EVALUATION OF INTERLABORATORY STUDY ON PCDDS, PCDFS AND DIOXIN LIKE PCBS IN THE SEDIMENT REFERENCE MATERIAL (11th round FY 2013 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 100 accredited laboratories for dioxin by MLAP (Specified Measurement Laboratory Accreditation Program) system of Ministry, of Economy, Trade and Industry (METI) in Japan.Ministry of the 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 65 private dioxin testing laboratories in 2014 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, R-8:sediment in 2010, R-9:flyash in 2011, R-10:flyash and fly ash extract in 2012 and R-11: sediment in 2013 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-11, FY 2013) conducted by UTA group for PCDDs, PCDFs and DL- PCBs in sediment sample.

Materials and methods

The sediment reference material the eleventh round robin study (R-11) was sent to 58 laboratories. The sediment was collected, dried, milled, homogenized and packed in 50 g portions.
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 internal standard substance 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 17043(JIS Q 17043). 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 11th round robin (R-11, 2013) are summarized in Table 1. It was reported totally 58 laboratories within the deadline. CV % rob in R-11 ranged from 3.7% to 11.3% for PCDDs/DFs, 4.5% to 8.3 % for DL-PCBs.

Table 1. Statistical analysis of the 11th round robin (R-11, 2013) study results of PCDDs/PCDFs and DL-PCBs.

PCDDs/DFs, DL-PCBs	MEDIAN (pg/g)	NIQR	CV(%) rob	MIN (pg/g)	MAX (pg/g)	AVERAGE (pg/g)	SD	N
2378-TeCDD	1.32	0.096	7.301	0.89	2.20	1.35	0.17	57
12378-PeCDD	7.62	0.428	5.622	5.06	10.24	7.66	0.74	58
123478-HxCDD	12.10	0.797	6.586	10.16	14.30	12.01	0.87	58
123678-HxCDD	28.60	1.612	5.638	24.30	33.90	28.48	1.83	58
123789-HxCDD	24.20	1.316	5.437	20.90	28.20	24.35	1.37	58
1234678-HpCDD	718.00	47.073	6.556	651.00	862.00	725.16	47.77	58
OCDD	12262.50	634.738	5.176	1273.00	14700.00	12137.90	1614.40	58
2378-TeCDF	12.75	1.075	8.430	10.80	20.20	12.87	1.43	58
12378-PeCDF	11.05	3.666	33.174	8.41	22.50	12.59	3.25	58
1,2,3,7,8-PeCDF *a)	10.60	0.990	9.336	8.41	13.80	10.85	1.08	43
1,2,3,7,8-PeCDF *b)	17.00	0.630	3.707	15.60	22.50	17.59	1.85	15
23478-PeCDF	16.80	1.371	8.163	14.30	20.70	16.82	1.32	58
123478-HxCDF	25.65	1.761	6.864	21.60	31.00	25.74	2.00	58
1,2,3,4,7,8-HxCDF *a)	25.30	1.520	6.007	21.60	30.40	25.19	1.73	43
1,2,3,4,7,8-HxCDF *b)	26.80	1.631	6.085	24.10	31.00	27.33	1.94	15
123678-HxCDF	24.95	1.816	7.279	21.40	27.90	24.95	1.55	58
123789-HxCDF	2.30	0.259	11.281	1.77	3.15	2.34	0.29	57
234678-HxCDF	35.70	3.391	9.500	29.20	46.40	36.11	3.85	58
1234678-HpCDF	145.50	7.228	4.967	131.00	169.00	146.53	7.68	58
1234789-HpCDF	24.60	1.446	5.876	21.90	30.80	24.76	1.66	58
OCDF	265.00	15.938	6.014	231.00	305.00	264.28	16.16	58
344'5-TeCB(#81)	132.50	7.969	6.014	110.00	740.00	144.38	79.95	58
33'44'-TeCB(#77)	5791.50	345.446	5.965	5015.00	29500.00	6194.26	3128.42	58
33'44'5-PeCB(#126)	64.65	3.521	5.447	54.20	320.00	69.39	33.86	58
33'44'55'-HxCB(#169)	5.87	0.499	8.500	4.72	31.00	6.34	3.35	58
2'344'5-PeCB(#123)	219.00	19.088	8.716	176.00	1225.00	236.81	133.56	58
23'44'5-PeCB(#118)	9176.50	519.837	5.665	7153.00	50000.00	9890.24	5392.54	58
233'44'-PeCB(#105)	3977.50	216.089	5.433	3105.00	21250.00	4250.21	2284.00	58
2344'5-PeCB(#114)	287.50	15.382	5.350	243.00	1550.00	310.34	166.59	58
23'44'55'-HxCB(#167)	309.00	19.459	6.297	270.00	1650.00	333.16	177.01	58
233'44'5-HxCB(#156)	795.50	52.447	6.593	705.00	4350.00	864.00	467.99	58
233'44'5'-HxCB(#157)	198.00	11.120	5.616	176.00	1025.00	214.78	109.05	58
233'44'55'-HpCB(#189)	63.25	4.355	6.886	56.20	323.00	67.67	34.30	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.: separate single peak

(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

Table 2 describes the trends of CV% rob from the 1st to 11th round robin study. 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). 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-11 study the use of such columns is 74% while it was only24% during R-2).

Table 2. Trends of the round robin study results (CV % rob) from the 1st to 11th round robin study

PCDDs/DFs, DL-PCBs	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	2011 (9th) flyash	2012 (10th) flyash	2012 (10th) flyash ext.	2011 (11th) sediment
2378-TeCDD	8.5	15.8	7.5	24.8	15.4	11.4	15.0	15.6	7.1	8.7	10.0	7.3
12378-PeCDD	6.3	16.7	5.9	16.6	10.3	9.6	9.3	7.2	6.7	7.2	5.3	5.6
123478-HxCDD	10.3	15.8	8.5	16.2	10.7	10.0	7.6	6.9	7.5	6.6	6.5	6.6
123678-HxCDD	8.7	16.6	9.7	13.3	10.4	9.9	6.9	6.7	5.7	4.4	6.4	5.6
123789-HxCDD	8.3	17.5	6.6	13.4	6.8	10.8	8.0	9.2	5.8	4.9	4.4	5.4
1234678-HpCDD	6.3	16.5	9.0	15.4	10.2	8.9	6.3	6.4	6.8	5.2	4.0	6.6
OCDD	8.5	11.5	6.4	13.9	7.5	8.3	6.7	8.5	9.0	5.5	5.4	5.2
2378-TeCDF	9.1	17.9	9.1	15.6	8.8	13.8	11.0	10.7	7.9	10.1	8.7	8.4
12378-PeCDF	10.0	23.4	11.1	22.2	23.6	38.8	32.2	27.1	35.1	19.9	39.0	9.3
1,2,3,7,8-PeCDF(※a)	-	11.0	7.8	14.1	9.8	12.6	5.7	9.7	4.9	9.6	5.2	3.7
1,2,3,7,8-PeCDF(※b)	-	15.0	9.0	16.2	7.1	9.8	9.2	9.4	6.8	9.2	8.1	8.2
23478-PeCDF	6.1	13.7	6.2	9.7	10.3	9.2	7.5	11.6	5.6	7.3	5.0	6.0
123478-HxCDF	6.3	15.2	8.9	11.5	13.0	10.8	9.9	8.8	15.5	9.7	20.1	6.1
1,2,3,4,7,8-HxCDF(※a)	-	5.6	9.1	9.9	8.6	9.2	9.0	8.1	6.7	5.1	3.6	7.3
1,2,3,4,7,8-HxCDF(※b)	-	14.9	7.2	13.2	8.0	10.8	5.6	9.9	6.9	6.2	5.3	11.3
123678-HxCDF	6.3	10.7	9.3	14.5	6.5	10.6	8.2	9.4	5.0	5.6	4.4	9.5
123789-HxCDF	12.9	17.4	10.3	16.9	14.7	15.8	13.7	12.3	9.8	10.0	7.5	5.0
234678-HxCDF	6.6	10.4	10.0	21.8	10.1	10.3	10.4	10.0	9.1	10.2	5.1	5.9
1234678-HpCDF	7.4	10.5	7.9	16.2	10.1	9.9	9.1	7.7	5.2	6.9	5.4	6.0
1234789-HpCDF	7.5	11.5	10.2	15.2	9.5	9.8	7.9	7.3	8.4	7.3	5.7	7.3
OCDF	7.0	10.7	11.6	11.5	10.1	10.2	9.0	6.6	8.9	5.6	3.2	5.6
344'5-TeCB(#81)	11.5	12.9	9.0	16.1	10.2	10.0	5.6	11.9	4.4	8.1	6.8	6.0
33'44'-TeCB(#77)	8.2	8.3	9.3	11.6	5.7	10.4	6.2	10.6	5.2	6.7	7.6	6.0
33'44'5-PeCB(#126)	8.6	8.9	9.4	15.9	9.6	9.7	8.9	10.9	7.9	6.9	7.2	5.5
33'44'55'-HxCB(#169)	8.4	23.1	18.7	18.5	16.0	7.6	10.5	15.0	7.6	6.2	7.5	8.5
2'344'5-PeCB(#123)	11.2	10.7	10.0	14.8	8.8	12.9	9.0	7.3	6.9	6.3	8.8	8.7
23'44'5-PeCB(#118)	6.9	8.3	18.1	13.0	6.9	20.1	5.7	7.1	7.7	17.9	9.9	5.7
233'44'-PeCB(#105)	8.3	8.4	18.5	12.3	8.7	12.2	6.2	5.8	8.4	8.3	6.8	5.4
2344'5-PeCB(#114)	9.8	12.2	20.6	19.0	11.0	12.6	5.9	10.9	9.1	12.9	8.0	5.4
23'44'55'-HxCB(#167)	8.1	8.3	9.8	10.0	10.8	9.3	7.5	7.1	6.7	6.3	6.8	6.3
233'44'5-HxCB(#156)	8.3	8.2	8.9	9.3	7.2	9.4	6.2	7.6	7.6	7.5	8.5	6.6
233'44'5'-HxCB(#157)	8.8	11.5	9.9	9.4	11.3	7.6	6.0	5.0	8.1	7.7	7.3	5.6
233'44'55'-HpCB(#189)	7.2	9.8	7.7	8.2	9.0	8.3	7.1	8.9	5.3	5.9	6.8	6.9
PCDDs/DFs	8.0	13.9	8.5	15.4	9.9	10.6	8.9	9.1	7.1	7.1	5.8	6.8
DL-PCB	8.8	10.9	12.5	13.2	9.6	10.9	7.1	9.0	7.1	8.4	7.1	6.4
PCDDs/DFs, DL-PCB	8.3	12.7	10.2	14.5	9.8	10.7	8.1	9.1	7.1	7.6	6.3	6.7

1,2,3,7,8-PeCDF,1,2,3,4,7,8-HxCDF column for analysis

(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: separate single peak

(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

Figure 1 shows Z-score exceed >±3 laboratory numbers in individual congeners (total 58 laboratories R-11 in 2013). Generally results from around 90% of the laboratories showed <±2 Z-score in individual congeners data. Furthermore, reproducibility data on extraction procedure (≦30%) and injection (≦10%) showed appreciable results from many laboratories.

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 , 32 / 66 (total) for R-8 , 25/ 63(total) for R-9 , 27(fly ash) and 23(fly ash ext.)/ 63(total) for R-10 , 21/58(total) for R-11. These trends indicate that individual laboratories maintain QA/QC systems for Z-score in inter-laboratory round robin study.

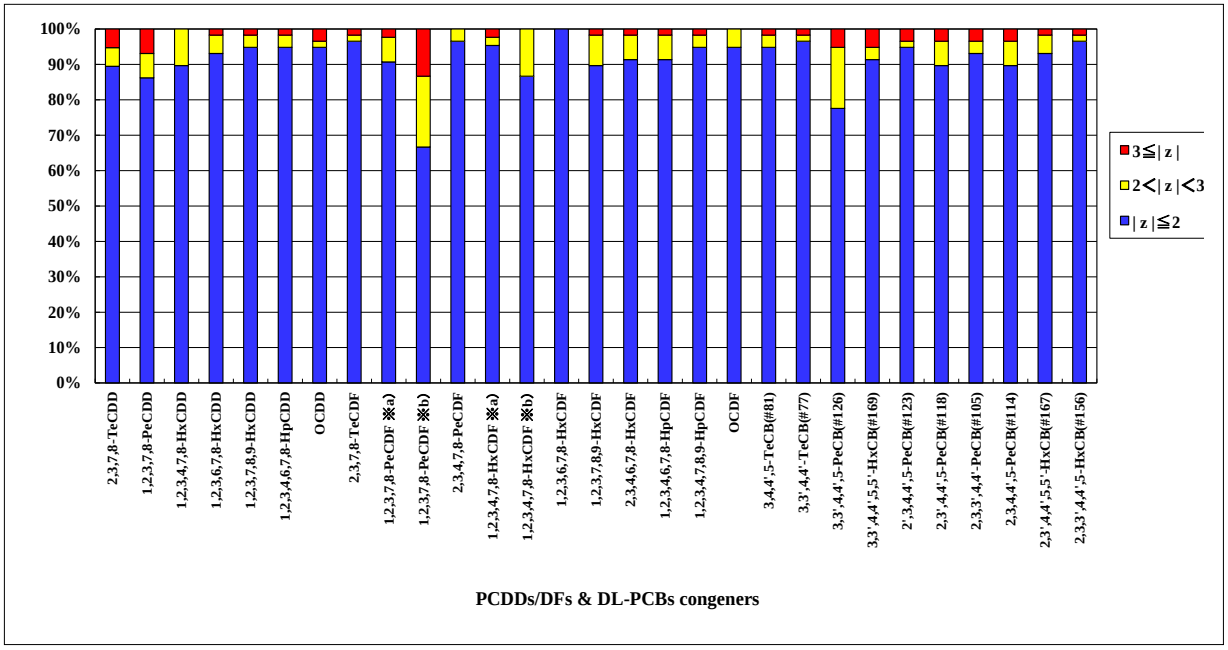

Fig. 1. Z-score exceed >±3 laboratory numbers in individual congeners (total 58 laboratories R-11 in 2013).
1,2,3,7,8-PeCDF,1,2,3,4,7,8-HxCDF column for analysis
(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: separate single peak
(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

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