Evaluation of Interlaboratory Round Robin Study (2000-2003) in Japan

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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 150 dioxin testing laboratories available in Japan consequently, Ministry of Environment (MOE) and Ministry of Economy Trade and Industry (METI) have began to investigate quality of dioxin testing laboratory and to upgrade their skills with in 4 years. On the other hands, Research Group for Dioxin Analysis which have technical experts from 33 private dioxin testing laboratories had carried out inter-laboratory round robin 4 times since 1998. 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 for not only dioxins but other trace level analysis of well known persistent organic pollutants (POPs), endocrine disrupting chemicals (EDCs) and ubiquitous contaminants in the environment. Former research group had run final round (4^{th}) and new UTA carried out first round studies in 2001 And 2003, respectively. Percentage relative standard deviations (RSD) for each polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) have become smaller than past studies.

Methods and Materials

On the last round robin study by former research group (R-1), two sediment samples which had high and low concentration, respectively were sent to 40 members, and on the other hand, for new UTA round robin study (R-2), one fly ash extract solution was sent to 83 members.

Sediment samples had been dried and packed in to 200-g portions while, fly ash extracts has been packed two 1-mL ampoules. All member laboratories were ask to consider the samples as a routine analysis using the normal extraction and clean up protocol in addition to normal 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 special result form was sent to all members in which, the following details were requested from each laboratories includes; 1. The obtained analytical data, 2. Complete analytical procedure that each laboratory followed and 3. chromatograms of each sample.

Results and Discussion

The results for the first robin study (R-1) were presented on isomer/congener specific basis with median, normalized semi-interquartile range (NIQR) and Z-score are summarized in Table 1. Every data set were used to identify obvious outliers. Obvious outliers were defined as having each Z-score over 2.

Table 1 Median, normalized interquartile range (NIQR) and c.v. of round robin study-1 (R-1).

Sediment (pg/g)	High concentration sediment			Low concentration sediment		
	Median	NIQR*	c.v.(%)	Median	NIQR*	c.v.(%)
2,3,7,8-TeCDD	0.85	0.26	30.6%	0.24	0.05	19.6%
1,2,3,7,8-PeCDD	5.4	0.53	9.9%	1.6	0.25	15.5%
1,2,3,4,7,8-HxCDD	7.9	0.77	9.8%	2.3	0.34	14.8%
1,2,3,6,7,8-HxCDD	37	3.8	10.3%	4.4	0.70	16.0%
1,2,3,7,8,9-HxCDD	15	1.5	9.5%	4.9	0.53	10.7%
1,2,3,4,6,7,8-HpCDD	1400	200	14.2%	66	9.9	14.9%
OCDD	16000	1500	9.3%	830	110	13.2%
2,3,7,8-TeCDF	6.4	0.95	14.9%	3.3	0.45	13.7%
1,2,3,7,8-PeCDF	11	1.8	16.0%	4.2	0.38	9.1%
2,3,4,7,8-PeCDF	9.4	1.3	13.9%	3.0	0.19	6.4%
1,2,3,4,7,8-HxCDF	29	2.7	9.3%	6.2	0.69	11.1%
1,2,3,6,7,8-HxCDF	19	1.5	8.0%	3.6	0.44	12.3%
1,2,3,7,8,9-HxCDF	1.9	0.60	32.1%	0.35	0.08	23.6%
2,3,4,6,7,8-HxCDF	28	5.3	18.9%	3.8	0.50	13.2%
1,2,3,4,6,7,8-HpCDF	430	44	10.4%	19	3.9	20.2%
1,2,3,4,7,8,9-HpCDF	43	7.1	16.3%	2.1	0.36	17.6%
OCDF	1700	140	8.4%	21	3.2	15.3%
#81	10	1.9	19.4%	2.8	0.70	24.9%
#77	350	32	9.3%	55	5.4	9.9%
#126	16	2.8	17.4%	3.6	0.40	11.2%
#169	3.7	0.47	12.8%	0.97	0.24	25.1%
#123	30	5.3	18.0%	5.0	0.91	18.1%
#118	1800	150	8.0%	273	37	13.4%
#105	670	84	12.5%	74	11	15.0%
#114	27	3.5	13.1%	3.6	1.2	33.4%
#167	73	6.6	9.0%	22.4	7.7	34.4%
#156	150	15	9.9%	43	3.4	8.0%
#157	41	14	34.9%	8.7	13	149%
#189	16	1.3	8.1%	11	1.1	9.5%
TEQ	50	3.3	6.5%	7.9	0.81	10.3%

As indicated earlier, R-1 study was carried out in 2001. MOE QA/QC program has already been enacted, but this program required only any records during sampling or to until reporting, and no on-site audit has been done. Coefficients of variations were ranged from 6.4% to 34.1% for PCDDs/DFs, 8.0% to 149% for DL-PCBs and 10.3% for TEQ. Coefficient of variation of 1,2,3,7,8,9-HxCDF is relatively greater than other PCDDs/DFs, since several laboratory could not separate 1,2,3,7,8,9-HxCDF peaks from fragment ion of HpCDF. Coefficient of variations of DL-PCBs were greater than those of PCDDs/DFs, since many laboratory have not be able to control and eliminate laboratory contamination of PCBs from ambient air.

Table 2 Median, normalized interquartile range and c.v. of Round Robin Study-2 (R-2)

Fly ash solution (pg/mL)	Median	NIQR	c.v.(%)
2,3,7,8-TeCDD	40	3.4	8.5%
1,2,3,7,8-PeCDD	170	11	6.2%
1,2,3,4,7,8-HxCDD	94	9.7	10.3%
1,2,3,6,7,8-HxCDD	130	10	8.1%
1,2,3,7,8,9-HxCDD	120	9.6	8.2%
1,2,3,4,6,7,8-HpCDD	380	23	6.1%
OCDD	280	24	8.6%
2,3,7,8-TeCDF	240	22	9.2%
1,2,3,7,8-PeCDF	670	60	8.9%
2,3,4,7,8-PeCDF	600	37	6.2%
1,2,3,4,7,8-HxCDF	660	40	6.0%
1,2,3,6,7,8-HxCDF	640	38	5.9%
1,2,3,7,8,9-HxCDF	54	6.7	12.4%
2,3,4,6,7,8-HxCDF	440	30	6.9%
1,2,3,4,6,7,8-HpCDF	1000	78	7.4%
1,2,3,4,7,8,9-HpCDF	150	11	7.3%
OCDF	240	17	7.1%
#81	30	3.1	10.4%
#77	190	16	8.3%
#126	130	11	8.3%
#169	52	4.4	8.4%
#123	20	2.1	10.8%
#118	460	30	6.6%
#105	260	22	8.5%
#114	27	2.5	9.4%
#167	38	3.0	7.8%
#156	100	6.9	6.9%
#157	45	3.9	8.7%
#189	65	4.5	6.9%
TEQ	810	36	4.4%

As mentioned earlier, R-2 study was carried out in 2003, and sample was distributed as an extracted solvents of fly ash. During this time, Japanese dioxin testing laboratory accreditation system (MLAP: Specified Measurement Laboratory Accreditation Program) has already been introduced. Probably, MLAP system might be possible explanation for the improvement and accuracy of dioxin analysis, since MLAP has required on-site audit and correction of improper process or quality system. Coefficients of variations in R-2 ranged from 6.0% to 12.4% ifor PCDDs/DFs, 6.6% to 10.8% for DL-PCBs and 4.4% for TEQ. Coefficient of variation of 1,2,3,7,8,9-HxCDF is relatively greater than other PCDDs/DFs, since several laboratory could not separate 1,2,3,7,8,9-HxCDF peaks from fragment ion of HpCDF, and this observation was same as R-1. Coefficient of variations of DL-PCBs were almost same as those of PCDDs/DFs, since many laboratory have tried to eliminate PCB contamination from ambient air.

In order to evaluate the reproducibility, measured toxicity equivalent quantities (TEQ) obtained by multiple analysis were compared and plotted in Fig.1 and Fig.2 for R-1 and R-2, respectively.

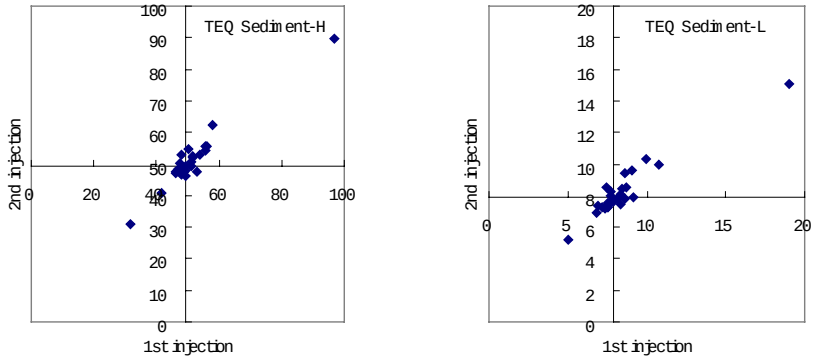

Fig. 1 Youden plot for R-1
Cross point of each axis indicate median of each injection.

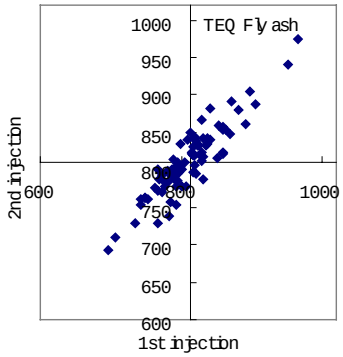

Fig. 2 Youden plot for R-2
Cross point of each axis indicate median of each injection.

Participants of these studies

List of members who have participated these studies was shown below.

Participants of Study R-1
Chugai Technos, Ebara Research, Environmental Control Center, Fukuda Hydrologic Center, Fukui Environmental Analysis Center, Japan Inspection, Kaneka Techno Research, Kankyo Sol-tech, Kankyo Techno, Kawaju Techno Service, Kobelco Research Institute, Kokan Keisoku, Kyoto Microbiological Institute, Kyushu Environmental Evaluation Association, Kyushu Techno Research, Metocean Environment, Mitsubishi Material, Miura, Nippon Total Science, Nittech Research, North Techno Research, Ryonichi Engineering, Sanzo Testing Center, Shimdzu Techno Research, Sumika Chemical Analysis Service, Taiheiyo Consultant, Teijin Eco Science, Toden Environmental Engineering, Toho Kaken, Toray Research Center, Towa Kagaku, Unitika Environmental Technical Center, Yagai Kagaku

Participants of Study R-2
BAB-Hitachi Industrial, BML, Chiba Prefectural Environment Foundation, Chugai Techinos, Dia Analysis Center, Ebara Research, Environment and Biochemistry Research Institute, Environmental Control Center, Environmental Science Research Niigata, Environmental Technology Service, Fukuda Hydrologic Center, Fukui Environmental Analysis Center, Green Laboratory, Gumma Analysis Center, Hiroshima Environment and Health Association, Ibiden Engineering, Industrial Analysis Service, Izumitec, Japan Food Research laboratories, Japan Inspection, Joetsu Environmental Science Center, Kaneka Techno Research, Kankyo Giken, Kankyohozen, Kankyo Kagaku Kenkyusyo, Kankyo Kogai Center, Kankyo Sogo Kenkyujo, Kankyo Sol-tech, Kankyo Techno, Kankyou Sogo Kenkyu Kiko, Kankyo Technos, Kawaju Techno Service, Kinki Bunseki Center, Kishimoto Clinical Laboratory Group, KN Lab. Analysis, Kobelco Eco Solution, Kobelco Research Institute, Kokan Keisoku, Kyoto Microbiological Institute, Kyushu Environmental Evaluation Association, Kyushu Techno Research, Metocean Environment, Mie Prefecture Environmental Conseruation Agency, Mitsubishi Material, Mitsui Chemical Analysis and Consulting Service, Miura, Nature Environment Support, Nihon Environmental Services, Niigata Prefecture Environmental Analysis Center, Nittech Research, Nippon Total Science, Nittetsu Techno Research, North Techno Research, NS Kankyo, Okinawa Prefectural Environmental Science Center, Oyakama-ken Kankyo Hozen Jigyodan, Riken Analysis Center, Ryomei Engineering, Ryonichi Engineering, Saga Prefectural Environmental Science Inspection Association, Seikan, Shimadzu Techno Research, Shinnikka Environmental Engineering, Shizuoka-ken Sangyo Kankyo Center, Sogo Mizu Kenkyujo, Sumiko Techno Research, Sumitomo Metal Technology, Takamizawa Analytical Chemistry Institute, Tatsuta Environmental Analysis Center, Techno Chubu, Teijin Eco Science, Term, Toden Environmental Engineering, Toho Kaken, Tohoku Ryokka Kankyo Hozen, Tokai Analytical Chemistry Institute, Tokai Technology Center, Tokai Techno, Tokyo Technical Service, Toray Research Center, Towa Kagaku, Unichemy, Unitika Environmental Technical Center, Yagai Kagaku,