EVALUATION OF INTERLABORATORY STUDY ON PCDD, PCDF AND DIOXIN LIKE PCB IN THE FLYASH AND FLYASH EXTRACT (16th round FY 2018 Research Group on Ultra Trace Analyses, JEMCA)

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Introduction

Inter-laboratory comparison is available for maintaining dioxin analytical quality/skills through testing by certified laboratories. 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 57 private dioxin testing laboratories in 2018 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 comparison studies annually since 2003, R-1,10:fly ash extract, R-2,4,5,12,16:soil, R-3,15:PUF fortified extract, R-6,9,10,14:fly ash, R-7,8,11:sediment, R-13:simulated drainage 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-16, FY 2018) conducted by UTA group for PCDDs, PCDFs and DL- PCBs in soil.

Materials and methods

The soil the sixteenth comparison study (R-16) was sent to 57 laboratories. 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 16th comparison (R-16) are summarized in Table 1. About the item (more than 10% of number of all reports) with many reports less than a minimum limit of determination, I did it with reference level handling this time. It was reported totally 57 laboratories within the deadline. CV% rob in R-16 ranged from 2.4% to 9.4% for PCDDs/DFs congeners, 5.9% to 14.1 % for DL-PCBs, and 6.2% for TEQ (not indicated in the table).
Figure 1 describes the trends of CV% rob from the 1st to 16th comparison 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-16 study the use of such columns is 93% while it was only 38% during R-5). In addition to 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF, 2,3,4,6,7,8-HxCDF and 2,3,4,4 ' , 5-PeCB (# 114) were also analyzed for data on columns that can separate other congeners. It shows the transition of the GC column used in Table 2.

Table 1. Statistical analysis of the 16th comparison (R-16, 2018) study results of PCDDs/PCDFs and DL-PCBs.

PCDDs/DFs, DL-PCBs	MEDIAN (pg/L)	NIQR	CV(%) rob	MIN (pg/L)	MAX (pg/L)	AVERAGE (pg/L)	SD	N
2,3,7,8-TeCDD	14.00	0.890	6.354	11.1	19.4	14.100	1.48	57
1,2,3,7,8-PeCDD	93.70	6.449	6.883	70.3	120	93.770	8.69	57
1,2,3,4,7,8-HxCDD	78.40	5.115	6.524	59.5	97.1	77.870	6.93	57
1,2,3,6,7,8-HxCDD	83.60	5.263	6.296	66.0	106	84.140	7.24	57
1,2,3,7,8,9-HxCDD	87.70	6.449	7.354	64.1	122	87.890	8.95	57
1,2,3,4,6,7,8-HpCDD	267.00	22.239	8.329	202	401	268.42	30.13	57
OCDD	160.00	11.120	6.950	138	224	161.61	14.43	57
2,3,7,8-TeCDF	30.70	2.150	7.003	23.4	36.9	30.74	2.404	57
1,2,3,7,8-PeCDF *a)	42.60	2.076	4.872	36	50.4	42.61	2.834	53
1,2,3,7,8-PeCDF *b)	63.85	4.244	6.647	56	70.2	63.48	5.933	4
2,3,4,7,8-PeCDF	60.90	4.596	7.547	49.2	78.6	61.66	5.769	57
1,2,3,4,7,8-HxCDF *a)	52.70	3.410	6.471	41.9	64.6	51.96	4.115	53
1,2,3,4,7,8-HxCDF *b)	61.50	1.483	2.411	60.1	66.3	62.35	2.726	4
1,2,3,6,7,8-HxCDF	62.00	4.596	7.413	51	77.3	61.94	4.995	57
1,2,3,7,8,9-HxCDF	5.60	0.467	8.340	4.13	16.1	5.81	1.556	57
2,3,4,6,7,8-HxCDF *a)	53.60	5.041	9.405	44.3	67.8	53.87	5.280	42
2,3,4,6,7,8-HxCDF *b)	62.00	4.225	6.815	55.2	74.9	63.79	4.923	15
1,2,3,4,6,7,8-HpCDF	109.00	8.154	7.481	86.6	143	108.8	9.860	57
1,2,3,4,7,8,9-HpCDF	15.50	0.964	6.217	12.1	21.6	15.53	1.464	57
OCDF	21.10	1.483	7.027	16.7	196	24.12	23.247	57
3,4,4',5-TeCB(#81)	3.50	0.208	5.930	2.84	4.64	3.56	0.289	57
3,3',4,4'-TeCB(#77)	20.50	1.483	7.232	17.3	24.2	20.65	1.535	57
3,3',4,4',5-PeCB(#126)	16.50	1.557	9.435	11.9	21.7	16.61	1.752	57
3,3',4,4',5,5'-HxCB(#169)	5.01	0.348	6.954	3.74	6.15	4.95	0.429	57
2',3,4,4',5-PeCB(#123)	1.88	0.146	7.808	1.36	2.45	1.87	0.179	56
2,3',4,4',5-PeCB(#118)	8.53	0.734	8.604	7.09	13.13	8.71	1.050	56
2,3,3',4,4'-PeCB(#105)	9.00	0.791	8.793	7.09	11.07	9.00	0.770	56
2,3,4,4',5-PeCB(#114) *a)	1.25	0.089	7.116	0.955	1.46	1.23	0.107	45
2,3,4,4',5-PeCB(#114) *b)	1.33	0.187	14.127	1.07	3.34	1.51	0.752	8
2,3',4,4',5,5'-HxCB(#167)	3.33	0.222	6.678	2.69	4.13	3.32	0.290	57
2,3,3',4,4',5-HxCB(#156)	5.25	0.385	7.342	4.36	6.69	5.32	0.448	57
2,3,3',4,4',5'-HxCB(#157)	3.74	0.259	6.937	3.10	4.69	3.77	0.305	57
2,3,3',4,4',5,5'-HpCB(#189)	3.68	0.274	7.453	2.99	4.61	3.66	0.336	57

(※a) Separate single peak

(※b) Including co-elute congeners

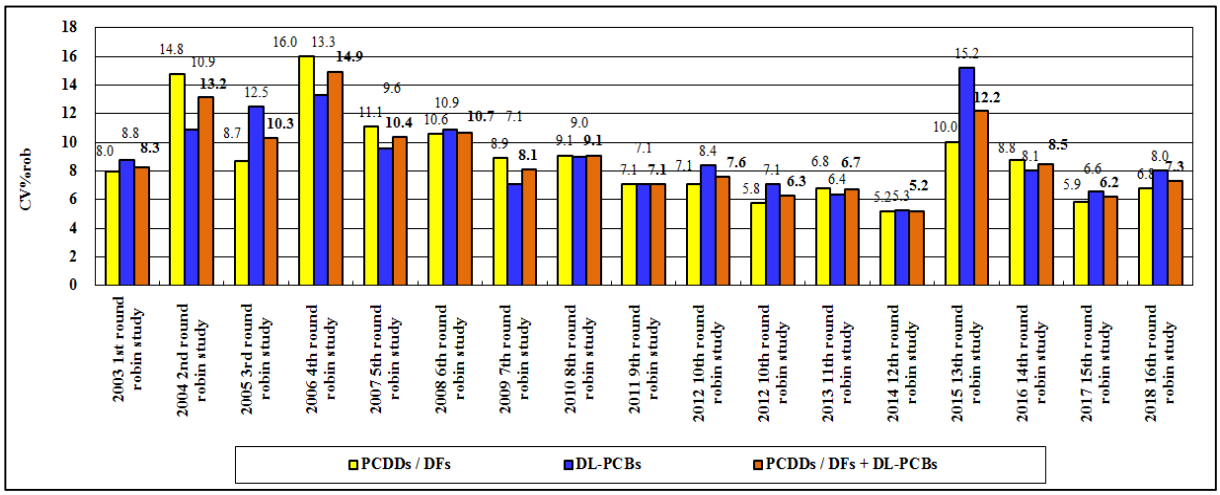

Fig. 1 Trends of the CV % rob. from R-1 to R-16 comparison study.

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-5 2007	R-6 2008	R-7 2009	R-8 2010	R-9 2011	R-10 2012	R-11 2013	R-12 2014	R-13 2015	R-14 2016	R-15 2017	R-16 2018
SP-2331, CP-Sil88 etc.	62.3	53.4	52.9	42.9	34.9	31.7	25.9	21.1	14.8	16.1	16.9	7.0
BPX-DXN, DB-5, BPX-5,RH-12ms etc.	37.7	46.6	47.1	57.1	65.1	68.3	74.1	78.9	85.2	83.9	83.1	93.0

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

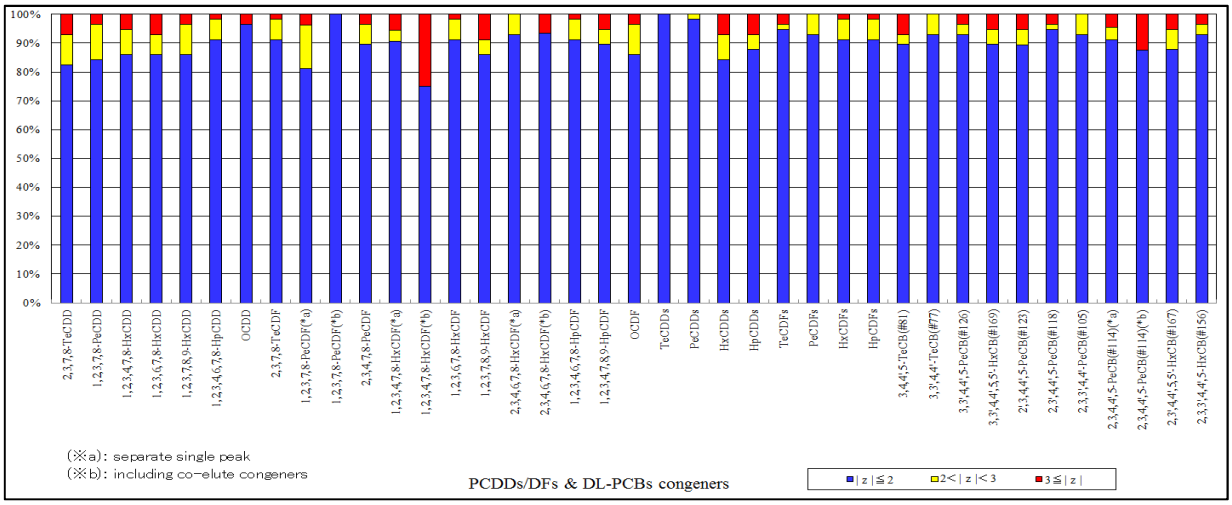

Fig. 2. *z*-score exceed >±3 laboratory numbers in individual congeners (total 57 laboratories R-16 in 2018).

Figure 2 shows z-score exceed ±3 laboratory numbers in individual congeners (total 57 laboratories R-16 in 2018). Generally results from around 90% of the laboratories showed <±2 z-score in individual congeners data(excluding 2 isomers). 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, 13 / 54 (total) for R13, 11 /57 (total) for R14, 17 /59 (total) for R15, 18 /57 (total) for R16.

These trends indicate that individual laboratories maintain QA / QC systems for z-score in inter-laboratory comparison.

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