Evaluation of interlaboratory study for PCDDs, PCDFs and Dioxin like PCBs in the soil reference material

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Introduction

Inter-laboratory round robin is available for maintaining dioxin analytical quality/skills by testing or certified laboratories. There are over 140 accredited Laboratory 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 examination program for order competence also. But it is more important to maintain QA/QC system and evaluate quality of daily analysis data continuously. There are some proficiency test for dioxin analysis by JSAC (The Japan Society for Analytical Chemistry), MOE and METI officially.
On the other hand, Research Group for Dioxin Analysis, which has technical experts from 33 private dioxin testing laboratories, had carried out inter-laboratory round robin 4 times since 1998 to 2002. These studies has been transferred to new research group namely, Research Group on Ultra Trace Analyses (UTA) which is accompanied organization of Japan Environmental Measurement & Chemical Analysis Association (JEMCA) in 2003. The UTA consists 83 private dioxin testing laboratories and has been subjected to grow up the technical potential not only for dioxins but other trace level analysis of well known POPs in the environment. UTA carried out first round studies (R-1) in 2003, second round studies (R-2) in 2004, third round studies (R-3) in 2005 and fourth round studies (R-4) in 2006 respectively for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs).
This paper summarizes and evaluate of recent interlaboratory study for PCDDs, PCDFs and Dioxin like PCBs in soil sample.

Materials and Methods

The fifth round study (R-5) in soil sample is used as "MLAP round robin (trial)" by JEMCA sponsored. Each UTA laboratory who participated in the "MLAP round robin (trial)" were brought together and were evaluated in 2007 fiscal year.
All member laboratories were ask to consider the samples as a routine analysis by official Japanese analytical method for dioxins with extraction and clean up individually in addition to duplicate HRGC-HRMS analysis of sample vial. 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 and the 12 DL-PCBs. A result form was sent to all participants in which the following details were requested from each laboratory : 1) the analytical results ; 2) a description of the analytical procedure and 3) the chromatograms for each sample.
Results of these studies are evaluated for median, normalized interquartile range (NIQR), coefficient of variation by Robust method (CV % rob) for each polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs). Furthermore calculated Z-score 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 for the round robin study were presented on isomer/congener specific basis with median, NIQR and CV% rob are summarized in Table 1. Every data set was used to identify obvious outliers. Obvious outliers were defined as having each Z-score over 2.
CV % rob in R-5 ranged from 11.1 % (6.5 % to 23.6 %) for PCDDs/DFs, 9.6 % (5.7 % to 16.0 %) for DL-PCBs and 7.2 % for total TEQ. Figure 1 describes the CV % rob obtained for each congener in the second, fourth and fifth round robin for the soil sample. Overall, as may be seen from Figure 1, the CV rob% obtained in the fifth round robin were significantly lower for most congeners than in the two previous exercises.

Table 1   Statistical analysis of the analytical results of PCDDs/PCDFs and DL-PCBs isomers

| PCDDs/DFs	Median (pg/g)	NIQR	CV % rob	DL-PCBs	Median (pg/g)	NIQR	CV % rob
2378-TeCDD	0.71	0.11	15.37	344'5-TeCB(#81)	4.00	0.41	10.19
12378-PeCDD	5.58	0.57	10.31	33'44'-TeCB(#77)	68.25	3.89	5.70
123478-HxCDD	5.35	0.57	10.74	33'44'5-PeCB(#126)	6.75	0.65	9.61
123678-HxCDD	9.60	1.00	10.42	33'44'55'-HxCB(#169)	1.28	0.20	15.99
123789-HxCDD	9.85	0.67	6.77	2'344'5-PeCB(#123)	7.40	0.65	8.77
1234678-HpCDD	51.00	5.19	10.17	23'44'5-PeCB(#118)	350.00	24.09	6.88
OCDD	87.00	6.49	7.46	233'44'-PeCB(#105)	170.00	14.83	8.72
2378-TeCDF	2.10	0.19	8.83	2344'5-PeCB(#114)	11.50	1.26	10.96
12378-PeCDF	4.40	1.04	23.59	23'44'55'-HxCB(#167)	24.00	2.59	10.81
23478-PeCDF	5.20	0.54	10.34	233'44'5-HxCB(#156)	64.00	4.63	7.24
123478-HxCDF	6.15	0.80	12.96	233'44'5'-HxCB(#157)	14.75	1.67	11.31
123678-HxCDF	6.55	0.43	6.51	233'44'55'-HpCB(#189)	6.60	0.59	8.99
123789-HxCDF	0.68	0.10	14.69				
234678-HxCDF	7.70	0.78	10.11				
1234678-HpCDF	22.00	2.22	10.11				
1234789-HpCDF	3.50	0.33	9.53				
OCDF	11.00	1.11	10.11	TOTAL TEQ	14.0	12.7	7.20
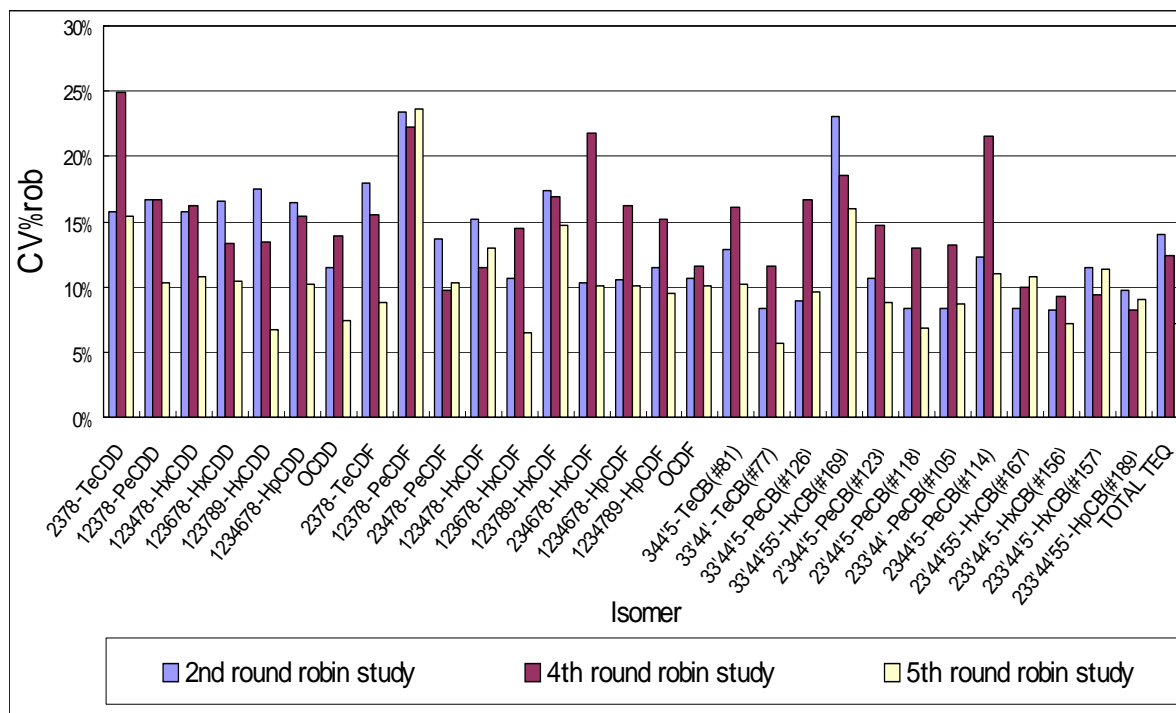
Fig. 1 Coefficient of variation by Robust (CV % rob)

This result is appreciable with the appearance of the improvement of the analysis technique of the UTA laboratories every year. The number of laboratories which presented report of corrective action >3 of Z-score, were 33 lab./77 lab. (total) for R-1, 30 lab./81 lab.(total) for R-2 , 33 lab./78 lab.(total) for R-3 ,23 lab./75 lab.(total) for R-4,and 33 lab./77 lab.(total) for R-5.

Figure 2 shows Z-score appearance rate of R-5 round robin study.

As may be seen from Tables 2 and 3, 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 for polar GC phase (SP-2331 or CP-Sil88). Laboratories numbers with the GC column which could isolate congeners are increased year by year, but the variation was a little bigger some use of the GC column which could isolate it by this round robin study.

Table 2. The table showing different results of 1,2,3,7,8-PeCDF when using different GC phase (e.g. polarity)

Type of GC-column	Lab. No.	Average (pg/g)	Max	Min	SD	Median	NIQR	CV% rob
SP-2331, CP-Sil88	48	4.64	5.50	3.80	0.42	4.63	0.33	7.11
BPX-DXN, DB-type, RH-12MS	29	3.30	6.20	2.20	0.66	3.20	0.32	9.85

Table3. The table showing different results of 1,2,3,4,7,8-HxCDF when using different GC phase (e.g. polarity)

Type of GC-column	Lab. No.	Average (pg/g)	Max	Min	SD	Median	NIQR	CV% rob
SP-2331, CP-Sil88	48	6.51	8.20	5.40	0.58	6.51	0.52	7.97
BPX-DXN, DB-type, RH-12MS	29	5.65	8.80	4.10	0.78	5.63	0.48	8.57

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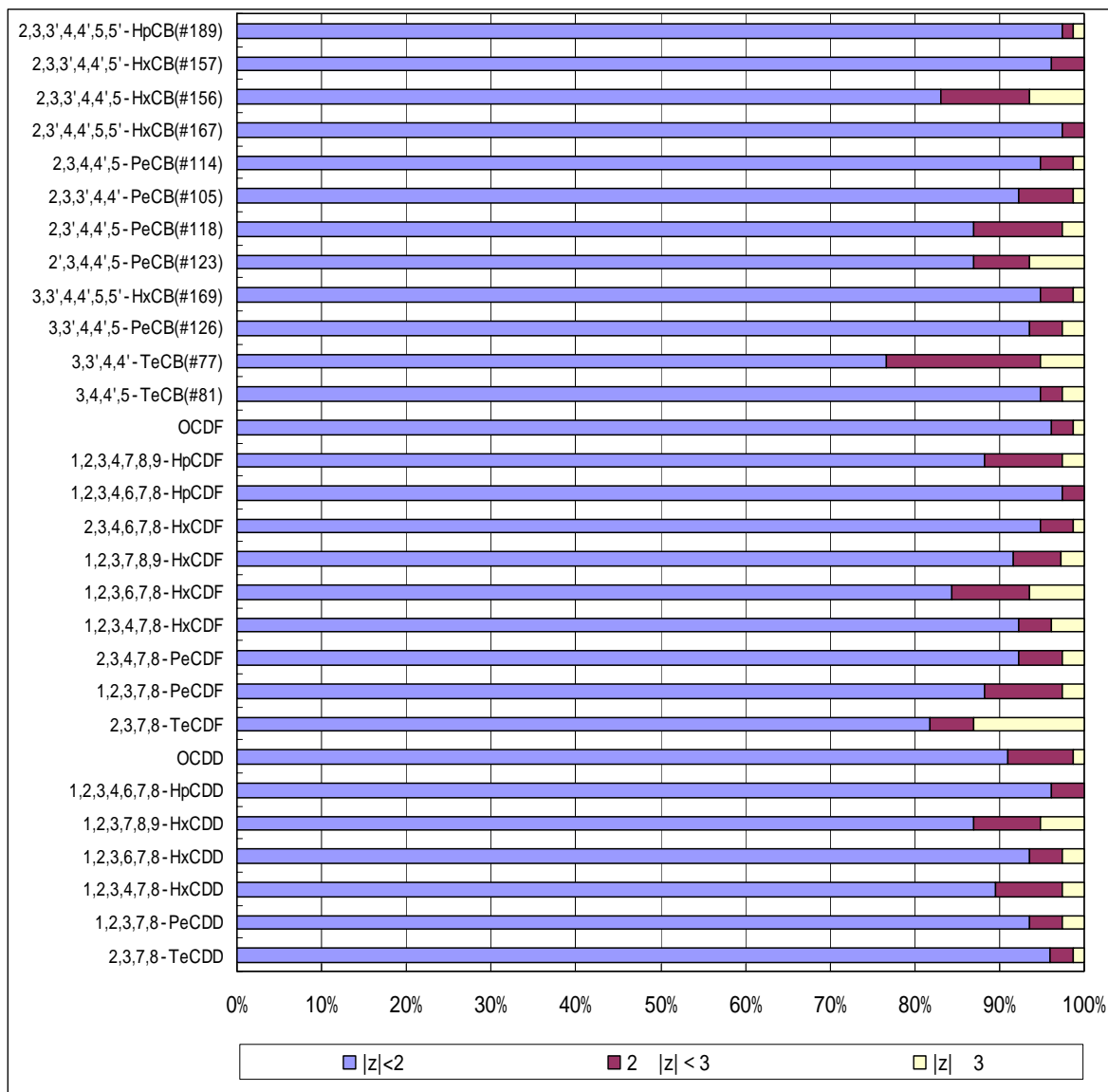
Figure. 2   Relative percentage of Z-score results in R-5 round robin study in 2007.