EVALUATION OF INTERLABORATORY STUDY ON PCDDS, PCDFS AND DIOXIN LIKE PCBS IN THE SOIL REFERENCE MATERIAL (12th round FY 2014 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 nearly 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 2015 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, R-11: sediment in 2013 and R-12:soil in 2014 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-12, FY 2014) conducted by UTA group for PCDDs, PCDFs and DL- PCBs in soil sample.

Materials and methods

The soil reference material the twelfth round robin study (R-12) was sent to 57 laboratories. The soil 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 12th round robin (R-12, 2014) are summarized in Table 1. It was reported totally 57 laboratories within the deadline. CV % rob in R-12 ranged from 2.6% to 7.8% for PCDDs/DFs congeners, 4.0% to 7.3 % for DL-PCBs, and 3.5% for TEQ (not indicated in the table).
It seems better CV% rob result for 12th round robin study as compared with the result of the past. These results indicate appreciable improvement of the analytical techniques and systems of UTA individual laboratories every year.

Table 1. Statistical analysis of the 12th round robin (R-12, 2014) 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
2,3,7,8-TeCDD	21.6	1.19	5.49	18.1	27.2	21.75	1.51	57
1,2,3,7,8-PeCDD	102.3	5.19	5.07	83.4	126.0	102.68	7.03	57
1,2,3,4,7,8-HxCDD	122.0	5.93	4.86	107.0	143.0	123.70	7.29	57
1,2,3,6,7,8-HxCDD	277.0	12.60	4.55	230.0	322.0	276.98	14.95	57
1,2,3,7,8,9-HxCDD	202.0	8.15	4.04	173.0	226.0	200.98	10.14	57
1,2,3,4,6,7,8-HpCDD	2025.0	105.26	5.20	1843.0	2248.0	2036.82	95.18	57
OCDD	3860.0	170.49	4.42	3415.0	4240.0	3824.79	193.84	57
2,3,7,8-TeCDF	188.0	11.12	5.92	157.0	211.0	187.65	12.76	57
1,2,3,7,8-PeCDF	358.0	29.65	8.28	301.0	852.0	441.70	172.95	57
1,2,3,7,8-PeCDF *a)	353.0	18.53	5.25	301.0	407.0	354.24	20.19	45
1,2,3,7,8-PeCDF *b)	760.5	43.74	5.75	711.0	852.0	769.67	44.90	12
2,3,4,7,8-PeCDF	491.0	23.72	4.83	413.0	551.0	492.28	25.46	57
1,2,3,4,7,8-HxCDF	1030.0	30.39	2.95	900.0	1265.0	1037.21	70.00	57
1,2,3,4,7,8-HxCDF *a)	1020.0	26.69	2.62	900.0	1223.0	1017.24	51.58	45
1,2,3,4,7,8-HxCDF *b)	1073.0	83.21	7.76	992.0	1265.0	1112.08	80.98	12
1,2,3,6,7,8-HxCDF	804.0	34.10	4.24	693.0	916.0	807.70	43.31	57
1,2,3,7,8,9-HxCDF	67.5	4.30	6.37	47.7	87.7	67.63	5.74	57
2,3,4,6,7,8-HxCDF	1001.0	77.84	7.78	851.0	1198.0	1008.02	78.13	57
1,2,3,4,6,7,8-HpCDF	4320.0	229.80	5.32	3725.0	4808.0	4303.25	224.55	57
1,2,3,4,7,8,9-HpCDF	672.0	37.80	5.63	592.0	778.0	673.33	39.61	57
OCDF	5838.0	229.80	3.94	4898.0	6840.0	5805.93	350.36	57
3,4,4',5-TeCB(#81)	374.0	19.27	5.15	331.0	420.0	374.02	19.81	57
3,3',4,4'-TeCB(#77)	548.0	25.20	4.60	462.0	615.0	549.46	26.65	57
3,3',4,4',5-PeCB(#126)	746.0	40.77	5.47	624.0	885.0	749.19	49.65	57
3,3',4,4',5,5'-HxCB(#169)	376.0	17.05	4.54	328.0	421.0	376.16	19.17	57
2',3,4,4',5-PeCB(#123)	107.0	7.64	7.14	91.2	123.0	107.91	7.08	57
2,3',4,4',5-PeCB(#118)	777.0	46.70	6.01	692.0	925.0	779.70	49.82	57
2,3,3',4,4'-PeCB(#105)	549.0	23.72	4.32	490.0	633.0	550.68	31.08	57
2,3,4,4',5-PeCB(#114)	261.0	10.38	3.98	230.0	365.0	262.88	19.97	57
2,3',4,4',5,5'-HxCB(#167)	275.0	20.02	7.28	240.0	324.0	275.41	19.12	57
2,3,3',4,4',5-HxCB(#156)	685.0	36.32	5.30	614.0	821.0	684.84	37.85	57
2,3,3',4,4',5'-HxCB(#157)	339.0	15.57	4.59	312.0	445.0	343.86	21.39	57
2,3,3',4,4',5,5'-HpCB(#189)	661.0	31.14	4.71	582.0	807.0	666.60	41.47	57

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

Figure 1 describes the trends of CV% rob from the 1st to 12th 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-12 study the use of such columns is 79% while it was only24% during R-2). It shows the transition of the GC column used in Table 2.

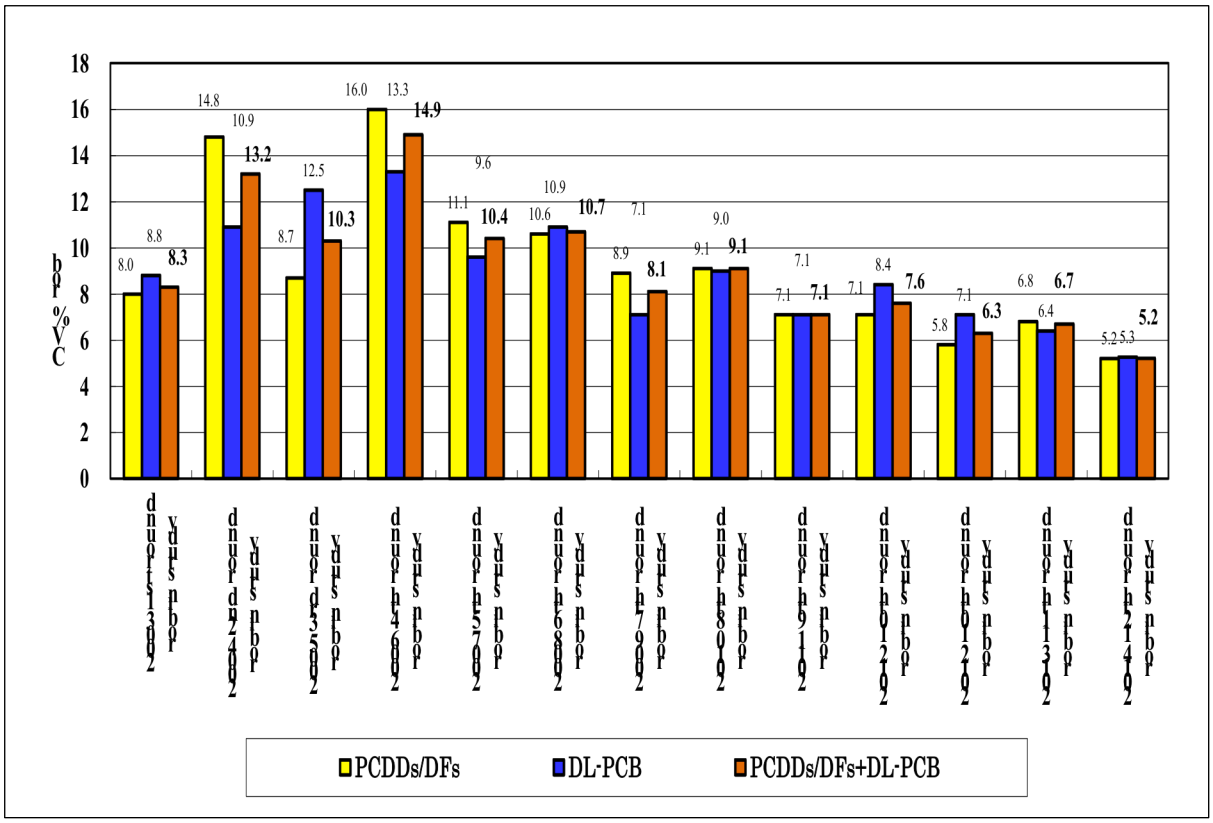

Fig. 1 Trends of the round robin study results (CV % rob)

Table 2. Trends (%) of GC column used for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF analysis

GC Column	R-2 2004	R-3 2005	R-4 2006	R-5 2007	R-6 2008	R-7 2009	R-8 2010	R-9 2011	R-10 2012	R-11 2013	R-12 2014
SP-2331, CP-Sil88 etc.	76.3	74	65.3	62.3	53.4	52.9	42.9	34.9	31.7	25.9	21.1
BPX-DXN, DB-5, BPX-5,RH-12ms etc.	23.8	26	34.7	37.7	46.6	47.1	57.1	65.1	68.3	74.1	78.9

Figure 2 shows Z-score exceed ±3 laboratory numbers in individual congeners (total 57 laboratories R-12 in 2014). 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-11,19/57 (total) for R-12. These trends indicate that individual laboratories maintain QA/QC systems for Z-score in inter-laboratory round robin study.

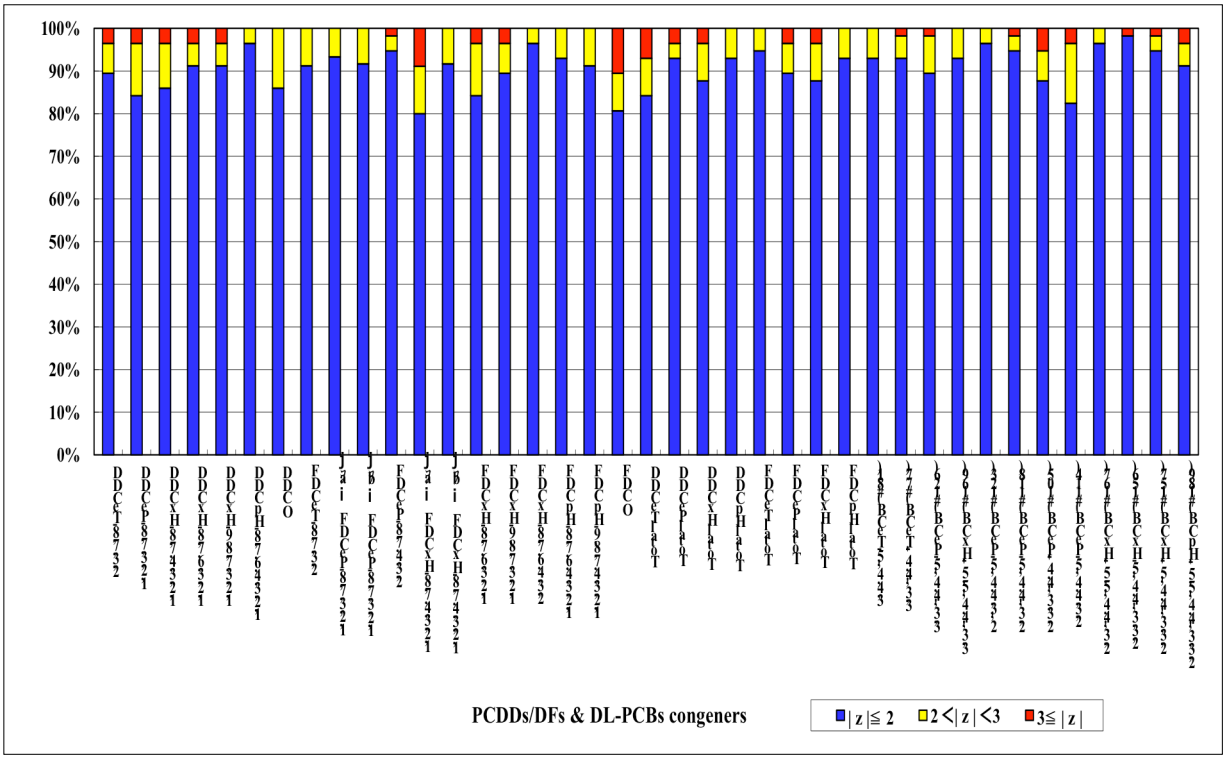

Fig. 2. Z-score exceed ±3 laboratory numbers in individual congeners (total 57 laboratories R-12 in 2014).

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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