaminated trout sample, the performance of the laboratories with respect to PBDEs was acceptable, but compared to the well established methods for PCDDs/PCDFs, where 84% of the laboratories achieved Z-scores within ±1, there is still room for improvements. A number of laboratories had difficulties when analysing background contaminated food samples, probably due to insufficient limits of detection or blank contamination.

Table 1. Statistical data from the calculation of consensus values for the eight PBDEs.

		Consensus median pg/g fw	Consensus mean pg/g fw	RSD %	Number in consensus	Number of NDs	Number of outliers
BDE-28	*Chicken*	0.62	0.66	59	10	6	6
	Trout	641	607	36	19	0	0
	Palm oil	4.7	4.6	59	10	6	5
BDE-47	*Chicken*	17	23	59	15	1	6
	Trout	95220	90596	38	21	0	0
	Palm oil	17	22	72	9	4	8
BDE-99	*Chicken*	20	23	51	18	1	3
	Trout	80681	78606	40	20	0	1
	Palm oil	33	38	67	12	4	6
BDE-100	*Chicken*	5.9	6.7	55	15	1	6
	Trout	40958	39220	38	21	0	0
	Palm oil	16	18	70	8	9	6
BDE-153	*Chicken*	4.7	5.1	39	19	1	1
	Trout	10200	9900	36	21	0	0
	Palm oil	9.5	8.3	58	6	10	7
BDE-154	*Chicken*	3.1	3.1	38	16	2	3
	Trout	12011	12005	41	21	0	0
	Palm oil	5.7	6.3	68	7	9	7
BDE-183	*Chicken*	2.7	2.9	30	12	6	4
	Trout	14	16	40	15	2	2
	Palm oil	5.6	7.1	90	7	12	7
BDE-209*	*Chicken*	64	73	37	4	3	2
	Trout	63	56	59	4	1	3
	Palm oil	390	390		1	5	2

Fw: fresh weight

ND: not detected

* Indicative value due to few reported values

RSD of the values used in calculation of consensus

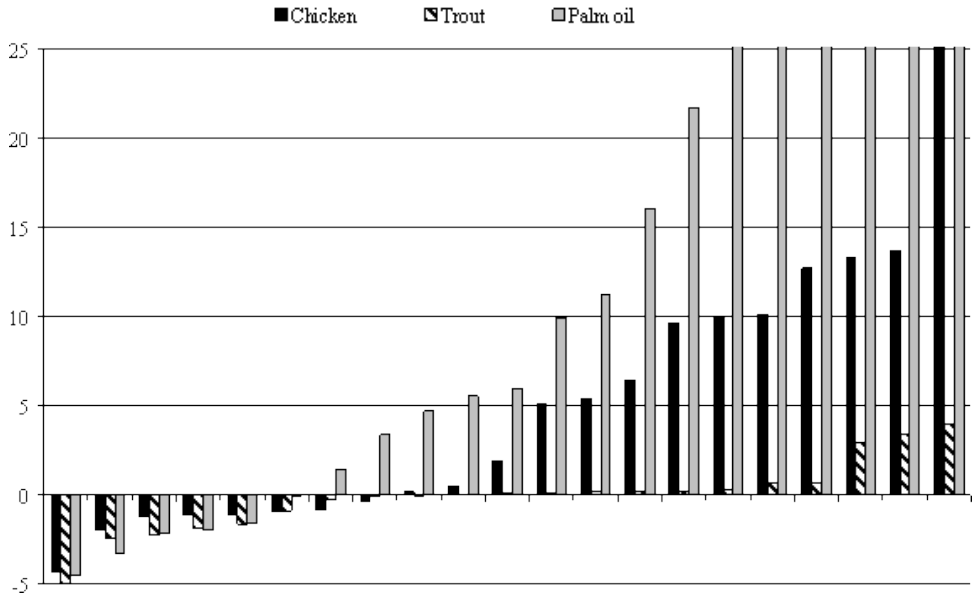

Figure 1: Z-score for the sum of tri- to hepta-BDEs for chicken, trout and palm oil, using as of 20% of the consensus.

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