

## **Ten years of QA/QC: The International Intercalibration Study of PCDD/DF and WHO TEF assigned PCBs in incineration and soil/sediment/sludge samples .**

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### **Introduction**

Laboratory intercalibration studies are essential for QA/QC of analytical data including dioxin analysis. The relatively low levels of PCDD/DFs, the elaborate sample extraction and clean up in addition to the detection by GC/MS requires special QA/QC considerations. Round robin or intercalibration studies for these compounds are also subjected to special criteria and needs. Since 1992 the International Intercalibration Study has been organised for this purpose, providing special incineration related and soil/sediment/sludge samples containing different levels of PCDD/DF and WHO TEF assigned PCBs. Started out with 10 participants in the 1<sup>st</sup> round of the study in 1992, now around 100 participant are taking part in this study. The study is since 1998 taking place on a yearly basis and has expanded from only incineration related samples to include also soil, sediment and sludge samples. In addition to 'real' samples also standard solution and extract have been included in the study to test different aspect of the analysis. During the ten years organising the study also gradually the target compounds have expanded from only the 2,3,7,8-substituted PCDD/DFs to including all WHO-TEF assigned dioxin-like compounds including the planar and mono-*ortho* PCBs. Throughout the 8 rounds organised an enormous amount of data has been compiled in reports, papers<sup>1</sup> and presented at international meetings. However most focus has been on the results of one specific round or sample. In order to study more long term trends and developments, the statistics of the first 7 rounds of the International Intercalibration Study have been studied in more detail and are presented here.

### **Material and Methods**

Real life samples were send to all participants to resemble a 'normal' routine sample as close as possible. These real samples consisted of Fly Ash, Soil, Sediment or Sludge samples which were dried, homogenised and packed in 3-20 g portions. Also soil or fly ash extracts were send to the participants occasionally to examine the influence of the extraction step on the final results. Also the influence of the final quantification step on the results was examined regularly by including standard solutions of known concentrations. All participating laboratories were ask to consider the samples as a routine sample and using the normal extraction and clean up protocol in addition to 'normal' QA/QC procedures. All laboratories were asked to report all 2,3,7,8-substituted PCDD/DFs and the 3 planar PCBs, as an option the mono *ortho* WHO TEF assigned PCB could be reported. A special results form was send to all participant in which not only all data described above could be reported but also the analytical procedure used for the analysis. All participants

were also encouraged to run the samples on two different GC columns, in order to avoid co-elution of certain isomers. Although high resolution GC/MS is the most common detection technique used, also results from low-resolution quadrupole and ion trap instruments were accepted. In the later studies also results from bioassay detection were accepted, but detection using bioassays was studied in more detail in a special designed bioassay intercalibration<sup>2</sup>. The results were presented on an isomer specific basis and the mean, median and RSD were calculated. In addition the total TEQ was calculated for each sample, this TEQ was used to identify obvious outliers. Obvious outliers were defined as having a TEQ value outside 2 times the RSD. After omitting of obvious outliers a new mean, median and RSD was calculated. All data was compiled in a yearly report that contained all data point and a graphical representation of the data indicating one and two times the RSD for each congener. All data was also made available on the Internet<sup>3</sup>

### Results and discussion

Throughout the seven round reported, the results of the 8<sup>th</sup> round will be presented at this meeting, a total of 43 samples were send. The results are summarised in Table 1, where the different samples are given in addition to the RSD for all samples (RSD all), the RSD after omitting obvious outliers (RSD) and the number of results included in the respective RSDs. In the first study 10 laboratories participated and of these 8 were able to report the results before the set deadline. No obvious outliers were detected so the same number is reported for the corrected RSD (RSD No outliers). The RSDs for the limited number of laboratories in the first rounds was relatively good and only a limited number of results were classified as outliers.

*Table 1. Summary the results of the 7 rounds organised since 1992. Including the %RSD of the total TEQ of all reported results and the %RSD after omitting obvious outliers.*

Year	Sample	RSD (all)	n	RSD (no outliers)	n
1 <sup>st</sup> Round	1994				
	Fly Ash Extract A	23%	8	23%	8
	Fly Ash Extract B	20%	8	20%	8
	Fly Ash Extract C	23%	8	23%	8
2 <sup>nd</sup> Round	1996				
	Fly Ash Extract A		25	11%	21
	Fly Ash Extract B		25	15%	21
	Fly Ash Extract C		25	12%	21
3 <sup>rd</sup> Round	1998				
	Fly Ash A	46%	30	33%	22
	Fly Ash B	43%	30	31%	22
	Fly Ash C	40%	30	23%	25
	Extract D	24%	30	24%	30
	Extract E	25%	30	25%	30
	Extract F	22%	30	22%	30
	Soil A	22%	29	16%	28
	Soil B	14%	29	14%	29
	Soil C	59%	29	59%	29
	Sewage Sludge D	110%	27	33%	21
	Sewage Sludge E	96%	28	33%	24
	Standard Z	37%	36	37%	36

Table 1. Continued.

	Year	Sample	RSD (all)	n	RSD (no outliers)	n
4 <sup>th</sup> Round	1999	Fly Ash A	49%	52	49%	52
		Fly Ash B	141%	52		
		Extract C	16%	51	16%	51
		Sediment A	34%	52	34%	52
		Sludge B	34%	50	34%	50
		Extract C	17%	51	17%	51
5 <sup>th</sup> Round	2000	Fly Ash A	46%	57	35%	50
		Fly Ash B	46%	57	32%	50
		Extract C	12%	56	12%	56
		Sediment A	62%	52	17%	48
		Sediment B	55%	51	18%	50
		Sediment C	263%	51	17%	44
6 <sup>th</sup> Round	2001	Standard E	18%	58	10%	50
		Fly Ash A	37%	63	32%	60
		Fly Ash B	85%	61	49%	59
		Fly Ash C	41%	62	31%	60
		Sludge A	96%	50	65%	49
		Clay B	90%	50	19%	49
7 <sup>th</sup> Round	2002	Sediment C	41%	49	26%	48
		Sediment D	39%	49	14%	48
		Standard F	19%	67	10%	63
		Standard H	29%	66	17%	62
		Fly Ash A	35%	80	19%	74
		Fly Ash B	40%	80	19%	74
7 <sup>th</sup> Round	2002	Fly Ash C	45%	80	40%	77
		Soil A	35%	68	18%	64
		Soil B	43%	66	20%	63
		Soil C	64%	68	64%	68
		Soil D	35%	66	18%	62
		Standard I	17%	93	11%	86

The results from Table 1 are graphically displayed in Figure 1. From this Figure clearly the increase of the number of laboratories in the study can be seen. This is reflected in the number of laboratories qualified going from 8 in the 1<sup>st</sup> round to 86 for the standard solution in the 7<sup>th</sup> round. The RSD corrected for outliers seems to be depended on the samples type and concentration. No clear relation with time was observed. Extracts and standard solutions seem easier to analyse indicating a large variance in the extraction procedure of the solid samples. In addition a significant higher RSD was seen when operating just above the detection limit for both fly ash and soil samples. Normally an RSD around 20% could be achieved except for some of the samples where the RSD was still over 60% after omitting outliers.

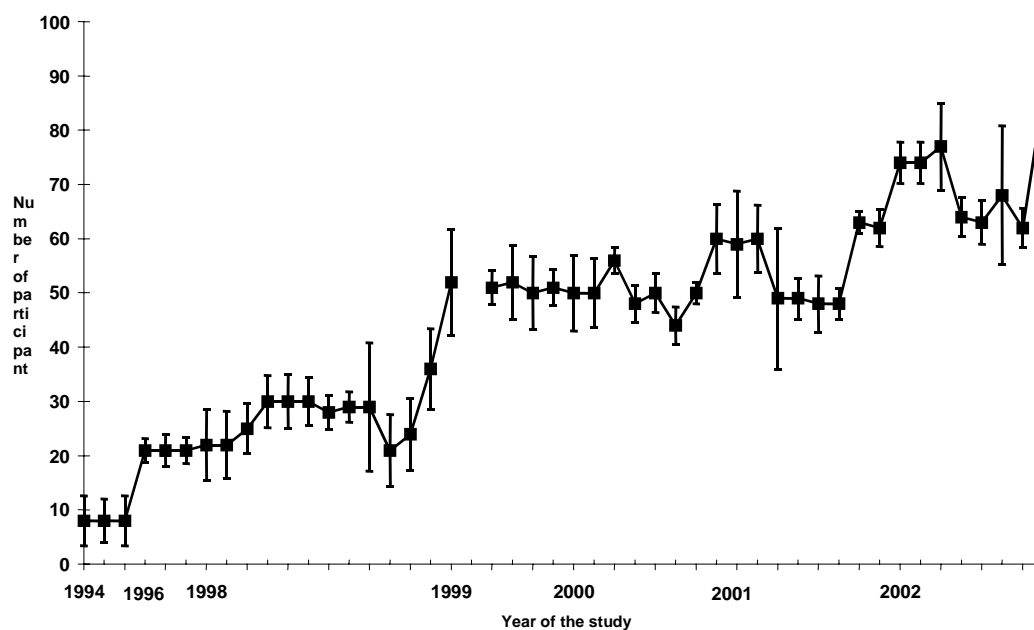


Figure 1. Number of participants in the different rounds of the International Intercalibration Study and the relative RSD of the data reported for the different samples after omitting obvious outliers.

The planar PCBs were reported by 70-80% of the participants since the 2<sup>nd</sup> round in 1996, the optional analysis of the WHO TEF assigned PCBs was first started in 1999 when around 45% of the reporting laboratories reported results for this compound class. In the 7<sup>th</sup> round in 2002 this number had gone up to the same number as the planar PCBs around 70-80% depending on the sample matrix.

### Acknowledgement

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### References

- <sup>1</sup> Bert van Bavel, Per Andersson, Nobuo Takeda and Christoffer Rappe. Results from and international intercalibration study on PCDDs and PCDFs in a fly ash extract. *Chemosphere* 32 (1996) 45-53.
- <sup>2</sup> Magnus Engwall, Gunilla Lindström and Bert van Bavel. Experiences from an international intercalibration of dioxin-like compounds in cod liver using bioassays. *Organohalogen Compounds* 2003 submitted.
- <sup>3</sup> [www.intercal.se](http://www.intercal.se)