A Small Scale Intercalibration Study on Organobromine Compounds in Japan: Results on Brominated Dioxins, Mixed Halogenated Dioxins and Brominated Flame Retardants

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Introduction

Recently, environmental problems relating to brominated flame retardants (BFRs) have become a matter of great concern due to their potential toxic risk on human and wildlife[1] and recent increase in levels of polybrominated diphenyl ethers (PBDEs)[2-4]. Many laboratories have started work on PBDEs and other BFRs such as tetrabromo-bisphenol A (TBBPA), tribromophenol (TBP) and hexabromocyclododecane (HBCD). International intercalibration studies on the analysis of PBDEs have been conducted[5-7]. The results of intercalibration studies indicated that determination of some higher brominated diphenyl ethers such as BDEs 183 and 209 was not under the control in most laboratories although these compounds are major in commercial Octa- and Deca- BDE products. Moreover, results on BFRs other than PBDEs are very much limited[7].

Another concern has been related to the thermal breakdown products of BFRs such as polybrominated and mixed brominated/chlorinated dibenzo-p-dioxins and dibenzofurans (PBDDs/DFs and mixed PXDDs/DFs). Considerable levels (ppm or even higher) of PBDDs/DFs were detected in waste television cabinets and other flame-retarded plastics[2]. Based on 'the Law Concerning Special Measures against Dioxins (applied since January 2000)', the Ministry of the Environment, Japan is working to promote studies on brominated dioxins, and conducted a pilot survey in the environment[8]. PBDDs/DFs and monobromo-polychloro dibenzo-p-dioxins and dibenzofurans (MoBPCDDs/DFs) were found in various environmental media with BFRs[2,8]. Although commercially available standards for these compounds are still limited, development of a good QA/QC system has become imperative.

To evaluate the accuracy and reliability in the analysis for organobromine compounds, an intercalibration study in which 10 laboratories in Japan participated was initiated since April, 2003. In this presentation, the results on PBDD/DFs, MoBPCDDs/DFs and PBDEs, in 'Mixed Standard Solutions' and 'Air-Dried Sediment' are reported.

Methods and Materials

Four groups of organobromine compounds were selected as target compounds; 1) PBDDs/DFs 2) MoBPCDDs/DFs, 3) PBDEs, and 4) TBBPA, dimethyl-TBBPA, TBP, tribromoanisole (TBA) and HBCD. Analysis of compounds grouped as 4) are yet to be completed, and the result will be

presented in future. To compare with organobromine target compounds, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/DFs) and coplanar PCBs (Co-PCBs) were also required to determine in some specific samples (i.e. 'Air-Dried Sediment' and 'Animal Fat' described below).

Four 'InterLab Samples' were designed in this study; 1) Mixed Standard Solutions (4 kinds of mixed solutions for PBDEs, PBDDs/DFs, PXDDs/DFs and other BFRs), 2) Air-Dried Sediment, 3) Waste TV Backplate, and 4) Animal Fat (homogenized blubber of finless porpoises). Among these samples, 1) and 2) were prepared and distributed to all the participants. Mixed Standard Solutions were made from commercial standard solutions purchased from CIL and Wellington Laboratories. Uncertainty of the concentrations of each compound was within 10% (as shown in data sheets provided with commercial solutions). The sample 'Air-Dried Sediment' was made from approx. 60 kg wet sediment collected from Osaka Bay followed by the method used for preparing NIES certified reference material[9]. Homogeneity of the sample was tested by analyzing major elements. No significant inhomogeneity was observed. The samples 'Waste TV Backplate' and 'Animal Fat' are being prepared and distributed.

The participants were asked to analyze the samples using their own analytical method(s). Triplicate results per determinand per samples were requested to evaluate variations/errors within laboratory. All the participants sent the description of their method and representative chromatograms along with results for each compound and sample to the coordinator. Guidelines for avoiding specific errors during analysis were provided to all the participants by the coordinator, for example, 1) pay attention to 'cut-off UV light' during the analysis, 2) use proper standards in particular for the analysis for higher brominated compounds, 3) check well the linearity of the calibration curves, and 4) follow the guidelines on QA/QC for the dioxin analysis suggested by JIS and the Ministry of the Environment, Japan, etc.

Results and Discussion

All participants that reported results used HRGC-HRMS(EI) or HRGC- LRMS(EI) and isotope-labeled standards for the determination of target compounds. The triplicate results from each laboratory were averaged, then the average concentrations and relative standard deviations (RSDs) between the laboratories were calculated and summarized for each compounds in 'Mixed Standard Solutions' (Table 1) and 'Air-Dried Sediment' (Table 2 and 3).

The results on 'Mixed Standard Solutions' revealed good agreement in both averaged concentrations reported by the participants and designed values for almost all the compounds analyzed. The RSDs for PBDDs/DFs, MoBPCDDs/DFs and PBDEs ranged from 4-20%, 8-27%, and 9-24%, respectively. The results for PBDEs were well compared with those reported in earlier international intercalibration studies[5-7]. This reflects general improvement in analytical methods and increasing number of authentic standards for organobromine compounds (e.g., $^{13}C_{12}$-labeled DeBDE standard

Table 1. Summary of results on 'Mixed Standard Solutions'

Compounds/Isomer	*n*	Average	*Design Value*	%RSD
PBDDs/DFs				
2,3,7,8-TeBDD	8	4.9	*5*	4
1,2,3,7,8-PeBDD	8	10	*10*	13
1,2,3,4,7,8-HxBDD	8	25	*20*	20
OBDD	7	48	*50*	14
2,3,7,8-TeBDF	8	9.8	*10*	10
2,3,4,7,8-PeBDF	8	5.9	*5*	16
1,2,3,4,7,8-HxBDF	8	27	*25*	9
1,2,3,4,6,7,8-HpBDF	7	50	*50*	11
MoBPCDDs/DFs				
2-MoB-3,7,8-TrCDD	7	4.7	*5*	12
1-MoB-2,3,7,8-TeCDD	7	21	*20*	8
2-MoB-3,6,7,8,9-PeCDD	7	15	*15*	14
1-MoB-2,3,6,7,8,9-HxCDD	7	21	*20*	27
1-MoB-2,3,4,6,7,8,9-HpCDD	7	30	*30*	24
3-MoB-2,7,8-TrCDF	7	9.7	*10*	17
1-MoB-2,3,7,8-TeCDF	7	25	*25*	17
PBDEs				
2,4,4'-TrBDE (#28)	7	10	*10*	10
2,2',4,4'-TeBDE (#47)	7	31	*30*	9
2,2',4,4',5-PeBDE (#99)	7	20	*20*	24
2,2',4,4',6-PeBDE (#100)	7	25	*25*	14
2,2',4,4',5,5'-HxBDE (#153)	7	17	*20*	21
2,2',4,4',5,6'-HxBDE (#154)	7	26	*25*	14
2,2',3,4,4',5',6-HpBDE (#183)	7	31	*30*	9
DeBDE (#209)	7	50	*50*	10

Average in ng/mL; *n* : number of data; %RSD: relative standard deviation in %.

is available, today). In particular the analysis for higher brominated compounds (e.g., OBDD), an advice was given to participants, to optimize the calibration curves to fit into the range of concentrations found in samples, because variation of relative response factors (RRFs) for higher brominated compounds was noted in some cases (Table 4).

Table 2. Summary of results on PBDDs/DFs, MoBPCDDs/DFs and PBDEs in 'Air-Dried Sediment'

Compounds/Isomer	*n*	Average	%RSD	Compounds/Homolog	*n*	Average	%RSD
PBDDs/DFs				**PBDDs/DFs**			
2,3,7,8-TeBDD	7	--	--	TeBDDs	7	14	24
1,2,3,7,8-PeBDD	7	--	--	PeBDDs	7	--	--
1,2,3,4,7,8-/1,2,3,6,7,8-HxBDD	7	--	--	HxBDDs	7	--	--
1,2,3,7,8,9-HxBDD	7	--	--	HpBDDs	6	--	--
OBDD	6	--	--	OBDD	6	--	--
2,3,7,8-TeBDF	7	--	--	TeBDFs	7	23	22
1,2,3,7,8-PeBDF	7	--	--	PeBDFs	7	30	35
2,3,4,7,8-PeBDF	7	--	--	HxBDFs	7	51	8
1,2,3,4,7,8-HxBDF	7	--	--	HpBDFs	6	49	36
1,2,3,4,6,7,8-HpBDF	6	51	38	OBDF	6	--	--
MoBPCDDs/DFs				**MoBPCDDs/DFs**			
2-MoB-3,7,8-TrCDD	7	--	--	MoB-TrCDDs	7	5.6	30
1-MoB-2,3,7,8-TeCDD	7	--	--	MoB-TeCDDs	7	7.3	18
2-MoB-3,6,7,8,9-PeCDD	7	--	--	MoB-PeCDDs	7	12	31
1-MoB-2,3,6,7,8,9-HxCDD	7	3.0	30	MoB-HxCDDs	7	11	32
1-MoB-2,3,4,6,7,8,9-HpCDD	7	33	17	MoB-HpCDD	7	50	17
3-MoB-2,7,8-TrCDF	7	--	--	MoB-TrCDFs	7	--	--
1-MoB-2,3,7,8-TeCDF	7	--	--	MoB-TeCDFs	7	--	--
				MoB-PeCDFs	6	4.1	36
				MoB-HxCDFs	6	6.0	23
				MoB-HpCDF	6	10	27
PBDEs				**PBDEs**			
2,4,4'-TrBDE (#28)	6	36	16	TrBDEs	5	220	36
2,2',4,4'-TeBDE (#47)	6	180	19	TeBDEs	5	600	10
2,2',4,4',5-PeBDE (#99)	6	170	25	PeBDEs	5	390	18
2,2',4,4',6-PeBDE (#100)	6	29	38	HxBDEs	5	600	33
2,2',4,4',5,5'-HxBDE (#153)	6	380	20	HpBDEs	5	2100	28
2,2',4,4',5,6'-HxBDE (#154)	6	69	15	OBDEs	5	2100	24
2,2',3,4,4',5',6-HpBDE (#183)	6	2000	25	NoBDEs	5	6200	17
DeBDE (#209)	6	170000	10	DeBDE	6	170000	10

Average in pg/g; *n*: number of data; %RSD: relative standard deviation in %.
--: Less number of results reported more than detection/quantification limits to caluclate average and %RSD.

Table 3. Summary of results on PCDDs/DFs and Co-PCBs in 'Air-Dried Sediment'

Compounds/Isomer	*n*	Average	%RSD	Compounds/Homolog	*n*	Average	%RSD
PCDDs/DFs				**PCDDs/DFs**			
2,3,7,8-TeCDD	7	0.80	8	TeCDDs	7	680	8
1,2,3,7,8-PeCDD	7	5	12	PeCDDs	7	170	9
1,2,3,4,7,8-HxCDD	7	8	19	HxCDDs	7	230	23
1,2,3,6,7,8-HxCDD	7	16	17	HpCDDs	7	680	6
1,2,3,7,8,9-HxCDD	7	14	15	OCDD	7	5100	9
1,2,3,4,6,7,8-HpCDD	7	320	6	TeCDFs	7	160	13
OCDD	7	5100	9	PeCDFs	7	160	12
2,3,7,8-TeCDF	7	4.6	12	HxCDFs	7	220	18
1,2,3,7,8-PeCDF	7	11	13	HpCDFs	7	300	7
2,3,4,7,8-PeCDF	7	9.8	5	OCDF	7	270	9
1,2,3,4,7,8-HxCDF	7	19	19				
1,2,3,6,7,8-HxCDF	7	16	18				
1,2,3,7,8,9-HxCDF	7	1.5	17				
2,3,4,6,7,8-HxCDF	7	22	15				
1,2,3,4,6,7,8-HpCDF	7	130	11				
1,2,3,4,7,8,9-HpCDF	7	18	7				
OCDF	7	270	9				
Co-PCBs							
3,4,4',5-TeCB(#81)	7	8.6	24				
3,3',4,4'-TeCB(#77)	7	390	11				
3,3',4,4',5-PeCB(#126)	7	31	9				
3,3',4,4',5,5'-HxCB(#169)	7	14	7				
2',3,4,4',5-PeCB(#123)	7	36	16				
2,3',4,4',5-PeCB(#118)	7	1700	10				
2,3,3',4,4'-PeCB(#105)	7	650	16				
2,3,4,4',5-PeCB(#114)	7	44	20				
2,3',4,4',5,5'-HxCB(#167)	7	88	6				
2,3,3',4,4',5-HxCB(#156)	7	220	12				
2,3,3',4,4',5'-HxCB(#157)	7	59	9				
2,3,3',4,4',5,5'-HpCB(#189)	7	19	13				

Average in pg/g; *n*: number of data; %RSD: relative standard deviation in %.
--: Less number of results reported more than detection/quantification limits to caluclate average and %RSD.

The results on 'Air-Dried Sediment' are also reasonable with RSDs from 8-38% for PBDDs/DFs, 17-36% for MoBPCDDs/DFs, 10-38% for PBDEs, 5-23% for PCDDs/DFs and 6-24% for Co-PCBs, although several isomers/homologues of PBDDs/DFs and MoBPCDDs/DFs were below detection limits. Despite limited number of standards available, homologs of organobromine compounds could be quantified as well as isomers determined by their authentic standards. Compared with 'Mix Standard Solutions', the RSDs for most of organobromine compounds were relatively high in the sediment sample, indicating possible errors in pretreatment of samples and/or interference by impurities in the GC-MS analysis. Particularly, higher variation of the concentrations of PeBDE (#100) than the other PBDE isomers would be due to its poor separation from other isomer peaks, which was often observed in the chromatograms provided (Figure 1). In spite of this, results for PBDEs reported in this study were well compared with those reported in earlier studies on sediment samples[5,6]. This again suggests progress in the quality of PBDE analysis. Compared with the results for PCDDs/DFs and Co-PCBs, the RSDs for most of organobromine compounds were high, indicating an insufficient QA/QC procedure for the analysis of organobromine compounds compared with common chlorinated dioxins.

Table 4 An example of concentrations of PBDDs in standard solutions for estimating calibration curves and relative response factors (RRFs)

	Concentraions (ng/ml) in standard solutions				
1,2,3,7,8-PeBDD (Native)	0.5	2	10	50	200
$^{13}C_{12}$-1,2,3,7,8-PeBDD (Surrogate)	50	50	50	50	50
	RRFs estimated at the concentraions above				
RRFs for 1,2,3,7,8-PeBDD	**0.941**	**0.904**	**0.997**	**0.990**	**0.964**

	Concentraions (ng/ml) in standard solutions				
OBDD (Native)	5	20	100	500	2000
$^{13}C_{12}$-1,2,3,4,7,8-HxBDD (Surrogate)	250	250	250	250	250
	RRFs estimated at the concentraions above				
RRFs for OBDD	**0.168**	**0.169**	**0.219**	**0.257**	**0.317**

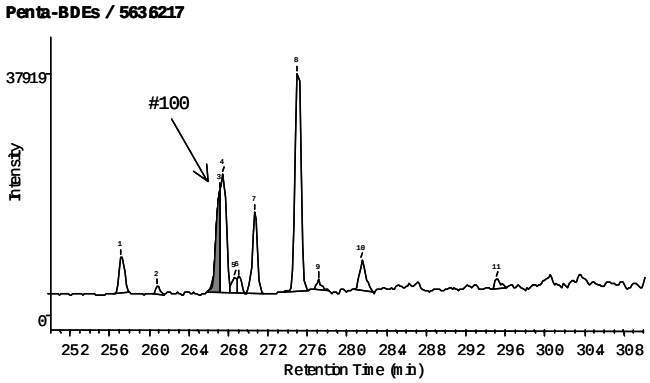

Figure 1. An example of a chromatogram for Penta-BDEs in the extract of air-dried sediment analyzed by HRGC-HRMS equipped with DB-17HT. A shaded portion in the figure was determined as a peak of BDE#100.

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