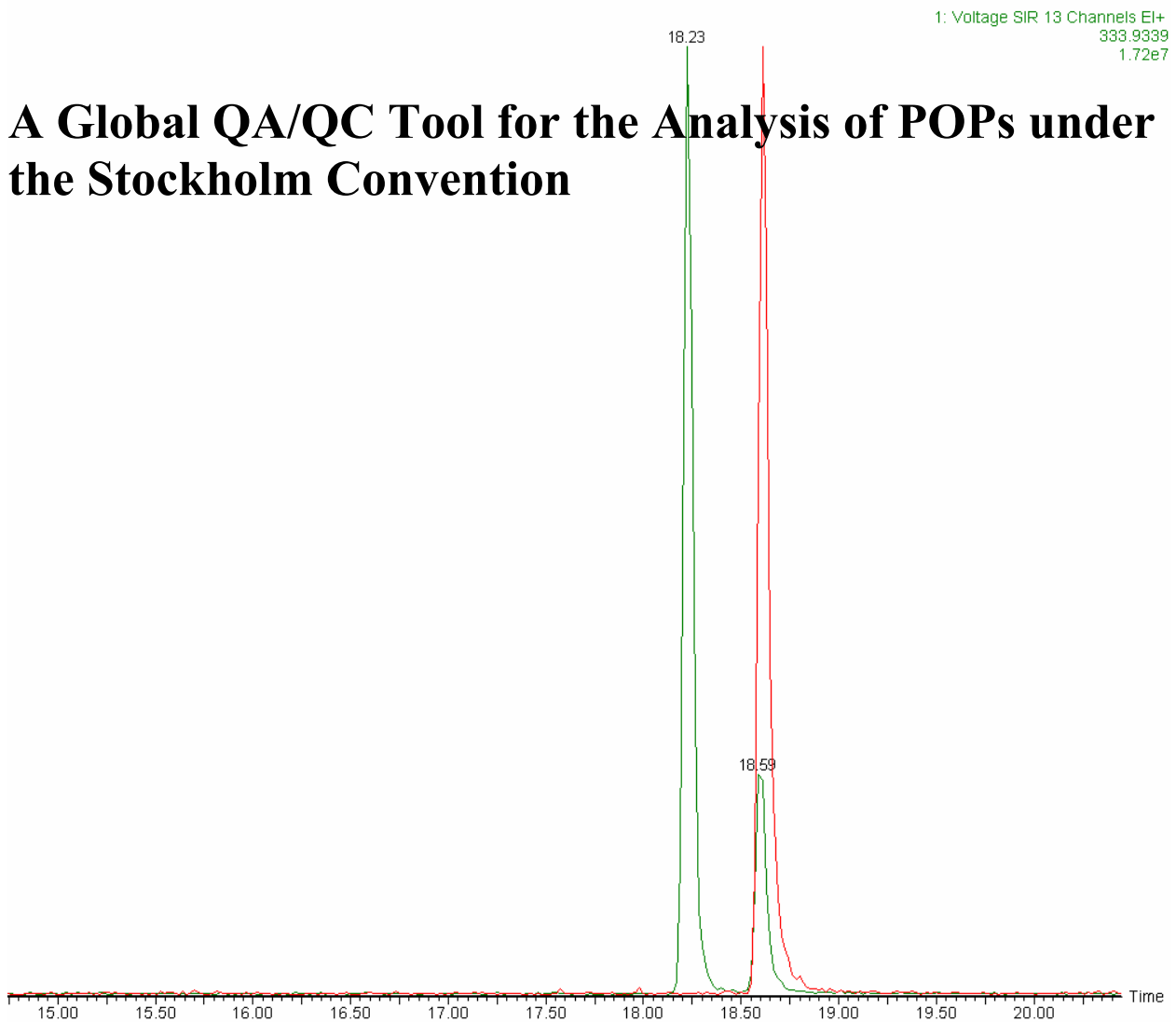




International Intercalibration Studies:

A Global QA/QC Tool for the Analysis of POPs under the Stockholm Convention



UNEP Chemicals

Geneva, December 2005

IOMC

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Title page: High resolution GC/MS chromatogram of 2,3,7,8-TCDD in a standard solution. Diagram courtesy of Dr. Bert van Bavel, Örebro University, Sweden

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Table of Content

	Page
Table of Content.....	i
List of Tables.....	ii
List of Figures.....	iii
Abbreviations and Acronyms.....	iv
1 Introduction.....	1
2 The TEF Concept for PCDD, PCDF and Dioxin-like PCB.....	2
3 Chemical Analyses.....	6
4 International Intercalibration Studies.....	11
4.1 General.....	11
4.2 Statistical Treatment of the Data.....	12
4.3 Z-Scores.....	16
4.4 Evaluation of Ten Rounds of International Intercalibration Studies (1994-2005).....	17
4.5 Regional z-Scores.....	21
5 Outlook and Future of Intercalibration Studies.....	23
6 Suggestions and Guideline before Participation in International Intercalibration Studies.....	25
7 A Practical Guideline for Starting Dioxin Laboratories.....	26
8 Annex 1: Results from International Inter-calibration Studies 1994-2005.....	28

List of Tables

		Page
Table 1:	Toxicity equivalency factors (TEFs) according the WHO (1998).....	3
Table 2:	Example of the TEQ calculation for a MSWI ash sample.....	4
Table 3:	TEFs for "dioxin-like" PCB (WHO 1998).....	5
Table 4:	Schedule International Inter-calibration on Soil/Sediment/Sludge and Incineration related samples	12
Table 5:	Compilation of the data of Ash sample of the 8th Round of the intercal study....	13
Table 6:	Qualification of z-scores after omitting obvious outliers outside 2x the RSD	14
Table 7:	Distribution of the participants of the 10th Round (2005) according to countries and regions	21
Table 8:	Regional z-scores (average of the absolute value) of the results of the 10 th Round and the number of results submitted by the participants per region	22
Table 9:	World wide interlaboratory comparison or intercalibration studies on PCDD/PCDF and other organic chemicals.....	23
Table 10:	RSDs from all samples analysed within the international intercalibration study on dioxin in solid samples 1994 to 2005.....	28
Table 11:	Total number of laboratories qualifying within 10% and 20% of the median consensus value of incineration and soil/sediment/sludge samples and extracts 1999-2005.....	30
Table 12:	Total number of laboratories qualifying within 5% and 10% of the median consensus value of standard solutions analysed between 1999 and 2005	31
Table 13:	Participants in the Soil/Sediment or Incineration Study 2005	32

List of Figures

	Page
Figure 1:	The chemical structure of PCDD and PCDF 2
Figure 2:	Example of the chemical structure of ‘dioxin-like’ PCB 4
Figure 3:	A typical sample clean up for dioxin analysis 6
Figure 4:	Clean up columns used for the analysis of dioxins and planar PCB in the 10 th Round of the international intercalibration study 2005 7
Figure 5:	A reconstructed selected ion recording (SIR) chromatogram (PCDD) of a sediment sample illustrating the enhanced separation of capillary columns (DB-5MS) 8
Figure 6:	GC columns used in the most recent round of the International Intercalibration (10 th Round 2005) 9
Figure 7:	The 3 SIR channels for TeCDF, showing mass (m/z) 303.9016 for the molecular ion (M) at the bottom, mass (m/z) 305.8987 for the most abundant ion in the molecular ion chlorine cluster (M + 2) in the middle, and mass (m/z) 317.9389 for the most abundant ion for the ¹³ C labelled internal standard of 2,3,7,8-TeCDF 10
Figure 8:	Data from the 8 th Round of the intercal study, high level fly ash B. 14
Figure 9:	Data from the 8 th Round of high level fly ash B 15
Figure 10:	Data from the 10 th Round, two identical standard solutions showing both the variation within the laboratories and the variation between the laboratories 15
Figure 11:	Z-scores calculated after omitting obvious outliers outside 2x the RSD. 17
Figure 12:	Number of participants in the international intercalibration study for each individual sample and the RSD after omitting obvious outliers during the period 1994-2005 18
Figure 13:	Number of participants within 10 and 20% of the median from the 4 th Round (1999) to the 10 th Round in 2005 for the fly ash samples. 19
Figure 14:	Number of participants within 10% and 20 % of the median since the 4 th Round (1999) for the soil samples 20
Figure 15:	Absolute z-scores of three selected laboratories adapted from data from the 6 th , 7 th , 8 th and 9 th Rounds of the international intercalibration study 25

Abbreviations and Acronyms

AHH	Aryl hydrocarbon receptor
AlOx	Alumina oxide
ASE	Accelerated solvent extraction
BFR	Brominated flame retardant(s)
CD	Compact disk
CRM	Certified reference material
EPA	Environmental Protection Agency
EU	European Union (25 Member States since 1 May 2004: Austria, Belgium, Czech Republic, Cyprus, Estonia, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Slovak Republic, Slovenia, Spain, Sweden, United Kingdom)
GC	Gas chromatography
GEF	Global Environment Facility
HBCCD	Hexabromocyclododecane
HCl	Hydrochloric acid
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry
IS	Internal standard
LRGC	Packed columns (low resolution gas chromatography)
LRMS	Low resolution mass spectrometry
M	Molecular ion
m/z	Molecular mass
MS	Mass spectrometry
MSWI	Municipal solid waste incinerator
ND	Not detected
ng	Nanogram
NIST	National Institute of Standards and Technology (Gaithersburg, MD, USA)
<i>p</i>	<i>para</i>
PBDEs	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo- <i>para</i> -dioxins
PCDF	Polychlorinated dibenzofurans
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
POPs	Persistent organic pollutants
QA/QC	Quality assurance/quality control
RRFs	Relative response factors
RS	Recovery standard
RSD	Relative standard deviation

SIR	Selected ion recording
SS	Sample standard
TEF	Toxicity Equivalency Factor
TEQ	Toxic Equivalent
UNEP	United Nations Environment Programme
WHO	World Health Organization

Homolog groups of the PCDD/PCDF:

TeCDD	Tetrachlorodibenzo- <i>p</i> -dioxin
PeCDD	Pentachlorodibenzo- <i>p</i> -dioxin
HxCDD	Hexachlorodibenzo- <i>p</i> -dioxin
HpCDD	Heptachlorodibenzo- <i>p</i> -dioxin
OCDD	Octachlorodibenzo- <i>p</i> -dioxin
TeCDF	Tetrachlorodibenzofuran
PeCDF	Pentachlorodibenzofuran
HxCDF	Hexachlorodibenzofuran
HpCDF	Heptachlorodibenzofuran
OCDF	Octachlorodibenzofuran

1 INTRODUCTION

Occurrence, distribution and formation of polychlorinated dibenzo-*para*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and other dioxin-like compounds have been discussed lively in the scientific literature since the early 1980. Now 25 years later PCDD/PCDF are routinely analysed in a large number of different types of samples. Nevertheless, dioxins are still in the news reporting high values especially due to accidental food contamination: levels above guideline concentrations in fish in certain areas or in eggs.

PCDD/PCDF have never been synthesised deliberately apart from the extreme small amounts for usage as analytical standards or toxicological tests. They are by-products of several industrial processes including production of herbicides (chlorinated phenoxy acids as in Agent Orange), chlorine bleaching of paper, chlorine production using mercury and carbon electrodes, and different incineration processes (hazardous and municipal waste incineration). In addition to dioxins resulting from human activity, recently also PCDD/PCDF in very old clay layers were found probably resulting from natural sources. However, the total amounts of 'naturally formed' dioxins are small compared to the anthropogenic sources.

The concentrations of PCDD/PCDF in environmental samples are normally at the ppt level (ng per kilogram or pg per gram), and thus some analytical skill is required detecting the dioxins among many interferences. A large number of national dioxin inventories have been done in the western world including Europe, the US, Canada and Japan. Much less data is available from developing countries in Africa, South and Central America or Asia. When now national implementation plans are done by Parties of the Stockholm Convention and other countries, it is very important that the quality of the data from those activities is controlled. This is of extreme importance that the results of national inventories can be compared. Data from inventories and measured environmental concentrations from one country should be comparable with data from countries in other regions. The analytical variance should be as small as possible and quantifiable. This is necessary to ground solid decision making in which analytical errors are eliminated between nations and regions. Most recently, this was emphasised in the regulation of levels of PCDD/PCDF in feed and food within the European Union. Low limit values were set for different animal feed and food, both within the EU and for products exported to the EU. It is expected that limits for the dioxin like PCB are to be included in 2006.

An approach that has been working very well to both improve the analytical quality and to quantify the uncertainty in analytical data is the organisation of interlaboratory comparison studies. This will be discussed in detail in this report focussed on the analysis of dioxins in soil, sediment, sewage sludge, and incineration samples. This approach is also useful and being used for other target POPs such as PCB, pesticides (including DDT, chlordanes, and toxaphene), brominated flame retardants (BFRs), or even heavy metals. Dioxin analysis is one of the most complicated analyses and the perfect example of what can be achieved with strict QA/QC and long-term interlaboratory studies. All knowledge acquired from the dioxin field can be readily applied to other target compounds including the POPs included in the Stockholm Convention.

2 THE TEF CONCEPT FOR PCDD, PCDF, AND DIOXIN-LIKE PCB

Although often reported as only one single value, PCDD and the structurally similar PCDF are in reality 210 different compounds consisting of 75 PCDD congeners and 135 PCDF congeners. The structures of both compound classes are shown in Figure 1; they consist of two aromatic rings bond together by oxygen with different chlorine substitution on the aromatic rings.

All 210 congeners are thus different compounds and exhibit very diverse chemical, physical and toxicological properties. All PCDD/PCDF are persistent but only 2,3,7,8 chlorine substituted congeners bioaccumulate and are found to be toxic. Different samples contain complex mixtures of PCDD or PCDF congeners; fly ash samples can contain nearly all the congeners, which is also often the case for soil and sediment samples. The higher chlorinated PCDD (OCDD) for example dominates sewage sludge. Other samples contain only a limited number of congeners. Biological samples higher up the food chain including humans contain only congeners with chlorine substitution in the 2,3,7,8 positions.

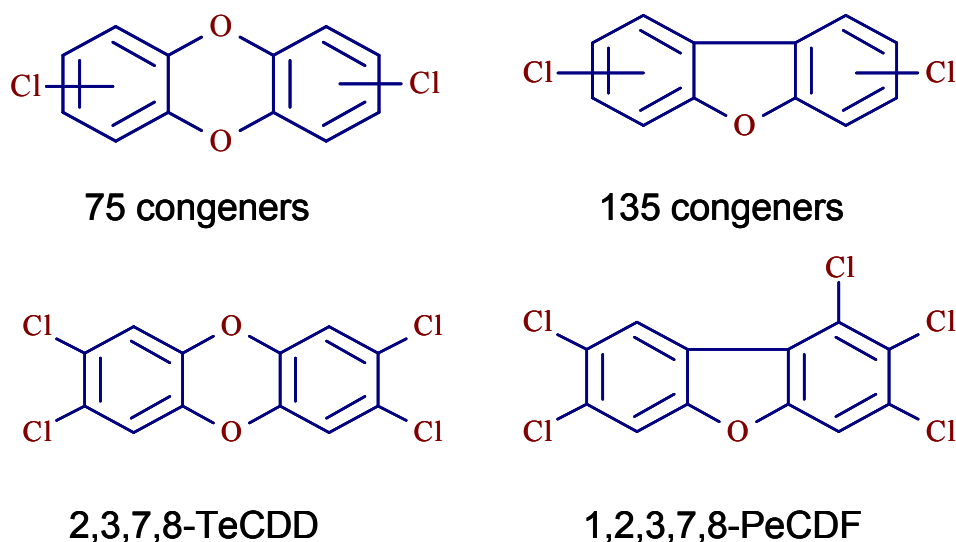


Figure 1: The chemical structure of PCDD and PCDF

PCDD and PCDF with chlorine substitution in the 2,3,7,8 positions have been found toxic and potent inducers of the AHH receptor. Non 2,3,7,8-chlorine substituted PCDD and PCDF show only very limited toxic responses. To get an overview of the ‘dioxin-like toxicity’ in the sample, the toxicity of the PCDD and PCDF with chlorine substitution in the 2,3,7,8-positions is often related to the most toxic dioxin; 2,3,7,8-TeCDD. This is the basis for the TEF concept where 2,3,7,8-TeCDD is assigned a toxicity equivalency factor (TEF) of 1, and the other 17 PCDD/PCDF have TEFs assigned ranging from 1 to 0.0001. The WHO-TEFs as established in 1998 are given in Table 1.

Table 1: Toxicity equivalency factors (TEFs) according the WHO (1998)

PCDD	TEF
2,3,7,8-TeCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0001
PCDF	
2,3,7,8-TeCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0001

When reporting the concentrations of PCDD and PCDF, the measured mass concentrations in an environmental sample are multiplied with the respective TEF for each of the congeners and a total toxic equivalent (TEQ) is calculated. This is illustrated in Table 2 where the toxic equivalent (TEQ) is calculated for a municipal solid waste incinerator ash sample.

$$\text{TEQ} = \sum_{i=1}^N C_i \times \text{TEF}_i$$

Using the formula above, the concentrations in ng/kg in the second column in Table 2 are multiplied by the TEF factor resulting in the levels expressed in ng TEQ/kg (column 4), these values are then summed up to give the total TEQ at the bottom of Table 2.

Several PCB can adopt a planar structure with the biphenyl ring located in the same plane geometry. This configuration is energetically favourable for PCB with no chlorine substitution in the *ortho* positions but can also be adopted by PCB with only one chlorine atom in the *ortho* positions. This is illustrated in Figure 2 showing both a planar or non *ortho* PCB with no chlorine atoms in the *ortho* positions and a mono *ortho* chlorine substituted PCB containing one chlorine atom in the *ortho* position. Adopting a co-planar structure these PCB resemble the planar chlorinated dioxins and furans and can bind to the AHH receptor in a similar way. This was recognized already in an early stage for three of the planar PCB, PCB #77, #126 and #169 and later for the mono *ortho* substituted PCB, PCB #105, PCB #114, PCB #118, #123, #156, #157, and #167. Also, an additional planar PCB, #81, was added to the WHO-TEF list in 1998.

Table 2: Example of the TEQ calculation for a MSWI ash sample

PCDD	Concentration (ng/kg)	TEF	TEQ (ng/kg)
2,3,7,8-TeCDD	12	1	12
1,2,3,7,8-PeCDD	28	1	28
1,2,3,4,7,8-HxCDD	30	0.1	3
1,2,3,6,7,8-HxCDD	72	0.1	7.2
1,2,3,7,8,9-HxCDD	41	0.1	4.1
1,2,3,4,6,7,8-HpCDD	610	0.01	6.1
OCDD	1850	0.0001	0.185
PCDF			
2,3,7,8-TeCDF	85	0.1	8.5
1,2,3,7,8-PeCDF	90	0.05	4.5
2,3,4,7,8-PeCDF	82	0.5	41
1,2,3,4,7,8-HxCDF	91	0.1	9.1
1,2,3,6,7,8-HxCDF	89	0.1	8.9
1,2,3,7,8,9-HxCDF	23	0.1	2.3
2,3,4,6,7,8-HxCDF	90	0.1	9
1,2,3,4,6,7,8-HpCDF	29	0.01	2.9
1,2,3,4,7,8,9-HpCDF	40	0.01	0.4
OCDF	160	0.0001	0.016
Total TEQ			147

The TEFs for the four coplanar PCB and eight *mono-ortho* substituted PCB are given in Table 3. Because of the TEF concept used to report dioxins and dioxin-like compounds it is essential that congener-specific analyses are performed. Co-elution or inferences can result in large errors and wrong TEQ values are obtained. Although the situation is extreme for PCDD and PCDF, only 17 toxic congeners to be analysed among 210 possible congeners at ppb, ppt or even ppq level also other compound classes including PCB, pesticide or brominated flame retardant (BFR) exhibit similar problems. It is therefore a real challenge for the analyst to come up with the ‘right’ and usable results.

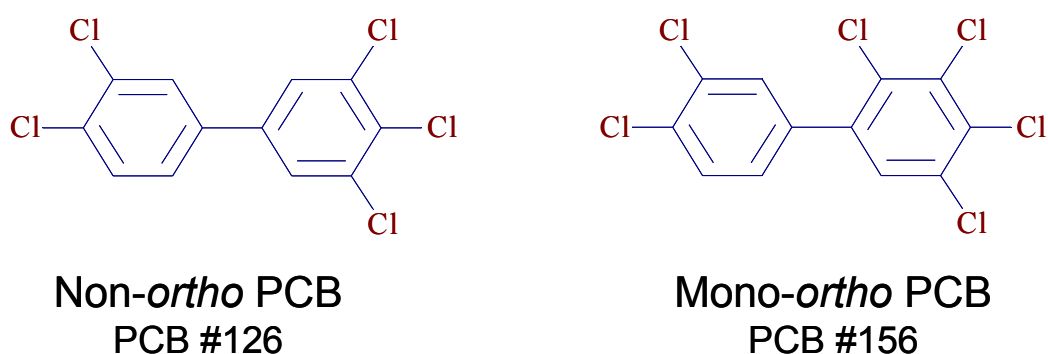


Figure 2: Example of the chemical structure of ‘dioxin-like’ PCB

Table 3: TEFs for "dioxin-like" PCB (WHO 1998)

coplanar or <i>non-ortho</i> PCB	TEF
PCB #77	0.0001
PCB #81	0.0001
PCB #126	0.1
PCB #169	0.01
<i>mono-ortho</i> PCB	
PCB #105	0.0001
PCB #114	0.0005
PCB #118	0.0001
PCB #123	0.0001
PCB #156	0.0005
PCB #157	0.0005
PCB #167	0.00001
PCB #189	0.0001

3 CHEMICAL ANALYSES

Congener specific analysis of PCDD/PCDF is best achieved by high resolution mass spectrometry (HRMS) coupled to high resolution gas chromatography (HRGC) after elaborate extraction and clean-up procedures. Soxhlet extraction using organic solvents (toluene, hexane, acetone) is the most used extraction technique for solid samples although accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE) also can be used. This was confirmed in the 10th Round of the international intercalibration study (2005) in which more than 100 laboratories participated. Only two laboratories used a different solvent than toluene (methylene chloride or a mixture of hexane/acetone) and only one laboratory used microwave assisted extraction. Nine laboratories used accelerated solvent extraction (ASE) or pressurised liquid extraction using toluene at elevated temperatures and pressure. For the analysis of ash samples there is some debate in the international literature if sample pre-treatment with acid (mainly HCl) is necessary. Ten participants (10%) decided not to use this treatment, although this procedure is highly recommended for complex samples such as fly ash. For sediments, the addition of copper to reduce sulphuric compounds might be necessary during the extraction stage or early in the clean-up stage.

Further clean-up of the extract is done by open column chromatography using acid/base modified silica and alumina oxide (AlOx) or Florisil. The final separation is done using carbon columns, which enable the planar compounds (PCDD, PCDF, and dioxin-like PCB) to be separated from the non-planar compounds. The open column clean-up procedure is very similar for many sample matrices after the extraction stage. Many laboratories use in-house methods based on the scheme in Figure 3. Recently also automated systems based on the same three open columns have become available.

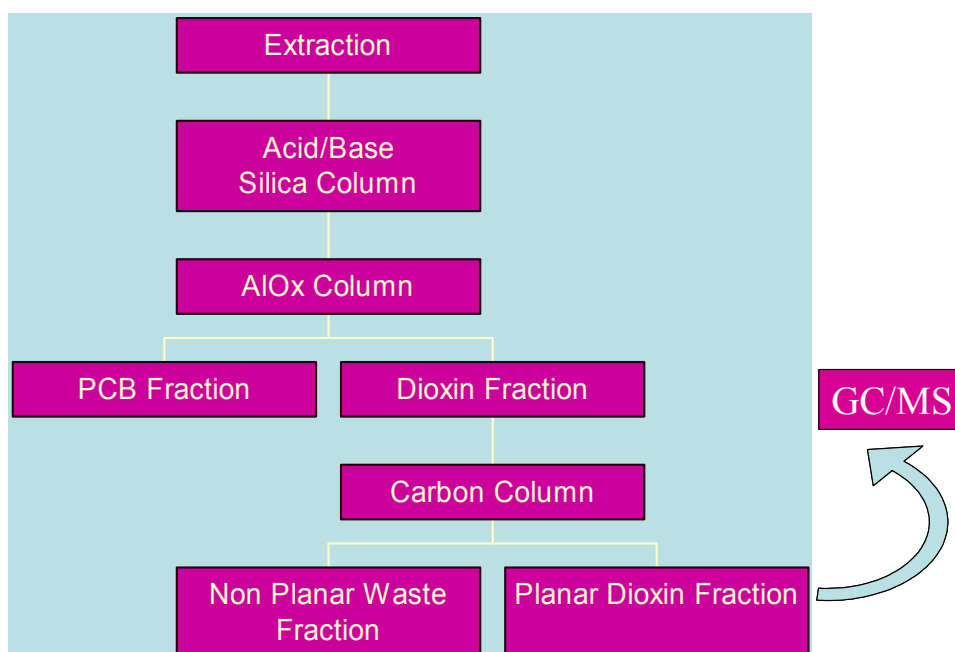


Figure 3: A typical sample clean-up for dioxin analysis

Although the sample clean-up and extraction procedures have improved and automated systems have become available many laboratories still use procedures based on the clean-up scheme in Figure 3. It should be noted that all steps normally take one day of work for a set from five to ten samples. This implies that it might take at least four days to get an extract ready for GC/MS analysis. The usage of different clean-up columns is given in Figure 4 where the clean-up methods used by the participants in the 10th Round of the international intercalibration study are summarized. Additional clean-up was performed by using sulphuric acid, silver nitrate or Florisil. An automated system (Powerprep) based on the multi silica column, the alumina oxide column, and the carbon column was used by ten of the participants.

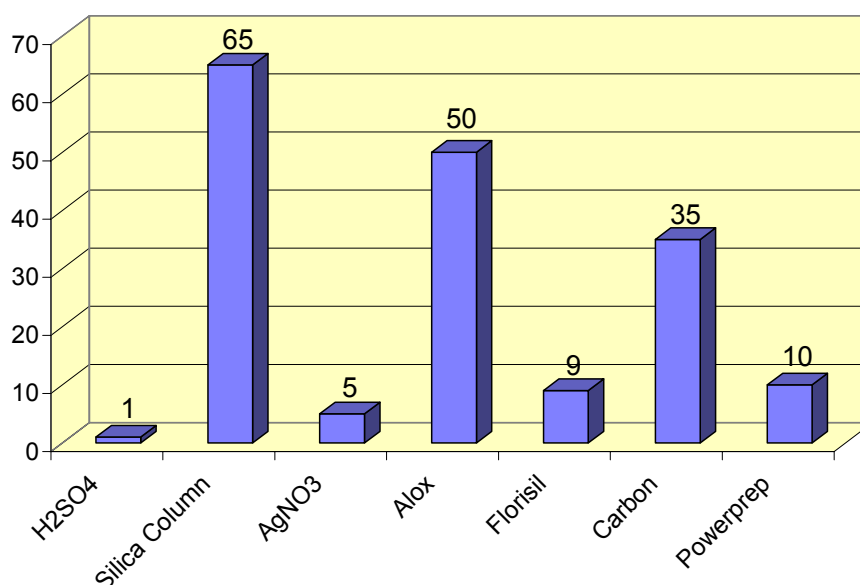


Figure 4: Clean up columns used for the analysis of dioxins and planar PCB in the 10th Round of the international intercalibration study 2005

When PCDD/PCDF were first found in environmental samples analyses were performed using low resolution mass spectrometry (LRMS) and packed columns (LRGC). This did not allow congener specific analysis and many interferences were present in the produced chromatograms. Since these first publications a lot has changed and the introduction of capillary columns and high resolution GC/MS has resulted in less interferences and baseline separation of nearly all the toxic 2,3,7,8-substituted PCDD and PCDF congeners. This finding is illustrated by a chromatogram of one of the samples from one of the last interlaboratory comparison studies in Figure 5.

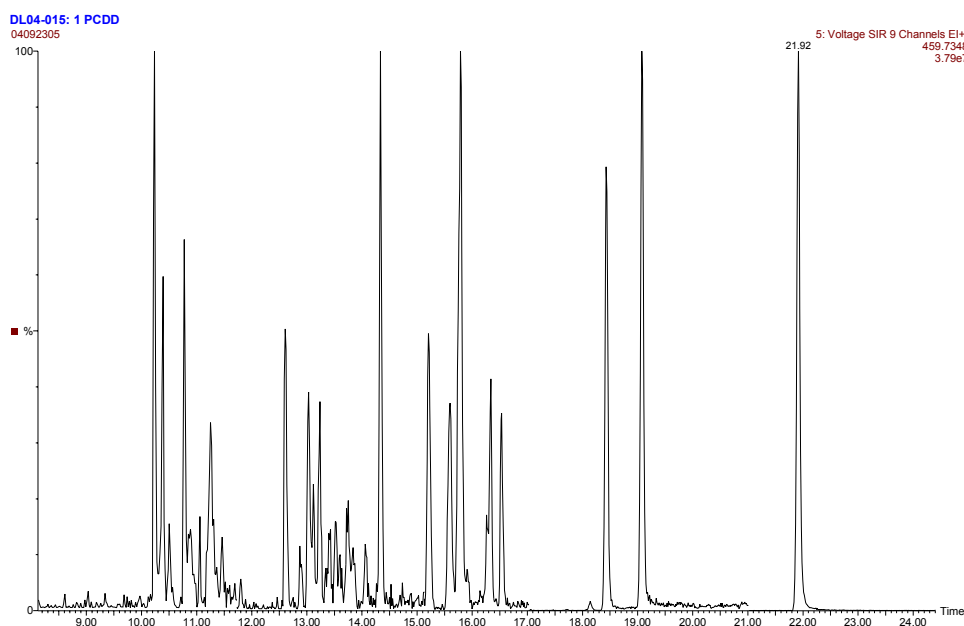


Figure 5: A reconstructed selected ion recording (SIR) chromatogram (PCDD) of a sediment sample illustrating the enhanced separation of capillary columns (DB-5MS)

Although separation of PCDD/PCDF on capillary columns has improved during the last decade, it is still difficult to achieve baseline separation of all toxic 2,3,7,8-substituted congeners in one GC run. Therefore, most laboratories run complex samples (soil, sediments, ash or emission samples) on a confirmation column after positive identification of the toxic congeners. Recently custom designed ‘dioxin’ columns have become available, reducing the need for confirmation columns.

However, the most used columns including DB-5MS or DB-5 do not separate all toxic congeners. It is not exactly clear how this affects the total TEQ results and this is again very depended on the sample type and the complexity of the dioxin pattern in the sample. Biological samples for example, especially higher up the food chain, merely contain the 2,3,7,8-substituted congeners exclusively. In Figure 6, the columns used for the analysis of the ash samples of the 10th Round of the international intercalibration are given. In addition 22 laboratories used a confirmation column to be able to completely separate all 2,3,7,8-substituted PCDD/PCDF.

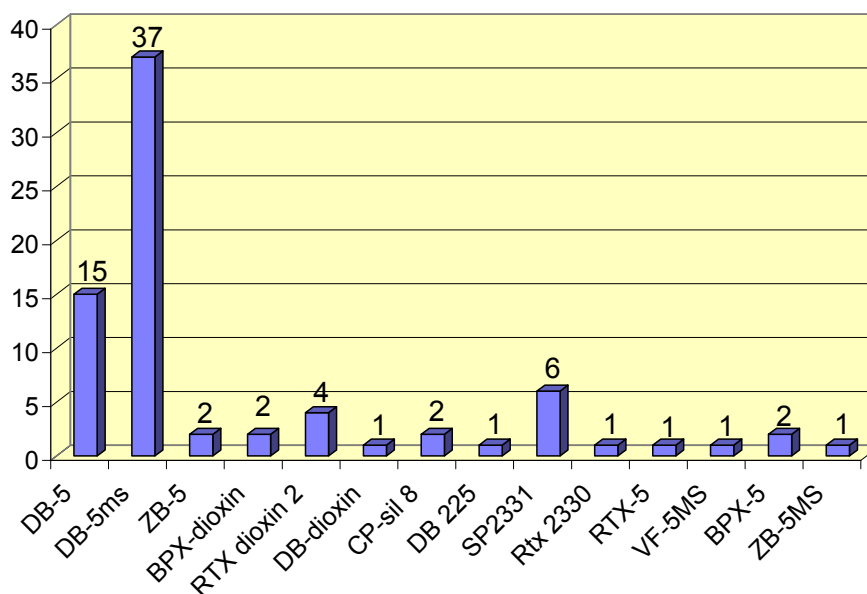


Figure 6: GC columns used in the most recent round of the International Intercalibration (10th Round 2005)

The usage of extensive sample clean-up and sample concentration was made possible through the availability of ¹³C labelled internal standards, these compounds behave exactly the same properties as their native counterparts but can be distinguished by mass spectroscopy. Normally, the twelve ¹²C carbon atoms in the two biphenyl rings are replaced by ¹³C carbon atoms resulting in an identical molecule with a mass of 12 units higher. All seventeen 2,3,7,8-substituted PCDD/F are now available as ¹³C marked internal standards in addition to several non 2,3,7,8-substituted ¹³C labelled PCDD or PCDF. These standards can be used as sample (SS), internal (IS) or recovery standards (RS). The usage of a ¹³C standard added before extraction is illustrated in Figure 7.

An important QA/QC criteria is also illustrated in Figure 7; the chlorine isotope ratio. Because of the natural occurrence of both ³⁵Cl and ³⁷Cl atoms, several POPs including PCDD/PCDF containing chlorine show a special 'chlorine cluster' when analysed by mass spectrometry. The abundance of the molecular ion (M) and the chlorine isotope (M + 2) of 2,3,7,8-TeCDF in Figure 7 should be within 15% of the theoretical ratio of 77%.

Nearly all laboratories use high resolution mass spectrometry operated at 10,000 resolution to achieve the best selectivity in combination with the best sensitivity. In the 10th Round of the International Intercalibration study only four laboratories used low resolution (quadrupole) instruments and two laboratories MS/MS (ion trap) instruments. Most standard methods require or recommend the use of high resolution mass spectrometry operated at 10,000 resolution to avoid interferences during GC/MS detection.

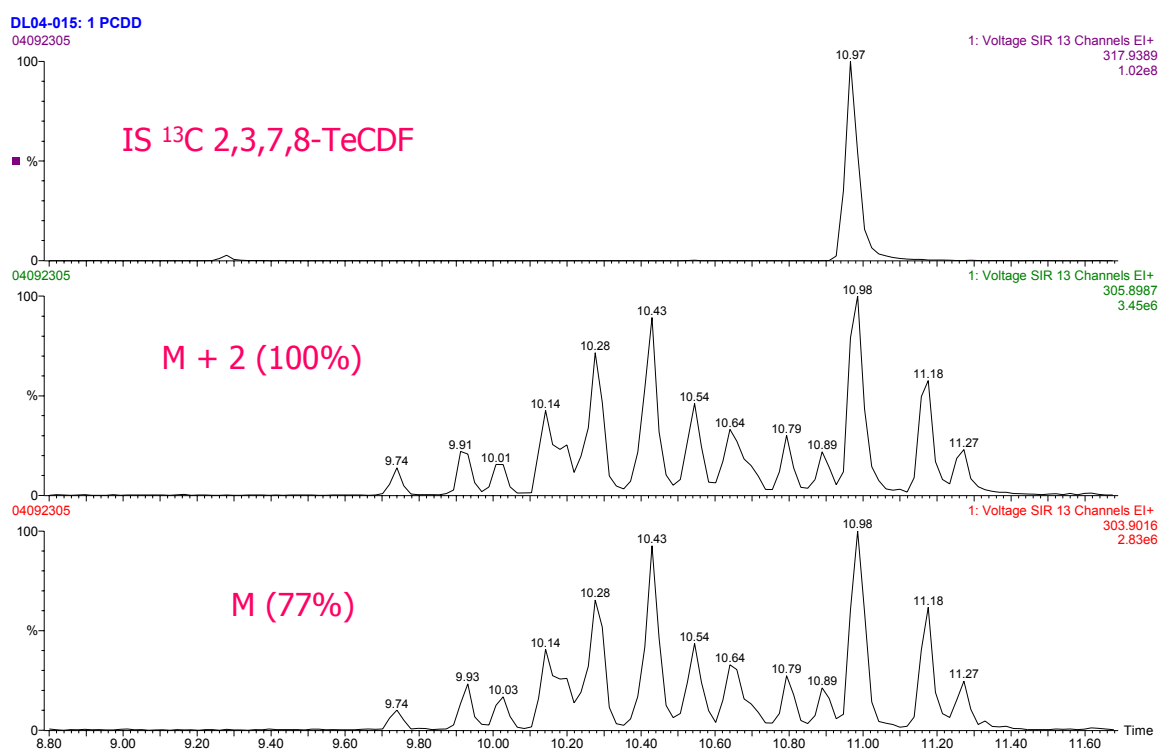


Figure 7: The 3 SIR channels for TeCDF, showing mass (m/z) 303.9016 for the molecular ion (M) at the bottom, mass (m/z) 305.8987 for the most abundant ion in the molecular ion chlorine cluster (M + 2) in the middle, and mass (m/z) 317.9389 for the most abundant ion for the ^{13}C labelled internal standard of 2,3,7,8-TeCDF

For the analysis of PCDD/PCDF, several standard methods are available from the US-EPA (EPA 1613), the European Union (EN 1948) or Japan (JIS). The majority of laboratories are using methods based on US-EPA method 1613. For example, for the samples distributed for the 10th Round of the international intercalibration study more than 70 percent of the participants used EPA-based methods. The QA/QC criteria of the standard methods are very similar and only differ on a few details. The QA/QC criteria are summarised in short below; more details can be found in the respective methods.

The recovery of the internal standards added before extraction should be within 50% to 150%. This recovery is calculated against 2-4 ^{13}C labelled recovery standards added just before the final GC/MS analysis. The recoveries indicate loss of the target compounds during sample handling, extraction and clean-up. The relative retention time of the target compound compared to the internal standard should be within a set time interval (1-5 s) for positive identification. The chlorine isotope ratio should be within 15% of the theoretical chlorine isotope ratio when measuring the two most abundant ions of the chlorine cluster to exclude co-elution of interferences. Additional QA/QC features are the linearity of a 3- or 5-point calibration curve showing relative response factors (RRFs) against the internal standard within 15%. The levels in laboratory blank samples run with each batch of samples should be less than 10% of the values found in the samples. It is also common that a certified reference material (CRM) or an in-house QA/QC sample is analysed with each batch of samples.

4 INTERNATIONAL INTERCALIBRATION STUDIES

4.1 General

With standardised methods in place and in combination with international or national accreditation according to ISO norms, the quality of the data produced is well documented but the quality of that data is not yet assured or accessed. External QA/QC can be achieved by participating in international intercalibration or interlaboratory comparison studies also referred to as round robin studies in the international literature. This kind of studies makes up important control criteria if properly organised. Therefore, international intercalibration studies are important QA/QC tools.

The basic idea of an interlaboratory study is to send representative samples without further information to a large number of laboratories. The participants analyse 'blind' samples with in-house methods and technology and report back to the organiser. This not only enables validation of the performance of the laboratories but also gives an overview of the state of art of the analyses. In addition to real samples, standard solutions and extracts are used to access specific analytical problems such as extraction efficiency or the control of calibration samples. The analysis of blind samples within international QA/QC studies gives better and more objective information than the analysis of CRMs or in-house QA/QC samples of which the levels are known. It is also important that the studies are organised on a regularly basis, preferable each year. For dioxin analysis two major studies are organised; the International Intercalibration on soil/sediment/sludge and fly ash organised by MTM Research Centre, Örebro University, Sweden and the study on food samples organised by the Institute of Public Health in Oslo, Norway.

Both studies are based on the same principle and are discussed below. A broad call to participate in the studies is send out in September/October each year and interested laboratories register for the appropriate study during this period. During October/November representative samples are produced and if necessary tested for homogeneity. In addition, extracts and standard solutions are prepared and tested. Normally three to four samples and a standard solution are sent for each study, covering different concentrations ranges and sample types. The samples are sent by an international carrier in special containers with absorbent material in the case of leakage or other accidents in December/January. For most shipments, this results in the samples being in the laboratory within 2-4 days. Due to more strict security since 2001, some delays have occurred during shipment. Additional paperwork done by the international carrier or the organiser has again assured that all packages arrive within a reasonable amount of time (2-4 days). The control of the shipments, through an Internet-based system, is essential. This way both the organiser and the participating laboratories are able to monitor the samples during shipment.

A period of three months to the end of March is given to the participants to analyse the samples and report the results through a results file in MSEXCEL format. This file is send in advance to all participants to facilitate the reporting of the results. The strict deadline at the end of March has to be enforced to be able to present the data at the yearly Dioxin symposium, which is typically held in August/September and to give all participants a possibility to check their results for writing mistakes or mistakes during data transfer to a database. During these annual Dioxin Symposia, the results are presented and discussed in an

informal lunch session. Taking both, comments and suggestions, from this meeting and reactions through @mail into account the final report is written during September/October. The report is made available in pdf-format in November through the internet and finally a printed copy is send to all participants. All results are presented with a code for each participating laboratory. This code will not be disclosed to third parties unless permission is given by the participating laboratory. The Food study organised by the Institute of Public Health in Oslo has a similar set-up and is also organised on a yearly basis.

Table 4. Schedule International Intercalibration on Soil/Sediment/Sludge and Incineration related samples

Time period	Activity
Sep/Oct 2005	Call to participate send by @mail
Oct/Nov 2005	Preparation samples
Dec 2005/Jan 2006	Shipment of samples
31 March 2006	Deadline to report results
April/May 2006	Control of results
June/July 2006	Validation results
Aug 2006	Presentation at International Dioxin Symposium
Sep/Oct 2006	Final report available on the internet

In international intercalibration studies, the laboratories are asked to treat the samples as routine samples and use in-house methods to resemble a 'normal' analysis as closely as possible. The participants use their own standard solutions and calibration standards and are to report all seventeen 2,3,7,8-substituted PCDD/PCDF, the four planar PCB, and the eight WHO-TEF assigned *mono-ortho* PCB all given in Table 1 and Table 3. In addition the PCDD/PCDF TEQ, the PCDD/PCDF + planar PCB TEQ and the total TEQ (PCDD/PCDF + all dioxin-like PCB) calculated by the formula given on page 3.

Detailed information on the method has to be reported in the results form on the extraction method used, the extraction solvent, the clean up method, the GC columns used, the GC/MS system, the number of standards and on which method the procedure was based. All the results files in EXCEL format are read into a database for further evaluation. When this process is done, a 'preliminary' results' file is send back to the participants for control of writing and transfer errors.

4.2 Statistical Treatment of the Data

Different approaches exist to evaluate the results in an international intercalibration study. The most basic way to evaluate the data is to calculate the mean, the median, the range of reported results (min, max), the standards deviation (RSD) and the relative RSD as a percentage $((RSD/mean) * 100\%)$. This is illustrated in Table 5 where the results of a high level fly ash sample of the 8th Round (2003) are given.

Table 5: Compilation of the data of Ash sample of the 8th Round of the intercal study

	Average	Median	Min	Max	SD	%RSD
2,3,7,8-TeCDD	2.9	3.1	0.4	7.0	1.1	38%
1,2,3,7,8-PeCDD	22.2	22.4	0.9	54.1	7.7	34%
1,2,3,4,7,8-HxCDD	27.6	28.3	3.1	69.1	9.6	35%
1,2,3,6,7,8-HxCDD	38.0	38.0	4.2	105.8	13.6	36%
1,2,3,7,8,9-HxCDD	46.9	44.7	5.5	137.6	20.2	43%
1,2,3,4,6,7,8-HpCDD	237.0	231.0	22.8	1371.0	156.6	66%
OCDD	287.7	261.0	16.4	2822.5	315.9	110%
<hr/>						
2,3,7,8-TeCDF	5.2	4.4	0.67	32.0	4.6	89%
1,2,3,7,8-PeCDF	11.4	11.6	1.60	27.0	4.5	40%
2,3,4,7,8-PeCDF	17.9	17.8	3.90	51.0	7.1	40%
1,2,3,4,7,8-HxCDF	27.1	26.1	3.40	92.0	13.9	51%
1,2,3,6,7,8-HxCDF	25.7	26.5	2.84	68.2	9.1	35%
1,2,3,7,8,9-HxCDF	6.8	2.2	0.02	57.6	11.6	169%
2,3,4,6,7,8-HxCDF	26.8	28.0	0.99	82.5	14.0	52%
1,2,3,4,6,7,8-HpCDF	122.9	122.3	9.21	289.6	45.5	37%
1,2,3,4,7,8,9-HpCDF	11.6	11.7	1.62	24.8	4.0	35%
OCDF	44.7	45.9	3.43	113.2	18.2	41%
<hr/>						
TEQ (PCDD/DF)	58.9	59.0	6.46	148.9	20.8	35%
<hr/>						
PCB #77	4.6	4.6	0.43	9.1	1.5	34%
PCB #126	5.0	5.0	1.65	10.6	1.6	32%
PCB #169	1.9	2.0	0.59	5.3	0.7	37%
PCB #81	0.9	0.9	0.32	2.4	0.4	40%
<hr/>						
TEQ (including coplanar PCBs)	63.0	60.4	25.37	149.5	20.2	32%
<hr/>						
Mono ortho PCBs						
PCB #105	3.7	2.2	1.02	70.4	9.5	257%
PCB #114	1.1	0.4	0.06	26.8	3.7	340%
PCB #118	3.8	2.1	0.64	60.2	8.5	222%
PCB #123	0.9	0.3	0.00	14.6	2.2	235%
PCB #156	3.9	2.6	0.71	63.5	8.3	215%
PCB #157	2.0	1.2	0.41	42.9	5.6	278%
PCB #167	1.6	1.0	0.27	27.1	3.6	230%
PCB #189	2.6	2.1	0.97	30.4	3.9	149%
<hr/>						
TEQ Total	63.3	61.2	25.37	149.5	20.7	33%

This works well if the data shows a 'normal' distribution. Other methods are also in use including robust statistics (WEPAL) and Cofino statistics (QUASIMEM). The difference in mean calculated by the two other methods is relatively small when the medium and median are close to each other. A critical point however is how outliers are identified in the 'raw' data file.

Two different approaches to validate the results are commonly used: a set value of the RSD or 'floating' RSD determined by the results. In order to study the improvement of the analysis over a long period of time, the second alternative results in RSDs depending on the degree of difficulty of the samples and the analytical skills of the laboratories. This is the preferred method for the more complex and challenging chemical analysis and is achieved by omitting so-called obvious outlier outside 2x the RSD from the mean on a PCDD/PCDF TEQ basis. For the example below this would be values outside 63.0 ± 41.6 (2x RSD). This is further illustrated in Figure 8 where the five outliers are marked with an arrow.

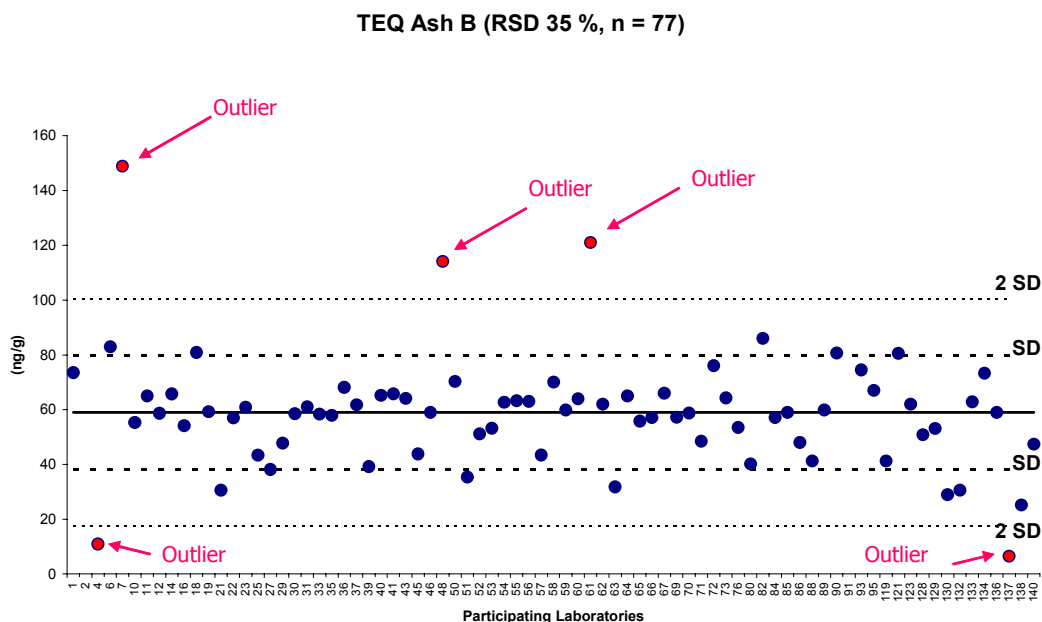


Figure 8: Data from the 8th Round of the intercal study, high level fly ash B. The laboratory code is given on the x-axes. The TEQ reported by each laboratory, the mean of all data, 1x the RSD and 2x the RSD are also given. Results outside 2x the RSD are considered outliers

These results outside 2x the RSD are deleted and a new value for mean value, median value, and standard deviation is calculated. This procedure results in a better RSD and five results that were not classified. For the example above, the RSD for the total PCDD/PCDF TEQ improved from 35% for all 77 laboratories reporting to 23% for 72 laboratories after omitting the five outliers. This is illustrated in Figure 9 where the number of classified results are plotted together with the mean, 1x RSD and 2x the RSD. The laboratories are classified as **good** if the results are within 1x the RSD, **satisfactory** when within 2x the RSD and **questionable** when within 3x the RSD. Outliers or results outside 3x the RSD are classified as **unsatisfactory**.

Table 6: Qualification of z-scores after omitting obvious outliers outside 2x the RSD

Z-score	Z-score	Qualification
$z\text{-score} < -3$	$z\text{-score} > 3$	Unsatisfactory
$-3 < z\text{-score} < -2$	$2 < z\text{-score} < 3$	Questionable
$-2 < z\text{-score} < -1$	$1 < z\text{-score} < 2$	Satisfactory
$-1 < z\text{-score} < 0$	$0 < z\text{-score} < 1$	Good/Excellent

The results on TEQ basis displayed from Figure 8 to Figure 10 contain valuable information for the participants on the quality of their data. Similar figures are also given for the individual PCDD/PCDF and PCB congeners. These figures are useful for the participants to find out which congeners might be responsible for the deviation from the mean TEQ value. It is important to evaluate the results on a congener specific basis. The total TEQ is a weighted average (see example in Table 2) and this might disguise problems on the individual congener level. In Figure 8 the raw data is displayed and the obvious outliers (not qualified) are identified, in Figure 9 the obvious outliers are removed and the qualified laboratories are

displayed. To study the variation within the laboratories, identical samples are distributed without further knowledge to the participating laboratories. This results in a figure both showing the within laboratory variation and the between laboratory variation. As an example, the results of a standard solution are given in Figure 9.

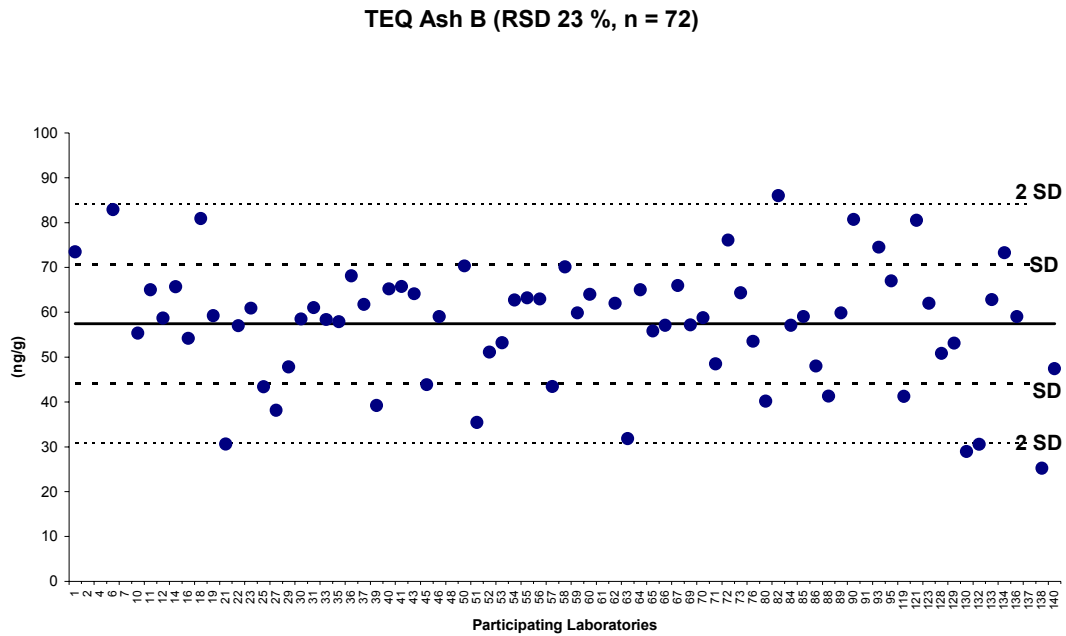


Figure 9: Data from the 8th Round of high level fly ash B
 The TEQ reported by each laboratory, the mean of all data, 1x the RSD and 2x the RSD after deleting the results outside 2x the RSD. Laboratory code displayed on the x-axis

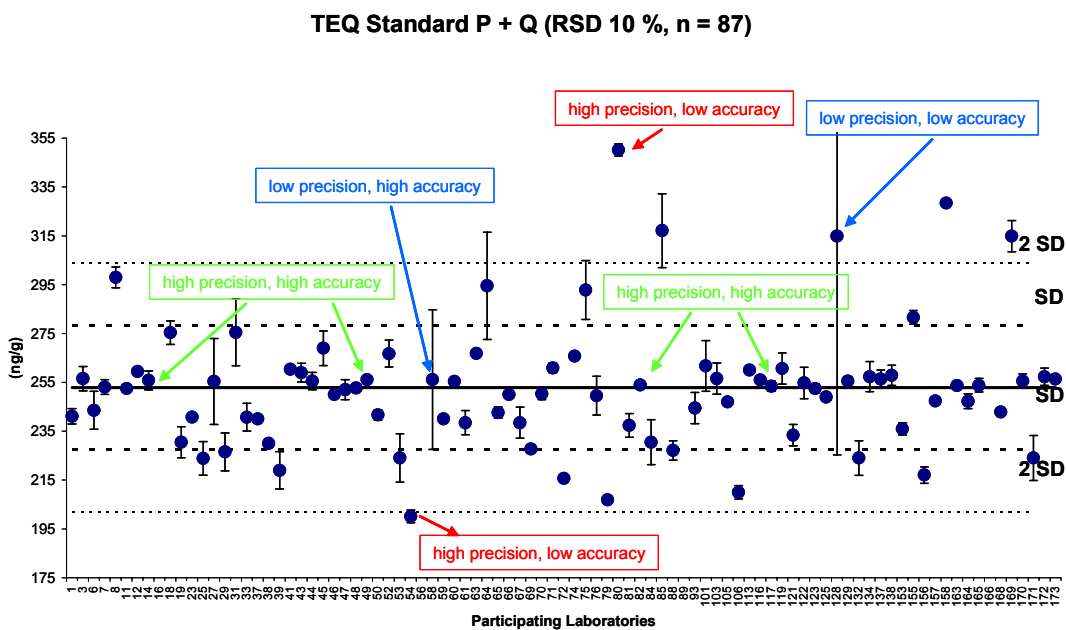


Figure 10: Data from the 10th Round, two identical standard solutions showing both the variation within the laboratories and the variation between the laboratories

In Figure 10 the performance of the laboratories can be distinguished according to accuracy (the closeness of a result to its true or accepted value) and precision (the closeness of data to other data that have been obtained in the same way). Although the laboratories marked in red show good precision, the results are not accurate and their mean result is far from the consensus value. On the other hand, one of the laboratories marked in blue shows good accuracy but low precision. The other lab marked in blue shows both low accuracy and precision. The laboratories marked in green are examples where the laboratories show both good precision (inner laboratory variation) and accuracy (closeness to the consensus value).

Another point of discussion is the treatment of non-detects (ND) when a detection limit or less than value is reported. Both 'lower bound' when NDs are not included in the total TEQ or 'upper bound' when the DL or the less than value, which is reported are used. The difference between upper bound and lower bound is generally small for environmental samples when enough sample volume is available but might be more problematic for human or other biological samples, which contain low levels and only limited material is available for analysis.

The usage of a floating RSD depending on the actual results submitted by the participants has two advantages over the usage of a set RSD. When the RSD is dependent on the reported results this gives an indication of the analytical quality at just that moment in time for a certain sample. When analytical methods are just established or implemented, this RSD is expected to be somewhat larger, while if standard methods have existed for longer period of time the RSDs will become smaller. It also results in more fair classification criteria depending on the performance of other laboratories or the kind of samples. Samples containing interferences and/or very small amounts of the target compounds are generally more difficult and result in larger RSDs.

4.3 Z-Scores

Another way to represent the data and to classify laboratories is to calculate so called z-scores, calculated as $z = (x-X) / SD$, where x = reported value, X = consensus value or mean value and SD the standard deviation. A graphical representation of z-scores calculated for a low level soil sample from the 8th Round of the International Intercalibration study is given in Figure 11. The overall RSD of the results for this sample was 20 % for 69 laboratories out of a total of 73. In this example the z-scores of 56 laboratories are between -1 and 1 and are classified as good, 12 laboratories are classified as satisfactory showing a z-score between 1 and 2 (lab codes 21, 41, 66, and 125 in Figure 11) or -1 and -2 (lab codes 8, 9, 50, 89, 155, 158), the results of two participants (10, 59) is questionable. The results of 5 laboratories were classified as unsatisfactory, z-score larger than 3 or -3 (lab codes 55, 140, 166).

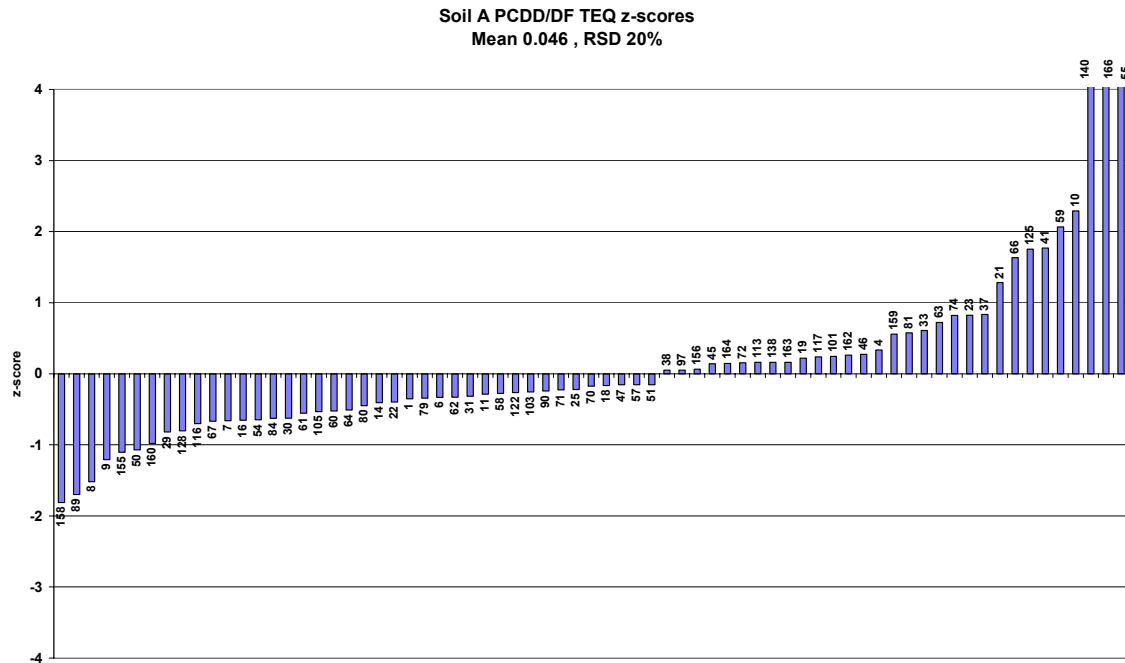


Figure 11: Z-scores calculated after omitting obvious outliers outside 2x the RSD. A z-score of 1 is classified as good, a z score between 1 and 2 as satisfactory and a z-score larger than 3 is unsatisfactory

The z-scores can be compared with other studies (QUASIME, Institute of Public Health, WEPAL) by studying the RSDs. In the statistics using a fixed RSD 25% is often used as a general criterion for the analysis of POPs in environmental samples independent of the target compounds, levels or complexity of the samples. A set RSD of 25% for a z-score of 2 might be somewhat optimistic for the complex dioxin analysis in low level samples. It is striking that the RSD based on the submitted results gets close to this optimal value (25%) and is in this way direct comparable.

4.4 Evaluation of Ten Rounds of International Intercalibration Studies (1994-2005)

In Figure 12 the relative RSDs for all 10 rounds of the dioxin intercalibration since 1994 are displayed together with the number of participants qualified after omitting obvious outliers. The data presented in this figure is included in detail in Appendix 1. From this figure an increase of in the number of participants since 1994 can be seen reflected in the number of laboratories qualified for each sample. This number increased from 8 in the 1st Round in 1994 to 87 for the standard solution in the 10th Round. Although initially an improved RSD was expected during the studied time period this was not seen in the data and Figure 12. The RSD is more dependent on the complexity of the samples and not related on the number of participants or the year when the exercise was organised. The lowest RSDs were achieved for standard solutions with an average RSD of 15% varying from 10% to 37% followed by the fly ash or soil extracts with an average of 19% ranging from 11% to 27%. The soil, sediment or sludge samples generally resulted in better RSDs than the fly ash samples with an average RSD of 27% varying from 13% to 65%. The fly ash samples were most complicated to analyse especially the low level samples and resulted in the largest variation between the

laboratories with an average RSD of 31% ranging from 19% to 49% in the years from 1994 to 2000. Low level sample were generally more difficult to analyse, but also complicated high level samples containing many inferences occasionally caused problems for the laboratories. In one sample large amounts of polychlorinated naphthalene's were present; this compound class has similar properties as the PCDD/PCDF during clean up and interferes even when using high resolution GC/MS detection.

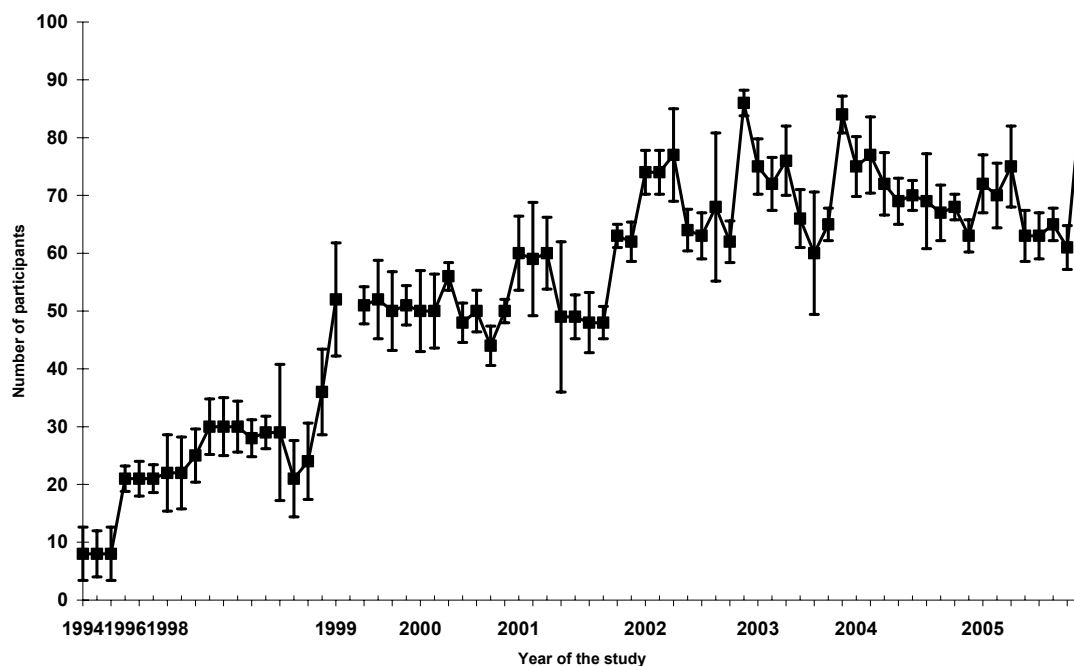


Figure 12: Number of participants in the international intercalibration study for each individual sample and the RSD after omitting obvious outliers during the period 1994-2005

In order to study the general analytical quality of the laboratories doing dioxin analysis the data from the last seven rounds of the QA/QC study was evaluated in more detail. For this evaluation the number of laboratories within 10% and 20% of the median were calculated as a percentage of the total number of participants. This data is in detail included in Appendix 2 and displayed in Figure 13 and Figure 14. In Figure 13 the data for all fly ash samples is displayed with the number of participants on the right y-axis and the percentages of participants within 10% or 20% on the left y-axis. The number of participants increased steadily until 2002 to around 70-80 laboratories. Note that many participants might analyse different matrices each year subscribing to the soil/sediment /sludge study one year and to the fly ash study another year. Also the percentage of laboratories within 10% or 20% of the median increased until 2002, and stayed basically the same during the period 2002-2004. The latest results from the 10th Round organised during 2005 differs and show somewhat lower percentages. The reason for this decrease is not directly evident. The samples for the fly ash study for 2005 were not more complicated than previous years. On average 52% of the participants were within 20% of the median and 32% within 10% of the median. But the results varied widely from 6% to 78% for results within 20% of the median value and 8% to 59% for results within 10% of the median.

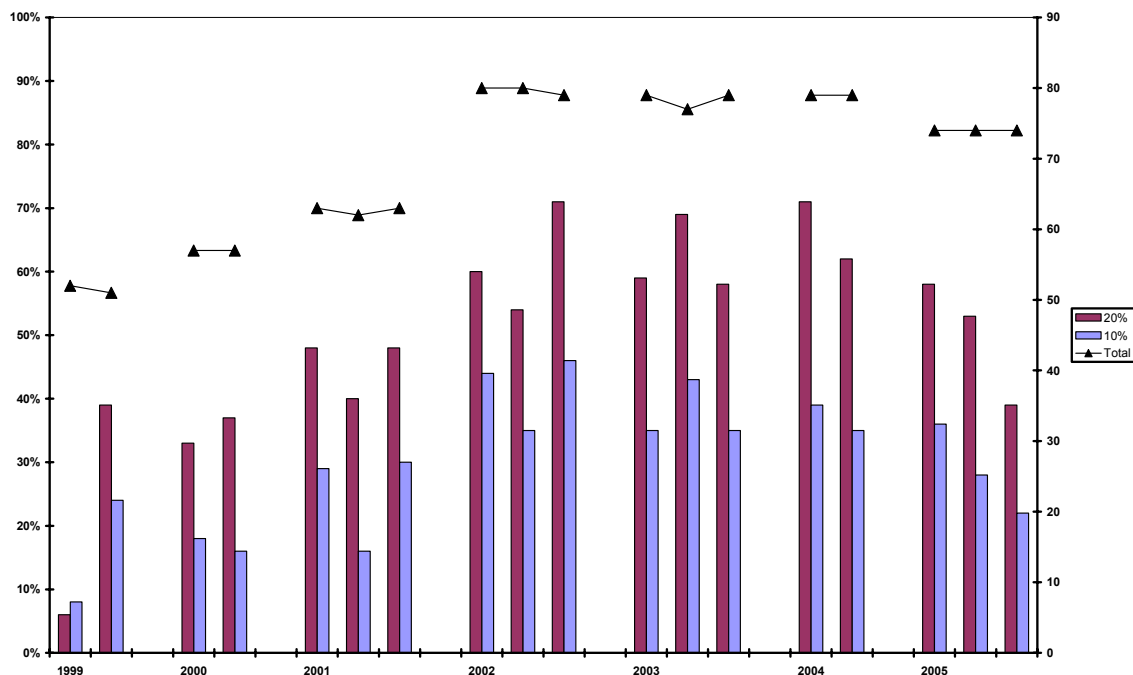


Figure 13: Number of participants within 10 and 20% of the median from the 4th Round (1999) to the 10th Round in 2005 for the fly ash samples.

The number of laboratories within 10% or 20% of the median for the soil, sediment, and sludge samples was generally larger than the numbers for the fly ash samples as illustrated in Figure 14. Already for the 4th Round (1999) more than 60% of the participants were reporting values within 20% of the median. On average 73% of the participants were reporting within 20% of the median (range 57-88%) and 50% within 10% of the median (range 31-74%) which are very good results taking into account that both low level samples and complex high level samples were included.

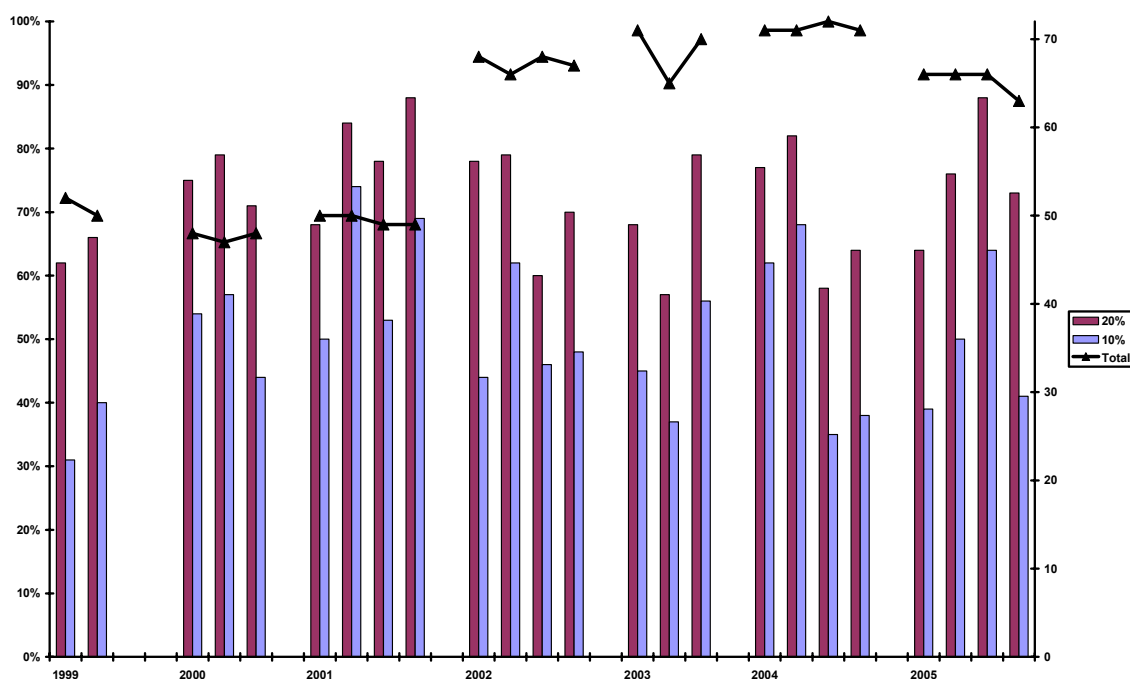


Figure 14: Number of participants within 10% and 20 % of the median since the 4th Round (1999) for the soil samples

Extraction was found to be a key issue when the results in Appendix 2 were validated in more detail. The three extracts distributed in the 4th, 5th and the 9th Rounds resulted in much better interlaboratory agreement than the solid samples. More than 90 % of the laboratories reported results within 20% of the median for a soil extract distributed in 1999, 89% of the participants were within 20 % of the median for a fly ash extract distributed in 2000 and finally 68% within 20% of the median for an extreme low level fly ash extract distributed in 2004.

For the standard solutions distributed throughout the years 2000-2005 the number of laboratories reporting between 10% of the median ranged from 48% to 79%, again depending on the concentration or complexity of the 'blind' standard solution send to the participants. In some cases co-eluting congeners to the 2,3,7,8-substituted congeners were included to increase the degree of difficulty.

4.5 Regional z-Scores

The z-scores of the 10th Round of the international intercalibration study were divided into seven regions according to Table 7 to study the analytical quality in different regions. Europe was divided into three regions consisting of the EU member states, the new member states and a group containing Norway, Switzerland, Turkey and Russia. Asia was divided into Japan and the rest of Asia including China and Hong Kong, Taiwan, Korea and Malaysia.

Table 7: Distribution of the participants of the 10th Round (2005) according to countries and regions

Region/Country	No of participants	Region/Country	No of participants
USA/Canada		EU New Member States (2)	
USA	7	Czech Republic	2
Canada	8	Poland	1
South America		Slovenia	1
Brazil	2	Hungary	2
		Other (Europe 3)	
EU (Europe 1)		Switzerland	1
England	4	Norway	1
Germany	4	Turkey	1
France	6	Russia	3
Sweden	4	Australia/New Zealand	
Belgium	4	Australia	2
The Netherlands	2	New Zealand	1
Italy	10	Asia	
Spain	4	Japan	9
Austria	1	China	3
Finland	3	Hong Kong	3
Denmark	1	Korea	5
		Taiwan	6
Total	102	Malaysia	1

The results of the regional z-scores are given in Table 8 in addition to the number of results submitted in the regions. The z-scores for each participant were calculated after omitting obvious outliers for the PCDD/PCDF TEQ. The average of the absolute value for each region was calculated. This results in a positive average z-score for each region as opposed to both negative and positive z-scores for the individual results which is given in Table 8.

The overall RSDs between the participating laboratories in the 10th Round of the dioxin interlaboratory study for the different samples were relatively good and varied between 9% and 35%. All regions showed, on average, good z-scores varying between 0.40 and 0.80. The highest regional z-scores were closely related to the number of participants from that region. It is therefore difficult to draw any conclusions on the ‘overall’ analytical quality per region. However it is obvious that in several regions; South and Central America, Africa, Asia (with the exception of Japan) and India, only limited analytical capability is available for advanced (PCDD/PCDF) POP analysis. With regard to Japan the analytical capability is larger than the number of laboratories (9) participating in the 10th Round world wide. A recent study within Japan organised by the Research Group on Ultra Trace Analysis (UTA) of the Japan

Environmental Measurement & Chemical Analysis Association (JEMCA) attracted 84 laboratories. Preliminary results from this study showed extreme good agreement between the laboratories for a fly ash extract (RSD, 6.5%).

Table 8: Regional z-scores (average of the absolute value) of the results of the 10th Round and the number of results submitted by the participants per region

	Standard P		Standard Q		Ash A		Ash B		Ash C	
	RSD	11%	RSD	9%	RSD	25%	RSD	28%	RSD	35%
	n	z-score	n	z-score	n	z-score	n	z-score	n	z-score
USA/Canada	14	0.43	14	0.57	10	1.26	10	0.72	11	1.01
Europe 1	40	0.82	38	0.73	35	0.62	33	0.72	30	0.93
Europe 2	4	0.64	4	0.80	-	-	1	0.05	1	0.88
Europe 3	4	0.52	5	0.51	5	1.14	5	0.74	2	0.90
Australia	3	0.29	3	0.07	2	0.94	2	0.62	2	0.14
Japan	7	0.36	7	0.55	5	0.79	5	0.55	5	0.37
Asia	16	0.65	16	0.76	14	0.83	13	0.71	14	0.64
South America	1	0.40	1	0.33	1	1.35	1	0.78	1	1.83
	Sediment A		Sediment B		Soil C		Sediment D		Total	
	RSD	22%	RSD	20%	RSD	14%	RSD	19%	n	z-score
	n	z-score	n	z-score	n	z-score	n	z-score	n	z-score
USA/Canada	11	0.55	11	0.67	12	0.65	11	0.76	104	0.74
Europe 1	30	0.90	29	0.82	29	0.76	27	0.93	291	0.80
Europe 2	1	0.68	1	0.19	2	0.36	2	0.08	16	0.46
Europe 3	2	0.34	2	0.41	2	0.22	2	0.26	29	0.56
Australia	3	0.68	3	0.23	3	0.42	3	0.19	24	0.40
Japan	5	0.32	5	0.46	5	0.20	4	0.37	48	0.44
Asia	13	0.85	13	0.89	13	0.86	12	0.74	124	0.77
South America	-	-	-	-	-	-	-	-	5	0.94

5 OUTLOOK AND FUTURE OF INTERCALIBRATION STUDIES

Interlaboratory or intercalibration studies are an important QA/QC tool for advanced POP analysis and have contributed that a growing number of laboratories are able to perform analysis with acceptable variation. Several studies have also contributed to better understanding of the variation in the results presented from different part of the world. Uncertainty between 10-25 % has to be expected when comparing results worldwide especially for advanced POP analysis. Intercalibration studies will also in the future be needed for both established and new laboratories to check their performance and 'prove' their capability. From an international quality assurance point of view world wide international studies are preferred, but local initiatives could also be useful to lift the analytical quality in just that region or country.

Table 9: World wide interlaboratory comparison or intercalibration studies on PCDD/PCDF and other organic chemicals

Organisation / Contact/ @mail / home page	Samples	Target Compounds	
International Intercal <i>Bert van Bavel</i> Bert.vanBavel@intercal.se www.intercal.se	Fly Ash Soil/Sediment/Sludge Standard Solutions	PCDD/DFs PCDD/DFs PCDD/DFs <i>PBDD/DF</i>	WHO PCBs WHO PCBs WHO PCBs <i>PBCDD/DF</i>
Norwegian Institute of Public Health <i>Georg Becher</i> Georg.Becher@folkehelsa.no Line.Smastuen.haug@fhi.no www.fhi.no	Food Standard Solutions	PCDD/DFs PCDD/DFs <i>PBDE</i>	WHO PCBs WHO PCBs <i>HBCD</i>
WEPAL /SETOC <i>Bram Eijgenraam</i> info.wepal@wur.nl www.wepal.nl	Soil/Sediment/Sludge	PCDD/DFs <i>PAH / Pesticides</i>	WHO PCBs <i>Bulk PCBs</i>
QUASIMEME <i>David Wells</i> <i>Jacob de Boer</i> quasimeme@wur.nl www.quasimeme.org	Fish and Shellfish Shellfish Sediment Fish Oil Solution/Biota/Sediment	PCDD/DFs PAHs PAHs Toxaphene BFRs (BDE, HCBd)	WHO PCBs Chlorinated Organics
Japanese Environmental Measurement & Chemical Association Research Group of Ultra Trace Analysis <i>Takumi Takasuga</i> t_takasuga00@shimadzu-techno.co.jp	Soil Standard Fly Ash Extract	PCDD/DFs PCDD/DFs PCDD/DFs	WHO PCBs WHO PCBs WHO PCBs

A number of large international studies open to laboratories worldwide are given in Table 9. These organisations often can give advice or suggest other studies to newly established laboratories. Concerning the POPs included in the Stockholm convention, studies on all compounds are available. For new POPs including the persistent brominated flame retardants (such as PBDEs) and persistent organic fluor compounds (such as PFOS, PFOA) new initiatives have recently started. In addition, new technological developments are evaluated in several international studies. As an example, the biological detection of dioxins using different kinds of bioassays was validated both between the 'bioassay' laboratories and the chemical analysis. Another example is the analysis of the PBDE replacement HBCD. This compound exists of three isomers, which are difficult to separate using gas chromatography. This issue is now being investigated in an intercalibration study. New POPs are expected to be included in the Stockholm Convention (see report of the 1st Meeting of the POPs Review Committee at <http://www.pops.int/documents/meetings/poprc/default.htm>), which is presently evaluating the proposal to include five additional POPs: chlordecone, γ -hexachlorocyclohexane (γ -HCH, lindane), hexabromobiphenyl (HxBB), pentabromo diphenyl ether (PeBDE), and perfluorooctane sulfonate (PFOS). World-wide interlaboratory comparison studies in an early stage will assure the quality of the analytical procedures and provide a base for solid decision making on both an international or regional level.

6 SUGGESTIONS AND GUIDELINE BEFORE PARTICIPATION IN INTERNATIONAL INTERCALIBRATION STUDIES.

To illustrate the benefits of long term participation in intercalibration studies the data for three laboratories have been adapted and plotted in Figure 14. The absolute value of the adapted z-scores has been plotted for 4 years (2001-2004). Laboratory A has been participating almost since the beginning of the study in 1992, laboratories B and C have more recently joined. As can be seen from Figure 14 laboratory A has been consistently under a z-score of 1 with the exception of the first sample from 2002. This pattern is typical for many of the more experienced laboratories performing well over a longer period of time but occasionally showing a larger z-score, although still satisfactory. Laboratory B resembles the pattern for a starting laboratory. In 2001 showing relatively high z-scores but gradually improved to surprisingly good results in the later years (2003, 2004). Laboratory C started well but did experience some problems in the year 2003 for the whole sample set with even one z-score over 2. Although speculative (no detailed information is available) this might indicate problems with the calibration standard which was corrected in the following year (2004).

The z-score calculated on the total PCDD/PCDF TEQ indicate if this value is in agreement with the other participants. However this is a so called weighted average (see Table 2) and individual results for the congeners might still be off. It is therefore still important to also evaluate the isomer specific results.

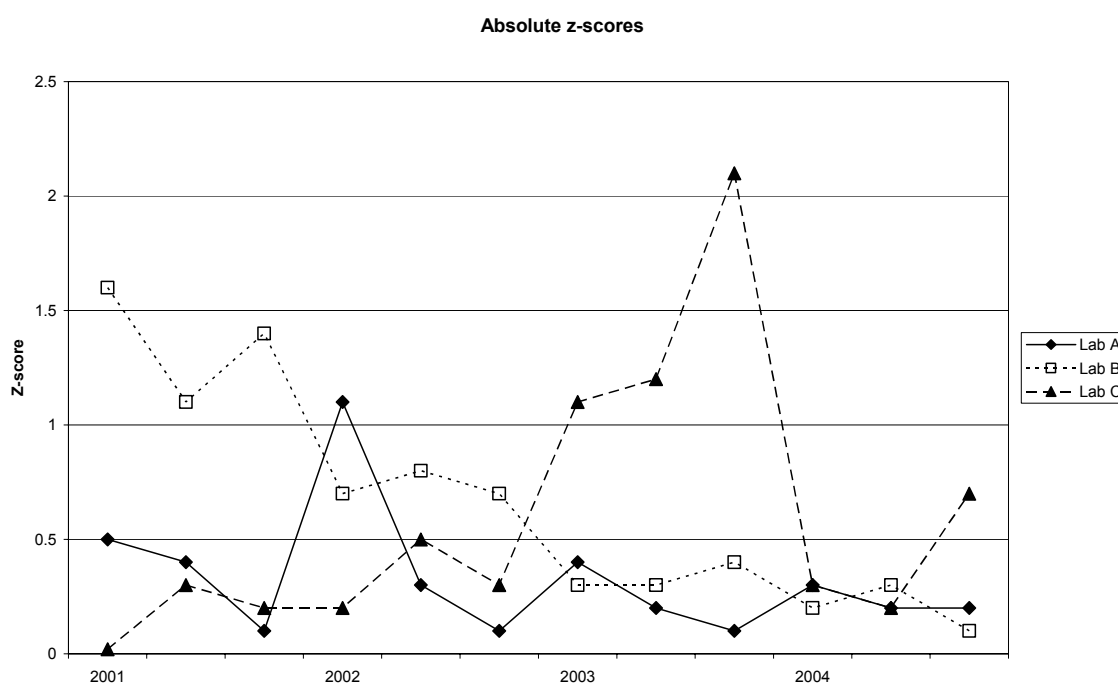


Figure 15: Absolute z-scores of three selected laboratories adapted from data from the 6th, 7th, 8th and 9th Rounds of the international intercalibration study

7 A PRACTICAL GUIDELINE FOR STARTING DIOXIN LABORATORIES

1. Research the literature. Information can be found in the Dioxin conference proceeding series (Organohalogen compounds). Since 1999 these proceedings are available on CD (www.dioxin2005.org). A lot of 'dioxin' articles are published in international journals such as Chemosphere and Environmental Science and Technology (ES&T).
2. For analytical procedures consult existing standard methods. For PCDD/PCDF EPA Methods 1613, 8290 and 23 are readily available from the internet (www.epa.gov). European guideline EN 1948 or different Japanese JIS methods are also available (but not free of charge or only in national language).
3. Take contact with a well established laboratory in the region and visit this laboratory. The investments to establishing a dioxin laboratory are substantial. A high resolution GC/MS system is not the only investment. The outcomes of a recent EU project (Difference) highlighted labour cost of the extraction and clean up phase as the largest cost per sample.
4. Contact and test high resolution GC/MS instruments, although low resolution instruments (*e.g.*, ion trap MS/MS) can be used for specific samples or applications, 90% of the laboratories world wide use high resolution instruments. Low levels samples including feed and food are almost exclusively run on high resolution instruments. Currently 4 suppliers are offering this instrumentation (Waters, Thermo Electron, JEOL and MSI) of which the first two dominate the market.
5. Education of laboratory personal in doing trace analysis is essential. Training on the high resolution GC/MS systems is normally not a problem and is offered by the different companies either at their facilities or on site. It is more difficult to train personal doing dioxin analysis at trace levels. Although automated systems such as the Powerprep (www.dionex.com) are available and gaining in popularity they are still not commonly used and are expensive. Most laboratories still use manual extraction and clean procedures adapted after one of the standard methods.
6. Consult established dioxin laboratories or the literature on the extraction procedures and clean up used and design a procedure that works for the local conditions. Decisions have to be made on extraction procedures (Soxhlet, open column, liquid/liquid, ASE), clean up steps (acid/base silica, AlOx, Florisil, carbon) and chromatographic columns (polar, non-polar, 30 m, 60 m).
7. One of the biggest problems during analysis is contamination; all chemicals from clean up gels to organic solvent have to be tested for dioxin contamination. It should also be kept in mind that high level samples potentially can contaminate low level samples and ideally should be extracted and handled in different laboratory locations.
8. All dioxin methods are based on the isotope dilution principle using ¹³C labeled internal standards. A wide variety of standards are available from two main suppliers, Wellington Laboratories and Cambridge Isotope Laboratories (www.well-labs.com and www.isotope.com) for the method used or the expected concentrations.

9. When blank test and standard runs are satisfactory a start can be made by testing 'real' samples. One of the first stages is to analyse certified reference material (CRM) of which the concentrations of dioxins are known. CRMs are available from the NIST, Sigma Aldrich or the standards suppliers mentioned above. In a start up phase it might also be useful to analyse material used in earlier intercalibration studies. Often the organisers of the intercalibration have material left over which can be sent for in house testing at low costs.
10. Running 'real' samples or CRMs might reveal co-elution or separation problems. Especially incineration related and soil/sewage/ sludge samples do not only contain the 2,3,7,8-substituted congeners and co-elution does occur. Often these samples have to be run on both a polar and/or non-polar column, although custom made 'dioxin' columns have become available with enhanced separation capacity. Biological samples in general human samples often only contain the 2,3,7,8-substituted PCDD/PCDF but the levels are significantly lower and column bleed could be an issue.
11. The final test will be to actually take part in a intercalibration study for the sample types relevant to the work expected to be done. It is not advisable to participate in several studies at once. A good strategy is to start with one or two matrices and slowly expand. It is very common that laboratories participate for different matrices every year, rotating between incineration related samples (fly ash), solid samples (soil/sediment/sludge) and biological samples (feed/food or human).
12. When the results are available always follow up the results on a congener specific basis. This will give detailed information on the extraction efficiency, cross contamination and calibration standards. From an analytical point of view the total TEQ is a weighted average which might not reveal problems on a congener specific level.

8 ANNEX 1: RESULTS FROM INTERNATIONAL INTER-CALIBRATION STUDIES 1994-2005

Table 10: RSDs from all samples analysed within the international intercalibration study on dioxin in solid samples 1994 to 2005

	Year	Sample	RSD (all)	n	RSD1	n
1 st 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 nd Round	1996	Fly Ash Extract A		25	11%	21
		Fly Ash Extract B		25	15%	21
		Fly Ash Extract C		25	12%	21
3 rd 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
4 th 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 th 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
		Standard E	18%	58	10%	50
6 th Round	2001	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
		Sediment C	41%	49	26%	48
		Sediment D	39%	49	14%	48
		Standard F	19%	67	10%	63
		Standard H	29%	66	17%	62

Table 10 (cont'd.)

	Year	Sample	RSD (all)	n	RSD1	n
7 th Round	2002	Fly Ash A	35%	80	19%	74
		Fly Ash B	40%	80	19%	74
		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
8 th Round	2003	Fly Ash A	68%	79	24%	75
		Fly Ash B	35%	77	23%	72
		Fly Ash C	48%	79	30%	76
		River Clay A	50%	70	25%	66
		Soil B	118%	64	53%	60
		Sediment C	22%	69	14%	65
		Standard L	29%	89	16%	84
9 th Round	2004	Fly Ash A	43%	75	26%	75
		Fly Ash B	51%	79	33%	77
		Fly Ash Extract C	41%	74	27%	72
		Sewage Sludge A	42%	71	20%	69
		River Clay B	23%	71	13%	70
		Sewage Sludge C	41%	69	41%	69
		Sediment D	45%	71	24%	67
		Standard M	29%	75	11%	68
		Standard O	25%	68	14%	63
10 th Round	2005	Fly Ash A	38%	76	25%	72
		Fly Ash B	43%	75	28%	70
		Fly Ash C	36%	76	35%	75
		Sediment A	34%	65	22%	63
		Sediment B	42%	65	20%	63
		Sediment C	33%	66	14%	65
		Sediment D	23%	63	19%	61
		Standard P + Q	20%	91	10%	87

Table 11: Total number of laboratories qualifying within 10% and 20% of the median consensus value of incineration and soil/sediment/sludge samples and extracts 1999-2005

	Total	20%	10%		Total	20%	10%	
4th Round	1999				1999			
	Ash A	51	39%	24%	Soil A	52	62%	31%
	Ash B	52	6%	8%	Soil B	50	66%	40%
	Extract C	51	78%	59%	Extract C	51	90%	57%
5th Round	2000				2000			
	Ash A	57	33%	18%	Soil A	48	75%	54%
	Ash B	57	37%	16%	Soil B	47	79%	57%
	Extract C	56	89%	70%	Soil C	48	71%	44%
6th Round	2001				2001			
	Ash A	63	48%	29%	Soil A	50	68%	50%
	Ash B	62	40%	16%	Soil B	50	84%	74%
	Ash C	63	48%	30%	Soil C	49	78%	53%
					Soil D	49	88%	69%
7th Round	2002				2002			
	Ash A	80	60%	44%	Soil A	68	78%	44%
	Ash B	80	54%	35%	Soil B	66	79%	62%
	Ash C	79	71%	46%	Soil C	68	60%	46%
					Soil D	67	70%	48%
8th Round	2003				2003			
	Ash A	79	59%	35%	Soil A	71	68%	45%
	Ash B	77	69%	43%	Soil B	65	57%	37%
	Ash C	79	58%	35%	Soil C	70	79%	56%
9th Round	2004				2004			
	Ash A	79	71%	39%	Soil A	71	77%	62%
	Ash B	79	62%	35%	Soil B	71	82%	68%
	Extract C	74	68%	54%	Soil C	72	58%	35%
					Soil D	71	64%	38%
10th Round	2005				2005			
	Ash A	74	58%	38%	Soil A	66	64%	39%
	Ash B	74	53%	28%	Soil B	66	76%	50%
	Ash C	74	39%	22%	Soil C	66	88%	64%
					Soil D	63	73%	41%

Table 12: Total number of laboratories qualifying within 5% and 10% of the median consensus value of standard solutions analysed between 1999 and 2005

		Total	10%	5%
5 th Round	2000			
	2,3,7,8-TCDD	58	53%	33%
6 th Round	2001			
	2,3,7,8-TCDD	66	67%	38%
	2,3,7,8-TCDD	65	48%	28%
7 th Round	2002			
	2,3,7,8-TCDD	92	51%	30%
8 th Round	2003			
	2,3,7,8-TCDD	88	60%	33%
9 th Round	2004			
	2,3,7,8-TCDD	74	65%	42%
	2,3,7,8-TCDD	68	60%	32%
10 th Round	2005			
	2,3,7,8-TCDD	89	79%	63%
	2,3,7,8-TCDD	89	78%	65%

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