EVALUATION OF INTERLABORATORY STUDY ON PCDD, PCDF AND DIOXIN LIKE PCB IN THE SEDIMENT REFERENCE MATERIAL (8th round FY 2010 Research Group on Ultra Trace Analyses, JEMCA)

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Introduction

Inter-laboratory round robin is available for maintaining the quality/skills of dioxin analysis through testing by certified laboratories. There are over 110 accredited Laboratories for dioxin by MLAP (Specified Measurement Laboratory Accreditation Program) system of Ministry of Economy Trade and Industry (METI) in Japan. Ministry of Environment (MOE) has another program for examining the order of competence also. But it is more important to maintain QA/QC system and evaluate quality of daily analysis data continuously. There are some official proficiency tests for dioxin analysis by JSAC (The Japan Society for Analytical Chemistry), MOE and METI in Japan.

Research Group on Ultra Trace Analyses (UTA) which is accompanying organization of Japan Environmental Measurement & Chemical Analysis Association (JEMCA) established in 2003. The UTA consists of 66 private dioxin testing laboratories in 2010 and is responsible for developing the analytical potential of not only dioxins but also other trace level analysis of well known POPs in the environment. UTA carried out inter-laboratory round robin studies annually since 2003, R-1:flyash extract in 2003, R-2:soil in 2004, R-3:PUF fortified extract in 2005, R-4:soil in 2006, R-5:soil in 2007, R-6:flyash in 2008 R-7:sediment in 2009, and R-8:sediment in 2010 for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs). This paper summarizes the recent inter-laboratory study (R-8, FY 2010) conducted by UTA group for PCDDs, PCDFs and DL- PCBs in sediment sample.

Materials and methods

The sediment reference material the seventh round robin study (R-8) was sent to 66 laboratories. The sediment sample used for round robin study (R-8) was collected, dried, milled, homogenized and packed in 50 g portions. Additional homogeneity tests were carried out for inorganic component and organic carbon before the samples were dispatched. All member laboratories were asked to handle the samples as per their routine on such samples following the official Japanese analytical method for dioxins in sediment (revised March 2009 by MOE) with duplicate extraction and clean up in addition to duplicate HRGC-HRMS analysis of sample vials. They were asked to adapt QA/QC procedures that they follow regularly. All member laboratories were asked to report all 2,3,7,8-substituted PCDD/DFs congeners, homologues and 12 DL-PCBs. A special result form was sent to all members in which, the following details were requested; 1. The analytical results obtained, including recovery percentage, 2. Complete analytical procedure followed and 3. SIM Chromatograms of each sample.
Results of these studies are evaluated for median, normalized interquartile range (NIQR), coefficient of variation by Robust method (CV % rob) for each PCDDs, PCDFs and DL-PCBs. Furthermore Z-score was calculated and evaluated by ISO/IEC Guide 43-1 (JIS Q 0043-1). Laboratories, which exceed >±3 of Z-score were required cause analysis and report of corrective action.

Results and discussion:

The results of statistical analysis in the 8th round robin (R-8, 2010) are summarized in Table 1. It was reported totally 63 laboratories within the deadline. Every data was used excepting ND congener data from some laboratories. CV % rob in R-8 ranged from 6.6 % to 15.6 % for PCDDs/DFs, 5.0 % to 15.0 % for DL-PCBs. Furthermore two lines are added for evaluating 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF data. As our earlier

report, significant differences were observed between laboratories, in particular for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF, depending upon the capillary column that was used for the analysis. The main causes of these differences are due to co-eluting congeners in polar GC phase (SP-2331 or CP-Sil88) (ex. 1,2,3,7,8-PeCDF co-eluting 1,2,3,4,8-PeCDF, 1,2,3,4,7,8-HxCDF co-eluting 1,2,3,4,7,9-HxCDF). During combined data processing for these congeners, the CV % rob value were clearly increased.
They have gradually increased number of laboratories to use GC columns that can separate other congeners in the analysis of 1,2,3,7,8- PeCDF and 1,2,3,4,7,8- HxCDF. (e.g. during R-8 study the use of such columns is 57% while it was only 24% during R-1).

Table 1. Results of statistical analysis in the 8th round robin (R-8, 2010) study.

PCDDs/DFs, DL-PCB	MEDIAN (pg/g)	NIQR	CV(%) rob	MIN (pg/g)	MAX (pg/g)	AVERAGE (pg/g)	SD	N
2378-TeCDD	2.98	0.46	15.6	2.17	5.87	3.08	0.624	62
12378-PeCDD	27.80	2.00	7.2	22.00	36.90	27.66	2.781	63
123478-HxCDD	38.70	2.67	6.9	30.90	49.10	38.97	3.571	63
123678-HxCDD	87.40	5.82	6.7	73.00	107.00	88.07	7.832	63
123789-HxCDD	86.70	8.01	9.2	69.00	110.00	88.37	8.321	63
1234678-HpCDD	2473.00	159.38	6.4	1850.00	3000.00	2498.37	191.301	63
OCDD	52825.00	4512.66	8.5	43575.00	84400.00	53841.27	6563.843	63
2378-TeCDF	3.42	0.37	10.7	2.17	7.92	3.42	0.760	62
12378-PeCDF	7.01	1.90	27.1	4.23	21.70	7.29	2.404	62
1,2,3,7,8-PeCDF *a)	5.90	0.57	9.7	4.23	21.70	6.39	2.808	35
1,2,3,7,8-PeCDF *b)	8.57	0.81	9.4	6.93	9.87	8.47	0.842	27
23478-PeCDF	5.67	0.66	11.6	4.27	26.90	6.41	3.378	62
123478-HxCDF	23.10	2.04	8.8	14.80	31.40	23.18	2.609	63
1,2,3,4,7,8-HxCDF *a)	22.65	1.83	8.1	14.80	28.10	22.90	2.482	36
1,2,3,4,7,8-HxCDF *b)	23.50	2.34	9.9	19.00	31.40	23.55	2.772	27
123678-HxCDF	20.40	1.93	9.4	16.70	29.80	20.80	2.428	63
123789-HxCDF	3.40	0.42	12.3	2.30	11.20	3.62	1.205	60
234678-HxCDF	19.00	1.91	10.0	14.50	29.80	19.42	2.802	62
1234678-HpCDF	250.00	19.27	7.7	201.00	304.00	250.40	21.274	63
1234789-HpCDF	38.60	2.82	7.3	31.00	59.40	38.84	4.066	63
OCDF	919.00	60.42	6.6	785.00	1138.00	925.37	73.038	63
344'5-TeCB(#81)	1.80	0.21	11.9	1.18	2.69	1.82	0.281	57
33'44'-TeCB(#77)	20.20	2.15	10.6	12.30	27.00	20.31	2.740	63
33'44'5-PeCB(#126)	3.81	0.42	10.9	2.69	5.39	3.88	0.519	62
33'44'55'-HxCB(#169)	0.96	0.14	15.0	0.66	2.97	1.04	0.339	56
2'344'5-PeCB(#123)	3.46	0.25	7.3	1.87	7.42	3.53	0.670	59
23'44'5-PeCB(#118)	141.00	10.01	7.1	102.20	174.00	141.43	12.308	63
233'44'-PeCB(#105)	58.60	3.37	5.8	43.80	70.60	58.77	4.913	63
2344'5-PeCB(#114)	3.13	0.34	10.9	1.94	6.86	3.27	0.660	61
23'44'55'-HxCB(#167)	8.64	0.61	7.1	4.66	11.20	8.69	0.843	62
233'44'5-HxCB(#156)	19.90	1.52	7.6	12.80	26.50	19.87	1.952	63
233'44'5'-HxCB(#157)	5.74	0.29	5.0	4.81	7.23	5.77	0.453	62
233'44'55'-HpCB(#189)	2.34	0.21	8.9	1.78	3.37	2.37	0.322	58

Used GC column for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF analysis
(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: single paek
(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

Figure 1 shows Z-score appearance rate of in individual congeners (total 63 laboratories R-8 in 2010). Generally results from around 90% of the laboratories showed <±2 Z-score in individual congeners data. Furthermore, reproducibility data were evaluated on extraction procedure (criteria ≦30 %) and injection (criteria ≦10 %) in individual laboratories. These results showed appreciable for many laboratories.
Table 2 describes the trends of CV % rob from the 1st to 8th round robin study. These CV % rob values were the same or better as our past results for PCDDs/DFs congeners and DL-PCBs. It observed that low level individual congeners has relatively high CV % rob (ex. 2,3,7,8-TeCDD, CV % 15.6%).
These results indicate appreciable improvement of the analytical techniques of UTA laboratories every year.
The trends number of laboratories whose results exceeded >±3 of Z-score of at least one data in individual congeners, were 20 / 77 (total) for R-1, 27 / 83 (total) for R-2, 33 / 78 (total) for R-3, 23 / 75 (total) for R-4, 32 / 77 (total) for R-5, 20 / 77 (total) for R-6, 11 / 70 (total) for R-7 and 32 / 63(total) for R-8. These trends indicate that individual laboratories maintain QA/QC systems for Z-score in inter-laboratory round robin study.

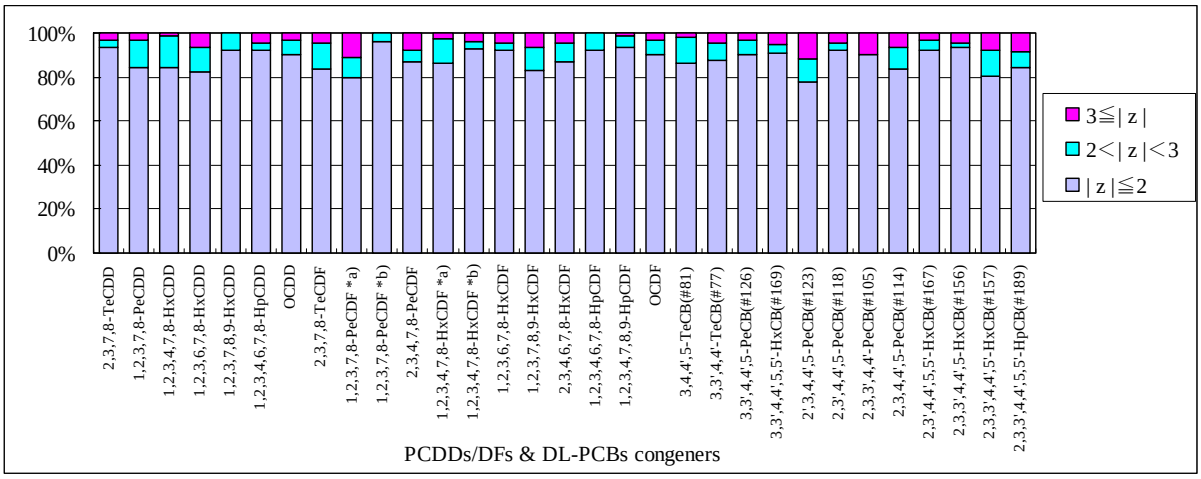

Fig. 1. Z-score appearance rate of in individual congeners (total 66 laboratories R-8 in 2010).

Used GC column for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF analysis
(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: single paek
(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

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Table 2. Trends of the round robin study results (CV % rob) from the 1st to 8th round robin study

PCDDs/DFs, DL-PCB	2003 (1st) flyash ext.	2004 (2nd) soil	2005 (3rd) PUF fortified	2006 (4th) soil	2007 (5th) soil	2008 (6th) flyash	2009 (7th) sediment	2010 (8th) sediment
2378-TeCDD	8.5%	15.8%	7.5%	24.8%	15.4%	11.4%	15.0%	15.6%
12378-PeCDD	6.3%	16.7%	5.9%	16.6%	10.3%	9.6%	9.3%	7.2%
123478-HxCDD	10.3%	15.8%	8.5%	16.2%	10.7%	10.0%	7.6%	6.9%
123678-HxCDD	8.7%	16.6%	9.7%	13.3%	10.4%	9.9%	6.9%	6.7%
123789-HxCDD	8.3%	17.5%	6.6%	13.4%	6.8%	10.8%	8.0%	9.2%
1234678-HpCDD	6.3%	16.5%	9.0%	15.4%	10.2%	8.9%	6.3%	6.4%
OCDD	8.5%	11.5%	6.4%	13.9%	7.5%	8.3%	6.7%	8.5%
2378-TeCDF	9.1%	17.9%	9.1%	15.6%	8.8%	13.8%	11.0%	10.7%
12378-PeCDF	10.0%	23.4%	11.1%	22.2%	23.6%	38.8%	32.2%	27.1%
1,2,3,7,8-PeCDF *a)			7.8%	14.1%	9.8%	12.6%	5.7%	9.7%
1,2,3,7,8-PeCDF *b)			9.0%	16.2%	7.1%	9.8%	9.2%	9.4%
23478-PeCDF	6.1%	13.7%	6.2%	9.7%	10.3%	9.2%	7.5%	11.6%
123478-HxCDF	6.3%	15.2%	8.9%	11.5%	13.0%	10.8%	9.9%	8.8%
1,2,3,4,7,8-HxCDF *a)			9.1%	9.9%	8.6%	9.2%	9.0%	8.1%
1,2,3,4,7,8-HxCDF *b)			7.2%	13.2%	8.0%	10.8%	5.6%	9.9%
123678-HxCDF	6.3%	10.7%	9.3%	14.5%	6.5%	10.6%	8.2%	9.4%
123789-HxCDF	12.9%	17.4%	10.3%	16.9%	14.7%	15.8%	13.7%	12.3%
234678-HxCDF	6.6%	10.4%	10.0%	21.8%	10.1%	10.3%	10.4%	10.0%
1234678-HpCDF	7.4%	10.5%	7.9%	16.2%	10.1%	9.9%	9.1%	7.7%
1234789-HpCDF	7.5%	11.5%	10.2%	15.2%	9.5%	9.8%	7.9%	7.3%
OCDF	7.0%	10.7%	11.6%	11.5%	10.1%	10.2%	9.0%	6.6%
344'5-TeCB(#81)	11.5%	12.9%	9.0%	16.1%	10.2%	10.0%	5.6%	11.9%
33'44'-TeCB(#77)	8.2%	8.3%	9.3%	11.6%	5.7%	10.4%	6.2%	10.6%
33'44'5-PeCB(#126)	8.6%	8.9%	9.4%	15.9%	9.6%	9.7%	8.9%	10.9%
33'44'55'-HxCB(#169)	8.4%	23.1%	18.7%	18.5%	16.0%	7.6%	10.5%	15.0%
2'344'5-PeCB(#123)	11.2%	10.7%	10.0%	14.8%	8.8%	12.9%	9.0%	7.3%
23'44'5-PeCB(#118)	6.9%	8.3%	18.1%	13.0%	6.9%	20.1%	5.7%	7.1%
233'44'-PeCB(#105)	8.3%	8.4%	18.5%	12.3%	8.7%	12.2%	6.2%	5.8%
2344'5-PeCB(#114)	9.8%	12.2%	20.6%	19.0%	11.0%	12.6%	5.9%	10.9%
23'44'55'-HxCB(#167)	8.1%	8.3%	9.8%	10.0%	10.8%	9.3%	7.5%	7.1%
233'44'5-HxCB(#156)	8.3%	8.2%	8.9%	9.3%	7.2%	9.4%	6.2%	7.6%
233'44'5'-HxCB(#157)	8.8%	11.5%	9.9%	9.4%	11.3%	7.6%	6.0%	5.0%
233'44'55'-HpCB(#189)	7.2%	9.8%	7.7%	8.2%	9.0%	8.3%	7.1%	8.9%
PCDDs/DFs	8.0%	14.8%	8.7%	15.8%	11.1%	12.2%	10.5%	10.1%
DL-PCB	8.8%	10.9%	12.5%	13.2%	9.6%	10.9%	7.1%	9.0%
PCDDs/DFs, DL-PCB	8.3%	13.2%	10.3%	14.7%	10.5%	11.7%	9.1%	9.7%

Used GC column for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF analysis
(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: single paek
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