CCQM-K25: Key Comparison – Determination of PCB Congeners in Sediment

Final Report
12 Dec 2003

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INTRODUCTION

Polychlorinated biphenyls (PCBs) consist of 209 possible congeners depending on the substitution of the chlorine atoms around the biphenyl molecule. PCBs have been widely used as industrial fluids, flame retardants, diluents, hydraulic fluids, and dielectric fluids for capacitors and transformers. As a class of compounds, they are environmentally stable and tend to bioaccumulate. Of the 209 possible congeners, approximately 150 congeners have been reported in the environment. Congener specific PCB methods, which are typically based on gas chromatography (GC) with electron capture detection (ECD) or mass spectrometric (MS) detection, are designed to measure selected priority congeners, but the congeners of interest change with the study and sponsoring agency.

A pilot comparison for PCB congeners in sediment was discussed at the April 2000 CCQM Organic Analysis Working Group meeting and conducted July 2000 to November 2000 (CCQM-P17). For the pilot study, four target PCB congeners were selected as representative of the measurement of individual congeners in environmental samples. The target congeners included some potential problematic GC separations, and they spanned the volatility range and the typical concentration range for the 150 congeners found in environmental samples. PCB 28 (2,4,4'-trichlorobiphenyl) is volatile and under certain conditions coelutes with PCB 31. PCB 101 (2,2',4,5,5'-pentachlorobiphenyl) has the potential coelution with a minor congener, PCB 90 (2,2',3,4',5-pentachlorobiphenyl). PCB 153 (2,2',4,4',5,5'-hexachlorobiphenyl) is typically one of the most abundant congeners and potentially coelutes with PCB 132 (2,2',3,3',4,6'-hexachlorobiphenyl). Finally, PCB 170 (2,2',3,3',4,4',5-heptachlorobiphenyl) is one of the less volatile congeners, is typically found at lower concentrations, and can potentially coelute with PCB 190 (2,3,3',4,4',5,6-heptachlorobiphenyl). The ability of a laboratory to measure these four congeners should indicate the ability to measure the suite of 150 PCB congeners found in sediments.

The results of the pilot study are described below. At the CCQM Organic Analysis Working Group meeting held at NIST in March 2001, a Key Comparison on the determination of selected PCB congeners in sediment was approved and outlined, following the successful 2000 Pilot Study (CCQM-P17). In January 2002, the designated coordinating laboratory, NIST, distributed sediment samples to the participating laboratories for CCQM-K25. The participating laboratories were to determine the four target PCB congeners in CCQM-P17 and a fifth congener, PCB 105 (2,3,3',4,4'-pentachlorobiphenyl), which was included to provide a congener with a lower concentration and which may change elution order with PCB 132 depending on the analytical conditions. Instructions and reporting forms were also sent to the participants.

Nine laboratories participated in CCQM-K25:

Centro Nacional de Metrologia (CENAM) [Mexico]
Federal Institute for Materials Research and Testing (BAM) [Germany]
Laboratory of the Government Chemist (LGC) [UK]
Institute for Reference Materials and Measurements (IRMM) [EU]
Korea Research Institute of Standards and Science (KRISS) [Korea]
National Analytical Reference Laboratory (NARL) [Australia]
National Institute of Standards and Technology (NIST) [US] *coordinating laboratory*

National Metrology Institute of Japan (NMIJ) [Japan]
National Research Council of Canada (NRC) [Canada]

All participants in the key comparison used gas chromatography/mass spectrometry (GC/MS) with carbon-13 labeled PCB congeners as internal standards/surrogates, with the exception of CENAM. CENAM used another PCB congener (PCB 103) as the internal standard.

PILOT STUDY SUMMARY

A pilot study (CCQM-P17) for the determination of PCB congeners in sediment was organized by NIST and NRC in 2000. Ten laboratories participated in the pilot study. The sediment sample analyzed in the study was prepared from material collected from six sites in the vicinity of New York Bay and Newark Bay. It was freeze-dried and sieved. The 61 μm to 250 μm sieve fraction was used for preparation of SRM 1944, New York/New Jersey Waterway Sediment. The < 61 μm sieve fraction was stored in bulk after homogenization and radiation sterilization (^{60}Co). A portion of the < 61 μm bulk material was bottled with 10 g sediment per bottle for use as the exercise material for CCQM-P17. Each participating laboratory received three jars of sediment along with instructions and an Excel spreadsheet for reporting results. Participants were instructed to use any technique for the analytical measurements along with their own calibration solutions and isotopically-labeled analogues for internal standards/surrogates. Results were received from nine participants prior to the March 2001 Working Group meeting, and one participant (KRISS) sent results in November 2001. The results are shown in Table 1. The comparability of the data was acceptable for a pilot comparison; the largest differences observed were for results from the one laboratory that used gas chromatography with electron capture detection (GC-ECD) rather than isotope dilution (ID) GC/MS. The participants met at the March 2001 Working Group meeting. (The KRISS representative at this meeting left the room during the discussion of this pilot study.) One of the guidelines established by the CCQM Organic Working Group is that the Key Comparison Reference Value (KCRV) be based on results from laboratories and methods validated in the pilot study. The method validated in the pilot study was based on GC/MS with carbon-13 labeled PCB congeners used as internal standards/surrogates, i.e., isotope dilution (ID) GC/MS. Based on the pilot study results, it was also decided that a standardized protocol for drying should be used in the Key Comparison. The CCQM approved the Organic Working Group's proposal to proceed with a Key Comparison on PCB Congeners in Sediment (CCQM-K25). The KCRV will be determined based only on results from ID-GC/MS and from laboratories that participated in the pilot study.

KEY COMPARISON

The CCQM-K25 Key Comparison study utilized a sediment sample prepared by mixing known quantities of two sediment materials. The sediment utilized for CCQM-P17 (5.00 g/sample) was mixed with the fines from SRM 1941a, Organics in Marine Sediment, (6.00 g/sample). The sediment fines from SRM 1941a were prepared in the same manner as described above for the sediment used in the pilot comparison except that the SRM 1941a sediment was collected in the Baltimore Harbor (Maryland) and was sieved to <150 μm. The target concentrations for the PCB congeners in the sediment used for the Key Comparison were about half of the concentrations in the CCQM-P17 exercise and are indicative of a moderately contaminated area. Each participant was sent three bottles of sediment, each bottle containing 11 g of sediment. The

participants were requested to analyze at least three aliquots of the sediment using a method based on ID-GC/MS. A protocol for drying was specified as follows:

> Correction for dry-mass should be obtained from a separate portion of the material of minimum mass of 1 g. The material should be dried in a ventilated oven at a temperature of 105 °C ± 2 °C. Dry the sediment for a minimum of 3 h. Then weigh and repeat drying until a constant mass is attained (successive weighings should not differ by more than 0.001 g). The loss of mass corresponds to the correction that should be applied. It is advisable to perform this procedure at the same time when weighing the aliquots for PCB measurements.

This study drying protocol was specified only to ensure that reported participant results were on a comparable basis and was NOT a recommendation of that specific drying protocol for any other purpose.

Laboratories used different methods for extraction and clean-up of the sediment, as well as different GC columns for the GC/MS analysis. These methods, along with identification of the internal standards and/or surrogates used are summarized in Table 2.

No calibration or internal standard materials were supplied by the coordinating laboratory for the Pilot or Key Comparison studies. Thus, each participant was responsible for selecting calibration materials for each congener that had a stated purity and uncertainty, which were to be incorporated in calculations of concentration and uncertainty.

RESULTS

Results were received from nine participants in the Key Comparison. A summary of the results including means and expanded uncertainties for all of the participants is provided in Table 3. Based on guidelines established by the CCQM Organic Analysis Working Group, Key Comparison Reference Values (KCRV) are to be established based on results from study participants that had their method(s) validated through participation in the preceding Pilot Study. It is recommended that the KCRV for each of the five congeners be assigned as the mean ± expanded uncertainty (U) of the eligible results. The U has been calculated by multiplying the standard deviation of the eligible results by the appropriate coverage factor (based on the degrees of freedom). CENAM's results were not included because they did not use ID-GC/MS. BAM and NRC reported a coelution of PCB 101 and PCB 90 so their results were not included in the calculation of the KCRV for PCB 101. In addition, BAM's results for PCB 28 were initially excluded in the calculation of the KCRV based on outlier testing. However, at the CCQM Organic Working Group meeting in November 2002, BAM reported that they had further investigated the potential sources of bias in their measurements and had found contamination with PCB 28 and PCB 101 in their sample preparation procedure. Thus the BAM results for both PCB 28 and PCB 101 were excluded in the calculation of the KCRV based on these findings (see appendix A for details of the BAM investigation). At the April 2003 meeting in Sèvres, it was decided that data with reported coelutions would be included in the tables but not in the graphs and not used for the calculation of the KCRV. All of the remaining results were used to calculate the KCRVs as shown in Table 3. Because all of the eligible results are included in the calculation of the KCRV, systematic biases that may exist in the individual laboratory

results, may bias the KCRV. Therefore, the KCRV may not be the best estimate of the true mass fraction of these five individual PCB congeners in the sediment.

The Tables of Equivalence, which enumerate the relationships among the results of the participants in this Key Comparison, are shown in Table 4. The degree of equivalence graphs are shown in Figure 1. Note that the participants were requested to report the concentrations on a dry-mass basis using oven drying as specified above in the drying protocol. The results for mass loss during drying ranged from 1.52% to 2.81% (relative). IRMM also used Karl Fischer titration for moisture determination and reported 2.87% moisture. However, IRMM used the oven drying results for the CCQM-K25 calculations.

Table 5 describes the uncertainty calculations for each of the participants. Each participant used different components of uncertainty and different approaches to the calculation of standard uncertainty. CENAM did not specify their sources of uncertainty. For the remainder of the NMIs, some of the common sources of uncertainty noted were the measurement precision, the purity of the standards used, and the extraction efficiency.

CONCLUSIONS AND HOW FAR DOES THE LIGHT SHINE?

This Key Comparison study demonstrated a high level of equivalence in capabilities of the participating NMIs to successfully measure five PCB congeners (congener numbers 28, 101, 105, 153, and 170) in a moderately contaminated sediment using GC/MS-based methods. NRC and BAM reported combined values for PCB 101 and a coeluting minor component, PCB 90. However, these laboratories were aware of the coelution problem and noted it on their reporting forms. BAM later reported a contamination problem with PCB 28 and PCB 101 (see Appendix A). The other six NMIs reported comparable results for PCB 101. LGC also had a problem with PCB 28 due to unresolved interferences. The KCRVs were determined based on results from all laboratories that used methods that had been validated in the preceding Pilot Study (in this particular case ID-GC/MS) and for which no unresolved interferences were reported or evident; The relative expanded uncertainties of the KCRVs ranged from 2% to 5% indicating excellent agreement among the participants that used ID-GC/MS. Results from the one laboratory that used GC/MS with a non-labeled PCB congener as the internal standard (CENAM) showed no systematic bias from the others.

The five PCB congeners measured in CCQM-K25 were selected to be representative of the approximately 150 congeners found in environmental samples and to provide the typical analytical measurement challenges encountered in the determination of individual PCB congeners, such as volatility losses during sample preparation and resolution from potential interferences during chromatographic separation. The abilities demonstrated by the laboratories that provided comparable measurements for all five congeners in this Key Comparison should be indicative of their ability to provide reference measurements for the typical suite of PCB congeners found in moderately contaminated sediments (> 5 ng/g dry basis).

Table 1. Results (ng/g dry basis) of Pilot Study CCQM-P17 PCBs in Sediment (2000)

PCB 28

Lab	Mean	U
BAM	63.9	2.0
CENAM	not reported	
IRMM	64.3	2.2
KRISS	64.0	2.9
LGC	55.5	4.2
NARL	62.0	5.3
NIMC	59.5	7.1
NIST	59.6	1.3
NRC	62.4	1.0
VNIIM	63.3	4.2
mean	61.6	
std dev	2.9	
CV (%)	4.7%	
U	6.0	

PCB 101

Lab	mean	U
BAM	52.9	1.8
CENAM	62.6	10.6
IRMM	48.6	1.1
KRISS	51.6	1.6
LGC	47.4	3.2
NARL	51.6	6.2
NIMC	51.6	6.7
NIST	48.6	1.3
NRC	52.4	1.2
VNIIM	77.0	10.8
mean[a]	51.9	
std dev	4.4	
CV (%)	8.6%	
U	8.9	

PCB 153

Lab	Mean	U
BAM	54.1	2.1
CENAM	61.5	12.4
IRMM	53.4	1.5
KRISS	not reported	
LGC	51	6.1
NARL	52.1	4.3
NIMC	52.5	6.8
NIST	53.7	2.0
NRC	53.2	0.6
VNIIM	58.6	5.1
mean	54.5	
std dev	3.4	
CV (%)	6.2%	
U	6.8	

PCB 170

Lab	mean	U
BAM	16.5	1.6
CENAM	24.3	13.2
IRMM	11.4	0.9
KRISS	not reported	
LGC	13.5	1.0
NARL	14.5	2.9
NIMC	13.6	1.7
NIST	13.9	0.4
NRC	15.0	2.8
VNIIM	not reported	
mean	14.1	
std dev	1.6	
CV (%)	11.1%	
U	3.7	

A The statistics for PCB 101 excludes VNIIM's data due to reported coelution.
B The statistics for PCB 170 excludes CENAM's data due to reported coelution.

Table 2. Summary of methods used by the laboratories for CCQM-K25, PCBs in Sediment

Lab	Amount of Sediment	Extraction	Extract clean-up
BAM	2.0 g	PFE (hexane:acetone, 1:1)	Multiple-layer silica gel column - elute with cyclohexane
CENAM	2 g to 4 g	Soxhlet (dichloromethane, DCM)	Silica SPE; copper; normal-phase HPLC
IRMM	1 g	PFE (hexane:acetone, 1:1)	Copper; sulphuric acidified silica - elute with hexane
KRISS	2.5 g	Soxhlet (DCM)	Copper; silica and amino SPE; normal-phase HPLC
LGC	1.946 g	PFE (hexane:acetone, 1:1)	Copper; silica SPE
NARL	0.50 g	PFE (DCM)	Copper; silica SPE
NIST	5 g	PFE (DCM)	Silica SPE; copper
NMIJ	2.0 g	PFE (hexane:acetone, 1:1)	Copper; silica SPE; normal-phase HPLC
NRC	1.49 g	PFE (DCM)	Copper; silica SPE

Lab	GC column for GC/MS analysis	IS/Surrogates	IS/Surrogates added when?
BAM	HT8 (50 m x 0.25 mm, 0.25 µm film)	$^{13}C_{12}$ PCB 28; $^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 105 $^{13}C_{12}$ PCB 105 ; $^{13}C_{12}$ PCB 180	Between extraction and clean-up
CENAM	DB-5 (60 m x 0.25 mm, 0.25 µm film)	PCB 103	Prior to extraction
IRMM	DB-17, DB-1701 (60 m x 0.25 mm, 0.25 µm film)	$^{13}C_{12}$ PCB 28; $^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 105 $^{13}C_{12}$ PCB 153 ; $^{13}C_{12}$ PCB 170	Prior to extraction
KRISS	HT-8 (50 m x 0.22 mm, 0.25 µm film)	$^{13}C_{12}$ PCB 28; $^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 153 ; $^{13}C_{12}$ PCB 170	Prior to extraction
LGC	HT-8 (50 m x 0.22 mm, 0.25 µm film)	$^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 105; $^{13}C_{12}$ PCB 153 ; $^{13}C_{12}$ PCB 170	Prior to extraction
		$^{13}C_{12}$ PCB 138	Prior to chromatographic analysis
NARL	HT-8 (50 m x 0.22 mm, 0.25 µm film) DB-Dioxin for PCB 90 (60 m x 0.25 mm, 0.15 µm film)	$^{13}C_{12}$ PCB 28; $^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 105 $^{13}C_{12}$ PCB 153 ; $^{13}C_{12}$ PCB 170 Br_2-DDE and F_2-DDE for blanks and QC	Prior to extraction Prior to chromatographic analysis
NIST	DB-17 (60 m x 0.25 mm, 0.25 µm film)	$^{13}C_{12}$ PCB 28; $^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 105 ; $^{13}C_{12}$ PCB 153; $^{13}C_{12}$ PCB 170	Prior to extraction
NMIJ	HT-8 (50 m x 0.22 mm, 0.25 µm film)	$^{13}C_{12}$ PCB 28; $^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 105 ; $^{13}C_{12}$ PCB 153; $^{13}C_{12}$ PCB 170	Prior to extraction
		$^{13}C_{12}$ PCB 180	Added as “syringe spike”
NRC	HT-8 (50 m x 0.22 mm, 0.25 µm film)	$^{13}C_{12}$ PCB 28; $^{13}C_{12}$ PCB 101; $^{13}C_{12}$ PCB 105 ; $^{13}C_{12}$ PCB 153; $^{13}C_{12}$ PCB 170	Prior to extraction

Table 3. Results for CCQM-K25 PCBs in Sediment

PCB 28 ng/g dry basis

Participant	Mean	standard uncertainty	Degrees of Freedom	k	U
BAM	40.74	0.54	199.7	1.97	1.06
IRMM	34.3	1.03	60	2	2.06
KRISS	32.9	0.69	4	2.78	1.91
NARL	34.53	0.83	18	2.10	1.74
NIST	32.42	0.29	2	4.30	1.24
NMIJ	31.9	0.4	13	2.16	0.9
NRC	35.8	0.38	60	2	0.76

Mean	33.6	excluding BAM (due to contamination problem reported subsequent to participant submission of results, see Appendix A)
Range (%)	11.6%	
Std unc	0.60	
Deg of freedom	5	
k factor	2.57	
U	1.6	
Rel U (%)	4.61%	
KCRV	**33.6 ng/g (dry basis) ± 1.6 ng/g (dry basis)**	

PCB 101 ng/g dry basis

Participant	Mean	standard uncertainty	Degrees of Freedom	k	U
BAM	35.69	0.99	170.80	1.97	1.95
CENAM	26.0	0.7	60	2	1.4
IRMM	30.4	0.54	60	2	1.07
KRISS	30.7	0.47	2	4.30	2.00
LGC	31.1	1.2	60	2	2.5
NARL	30.54	1.04	35	2.03	2.11
NIST	30.21	0.27	2	4.30	1.16
NMIJ	29.7	0.4	12	2.18	0.8
NRC	31.4	0.20	60	2	0.40

Mean	30.44	excluding CENAM, BAM, and NRC (CENAM did not use ID-GC/MS; BAM and NRC reported coelution of PCB 101 and PCB 90; subsequent to participant submission of results, BAM also reported contamination problem, see Appendix A)
Range (%)	4.60%	
Std unc	0.19	
Deg of freedom	5	
k factor	2.57	
U	0.50	
Rel U (%)	1.64%	
KCRV	**30.44 ng/g (dry basis) ± 0.50 ng/g (dry basis)**	

PCB 105 ng/g dry basis

Participant	Mean	standard uncertainty	Degrees of Freedom	k	U
BAM	10.21	0.35	12.90	2.18	0.76
IRMM	10.9	0.25	60	2	0.49
LGC	10.94	0.13	60	2	0.26
NARL	10.58	0.41	60	2.00	0.82
NIST	10.81	0.07	1.99	12.70	0.88
NMIJ	9.62	0.18	12	2.18	0.39
NRC	10.8	0.093	60	2	0.186

Mean	10.55
Range (%)	12.5%
Std unc	0.18
Deg of freedom	6
k factor	2.45
U	0.45
Rel U (%)	4.27%

KCRV **10.55 ng/g (dry basis) ± 0.45 ng/g (dry basis)**

PCB 153 ng/g dry basis

Participant	Mean	standard uncertainty	Degrees of Freedom	k	U
BAM	33.76	0.86	146.60	1.98	1.70
CENAM	32.3	0.9	60	2	1.7
IRMM	30.7	0.57	60	2	1.14
KRISS	31.0	0.58	2	4.30	2.49
LGC	33.52	0.36	60	2	0.72
NARL	32.41	0.88	25	2.06	1.81
NIST	31.70	0.24	2	4.30	1.02
NMIJ	30.2	0.5	8	2.31	1.0
NRC	31.9	0.26	60	2	0.52

Mean	31.9	excluding CENAM (CENAM did not use ID-GC/MS)
Range (%)	11.2%	
Std unc	0.45	
Deg of freedom	7	
k factor	2.36	
U	1.1	
Rel U (%)	3.35%	

KCRV **31.9 ng/g (dry basis) ± 1.1 ng/g (dry basis)**

PCB 170 ng/g dry basis

Participant	Mean	standard uncertainty	Degrees of Freedom	K	U
BAM	9.01	0.22	216.80	1.97	0.43
CENAM	9.8	0.4	60	2	0.8
IRMM	9.0	0.38	60	2	0.76
KRISS	8.6	0.11	6	2.45	0.28
LGC	9.22	0.12	60	2	0.24
NARL	9.21	0.37	35	2.03	0.75
NIST	9.19	0.05	1.96	12.70	0.67
NMIJ	8.69	0.17	7	2.36	0.41
NRC	8.98	0.089	60	2	0.178

Mean	8.99	excluding CENAM (CENAM did not use ID-GC/MS)
Range (%)	6.90%	
Std dev of mean	0.083	
Deg of freedom	7	
k factor	2.36	
U	0.20	
Rel U (%)	2.18%	
KCRV	**8.99 ng/g (dry basis) $\pm$ 0.20 ng/g (dry basis)**	

Table 4. Tables of Equivalence for CCQM-K25

TABLE OF EQUIVALENCE - PCB 28 in CCQM-K25

Measurand: Amount of PCB 28 in Sediment
Unit: nanograms/gram

	KCRV		BAM		IRMM		KRISS		NARL		NIST		NMIJ		NRC	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
BAM	7.098	1.727			6.440	2.309	7.840	1.952	6.210	2.010	8.320	1.244	8.840	1.336	4.940	1.301
IRMM	0.658	2.407	-6.440	2.309			1.400	2.529	-0.230	2.640	1.880	2.142	2.400	2.203	-1.500	2.187
KRISS	-0.742	2.115	-7.840	1.952	-1.400	2.529			-1.630	2.288	0.480	1.924	1.000	1.952	-2.900	1.927
NARL	0.888	2.142	-6.210	2.010	0.230	2.640	1.630	2.288			2.110	1.840	2.630	1.898	-1.270	1.880
NIST	-1.222	1.640	-8.320	1.244	-1.880	2.142	-0.480	1.924	-2.110	1.840			0.520	1.101	-3.380	1.033
NMIJ	-1.742	1.639	-8.840	1.336	-2.400	2.203	-1.000	1.952	-2.630	1.898	-0.520	1.101			-3.900	1.116
NRC	2.158	1.615	-4.940	1.301	1.500	2.187	2.900	1.927	1.270	1.880	3.380	1.033	3.900	1.116		

TABLE OF EQUIVALENCE - PCB 101 in CCQM-K25

Measurand: Amount of PCB 101 in Sediment
Unit: nanograms/gram

	KCRV		CENAM		IRMM		KRISS		LGC		NARL		NIST		NMIJ	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
CENAM	-4.442	1.450			-4.400	1.752	-4.700	1.779	-5.100	2.758	-4.540	2.504	-4.210	1.509	-3.700	1.609
IRMM	-0.042	1.146	4.400	1.752			-0.300	1.595	-0.700	2.617	-0.140	2.349	0.190	1.230	0.700	1.346
KRISS	0.258	2.186	4.700	1.779	0.300	1.595			-0.400	2.594	0.160	2.334	0.490	1.725	1.000	1.586
LGC	0.658	2.430	5.100	2.758	0.700	2.617	0.400	2.594			0.560	3.153	0.890	2.460	1.400	2.523
NARL	0.098	2.143	4.540	2.504	0.140	2.349	-0.160	2.334	-0.560	3.153			0.330	2.179	0.840	2.247
NIST	-0.232	0.921	4.210	1.509	-0.190	1.230	-0.490	1.725	-0.890	2.460	-0.330	2.179			0.510	1.062
NMIJ	-0.742	0.941	3.700	1.609	-0.700	1.346	-1.000	1.586	-1.400	2.523	-0.840	2.247	-0.510	1.062		

TABLE OF EQUIVALENCE - PCB 105 in CCQM-K25

Measurand: Amount of PCB 105 in Sediment
Unit: nanograms/gram

	KCRV		BAM		IRMM		LGC		NARL		NIST		NMIJ		NRC	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
BAM	-0.341	0.832			-0.690	0.883	-0.730	0.791	-0.370	1.082	-0.600	0.771	0.590	0.824	-0.590	0.777
IRMM	0.349	0.627	0.690	0.883			-0.040	0.560	0.320	0.953	0.090	0.520	1.280	0.616	0.100	0.531
LGC	0.389	0.483	0.730	0.791	0.040	0.560			0.360	0.858	0.130	0.302	1.320	0.456	0.140	0.317
NARL	0.029	0.897	0.370	1.082	-0.320	0.953	-0.360	0.858			-0.230	0.832	0.960	0.893	-0.220	0.839
NIST	0.259	0.460	0.600	0.771	-0.090	0.520	-0.130	0.302	0.230	0.832			1.190	0.417	0.010	0.251
NMIJ	-0.931	0.545	-0.590	0.824	-1.280	0.616	-1.320	0.456	-0.960	0.893	-1.190	0.417			-1.180	0.426
NRC	0.249	0.462	0.590	0.777	-0.100	0.531	-0.140	0.317	0.220	0.839	-0.010	0.251	1.180	0.426		

TABLE OF EQUIVALENCE - PCB 153 in CCQM-K25

Measurand: Amount of PCB 153 in Sediment
Unit: nanograms/gram

	KCRV		BAM		CENAM		IRMM		KRISS		LGC		NARL		NIST		NMIJ		NRC	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
BAM	1.861	1.931			1.460	2.458	3.060	2.034	2.760	2.171	0.240	1.839	1.350	2.448	2.060	1.768	3.560	1.978	1.860	1.773
CENAM	0.401	2.016	-1.460	2.458			1.600	2.113	1.300	2.241	-1.220	1.930	-0.110	2.510	0.600	1.864	2.100	2.060	0.400	1.869
IRMM	-1.199	1.477	-3.060	2.034	-1.600	2.113			-0.300	1.923	-2.820	1.337	-1.710	2.110	-1.000	1.248	0.500	1.541	-1.200	1.246
KRISS	-0.899	2.044	-2.760	2.171	-1.300	2.241	0.300	1.923			-2.520	2.172	-1.410	2.246	-0.700	2.701	0.800	1.968	-0.900	2.735
LGC	1.621	1.222	-0.240	1.839	1.220	1.930	2.820	1.337	2.520	2.172			1.110	1.934	1.820	0.909	3.320	1.300	1.620	0.880
NARL	0.511	2.019	-1.350	2.448	0.110	2.510	1.710	2.110	1.410	2.246	-1.110	1.934			0.710	1.875	2.210	2.062	0.510	1.877
NIST	-0.199	1.183	-2.060	1.768	-0.600	1.864	1.000	1.248	0.700	2.701	-1.820	0.909	-0.710	1.875			1.500	1.255	-0.200	0.800
NMIJ	-1.699	1.448	-3.560	1.978	-2.100	2.060	-0.500	1.541	-0.800	1.968	-3.320	1.300	-2.210	2.062	-1.500	1.255			-1.700	1.228
NRC	0.001	1.139	-1.860	1.773	-0.400	1.869	1.200	1.246	0.900	2.735	-1.620	0.880	-0.510	1.877	0.200	0.800	1.700	1.228		

TABLE OF EQUIVALENCE - PCB 170 in CCQM-K25

Measurand: Amount of PCB 170 in Sediment
Unit: nanograms/gram

	KCRV		BAM		CENAM		IRMM		KRISS		LGC		NARL		NIST		NMIJ		NRC	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
BAM	0.023	0.464			-0.790	0.906	0.010	0.871	0.410	0.488	-0.210	0.493	-0.200	0.860	-0.180	0.445	0.320	0.560	0.030	0.467
CENAM	0.813	0.816	0.790	0.906			0.800	1.092	1.200	0.829	0.580	0.833	0.590	1.082	0.610	0.806	1.110	0.868	0.820	0.818
IRMM	0.013	0.777	-0.010	0.871	-0.800	1.092			0.400	0.790	-0.220	0.795	-0.210	1.054	-0.190	0.766	0.310	0.832	0.020	0.779
KRISS	-0.387	0.303	-0.410	0.488	-1.200	0.829	-0.400	0.790			-0.620	0.335	-0.610	0.781	-0.590	0.286	-0.090	0.446	-0.380	0.302
LGC	0.233	0.294	0.210	0.493	-0.580	0.833	0.220	0.795	0.620	0.335			0.010	0.785	0.030	0.262	0.530	0.444	0.240	0.296
NARL	0.223	0.768	0.200	0.860	-0.590	1.082	0.210	1.054	0.610	0.781	-0.010	0.785			0.020	0.757	0.520	0.822	0.230	0.770
NIST	0.203	0.223	0.180	0.445	-0.610	0.806	0.190	0.766	0.590	0.286	-0.030	0.262	-0.020	0.757			0.500	0.409	0.210	0.210
NMIJ	-0.297	0.421	-0.320	0.560	-1.110	0.868	-0.310	0.832	0.090	0.446	-0.530	0.444	-0.520	0.822	-0.500	0.409			-0.290	0.422
NRC	-0.007	0.249	-0.030	0.467	-0.820	0.818	-0.020	0.779	0.380	0.302	-0.240	0.296	-0.230	0.770	-0.210	0.210	0.290	0.422		

Table 5. Participant Uncertainty Budgets for CCQM-K25

BAM

	Type	Degrees of Freedom
Weighing	A	48
Calibration	A	4
Standards	B	100
Extraction	B	100
Clean-up, losses	B	100
Blank sand	A	2
Water Content	A	5

CENAM
Not Specified

IRMM

Uncertainty of standards used
- standard purity
- std dev of the balance
- accuracy of the balance
- mass of standard
- mass of standard solution
- RSD for measure of 20 µL of standard using syringe

Uncertainty of sample mass
-mass of sediment sample used
- std dev of the balance
- accuracy of the balance

RSD of response factors determined
RSD of analyte concentrations
Uncertainty of analyte concentration for blank sample
- limit of detection determined
- average concentration of the analyte

Uncertainty of recovery of extraction, determined as an uncertainty for blank sample

KRISS

	Type	Degrees of Freedom
Dry mass correction factor	A	1
Balance linearity and precision	B	large
Purity of standards and self-consistency test of four replicate solutions	B	large
Standard deviation of response factors of three standard mixes	A	2
Area ratio of analyte to isotope labeled analogue from GC/MS-SIM measurement of the samples	A	2
Area ratio of analyte to isotope labeled analogue from GC/MS-SIM measurement of the standard mix	A	2

LGC

Standard uncertainty of the dry mass correction factor
Between subsample variation (2 subsamples per bottle x 3 bottles)
Contributions from the primary standard used, the masses used for the sediment, and the precision of the measurement

NARL

Balance linearity
Balance repeatability
Purity of the neat standards
Precision of preparing the stock solution
Method precision – based on three replicate results from three jars
Extraction efficiency
Moisture content
Matrix matching
For PCB 28 – correction for interference from PCB 53
PCB 101 – correction for presence of PCB 90 (determined independently on a different column)

NIST

	Type	Degrees of Freedom
Method precision	A	2
Moisture content	A	2
Measurement of calibration solutions	A	4
Certified concentrations of calibration solutions	B	large

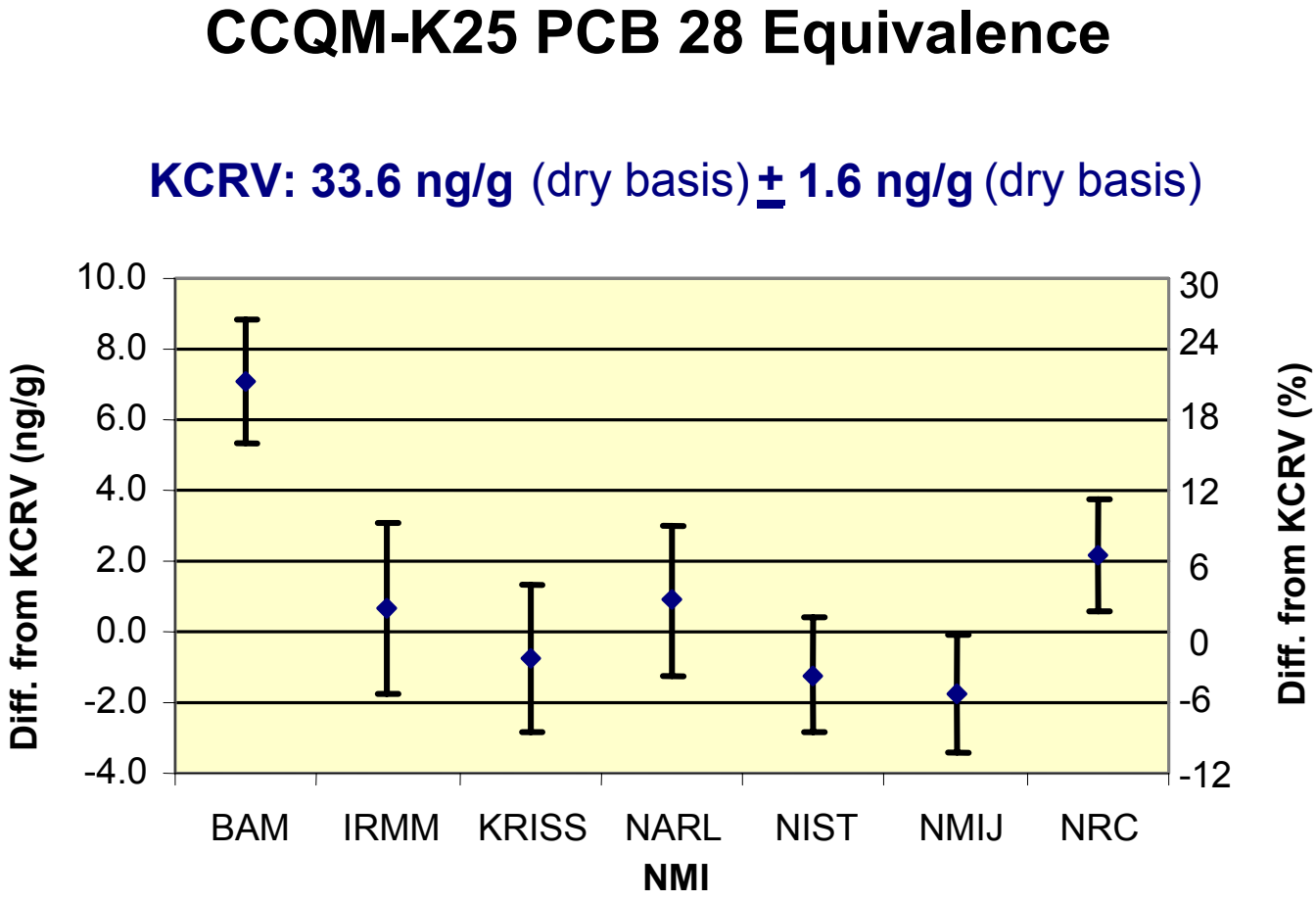
NMIJ

	Type	Degrees of freedom
Efficiency of sample preparation	A	8
Ratio of unlabeled to labeled congener in the samples to ratio of unlabeled congener to labeled congener in the calibration solutions	A	5
Weight of calibration solution taken for analysis	B	large
Concentration of congener in calibration solution	B	large
Weight of spiking solution added to calibrant	B	large
Weight of spiking solution added to sample	B	large
Moisture content	A	3
Weight of sample taken for analysis	B	large
Blank correction	A	3

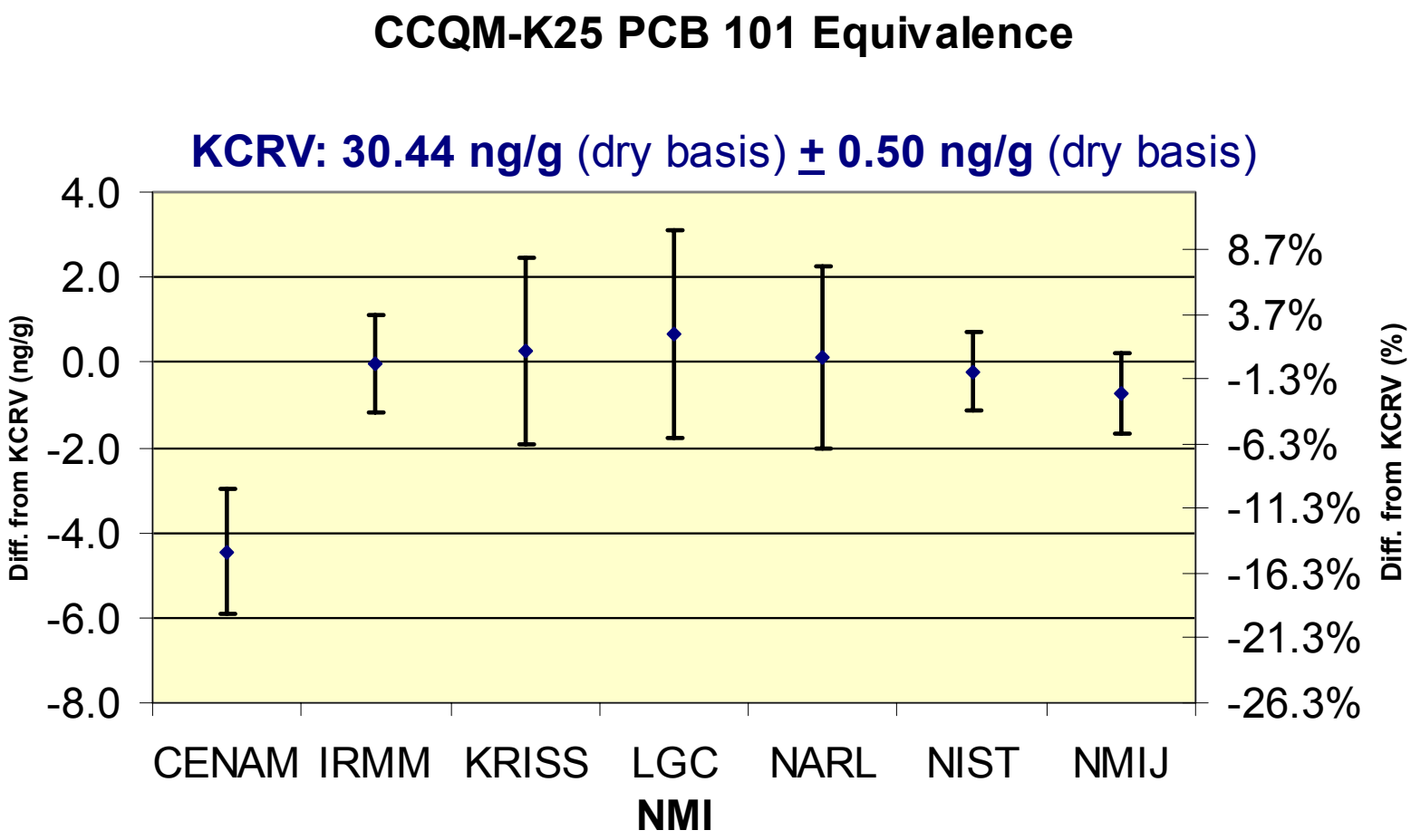
NRC	Type	Degrees of freedom
Weight of calibration solution taken for analysis	B	large
Weight of spiking solution added to calibrant	B	large
Weight of spiking solution added to sample	B	large
Weight of sample taken for analysis	B	large
Chemical purity	B	large
Moisture content	A	2
Method precision	A	5

Figure 1. Degrees of Equivalence Graphs for each Congener in CCQM-K25. The KCRV is the mean ± expanded uncertainty (U) of the eligible results

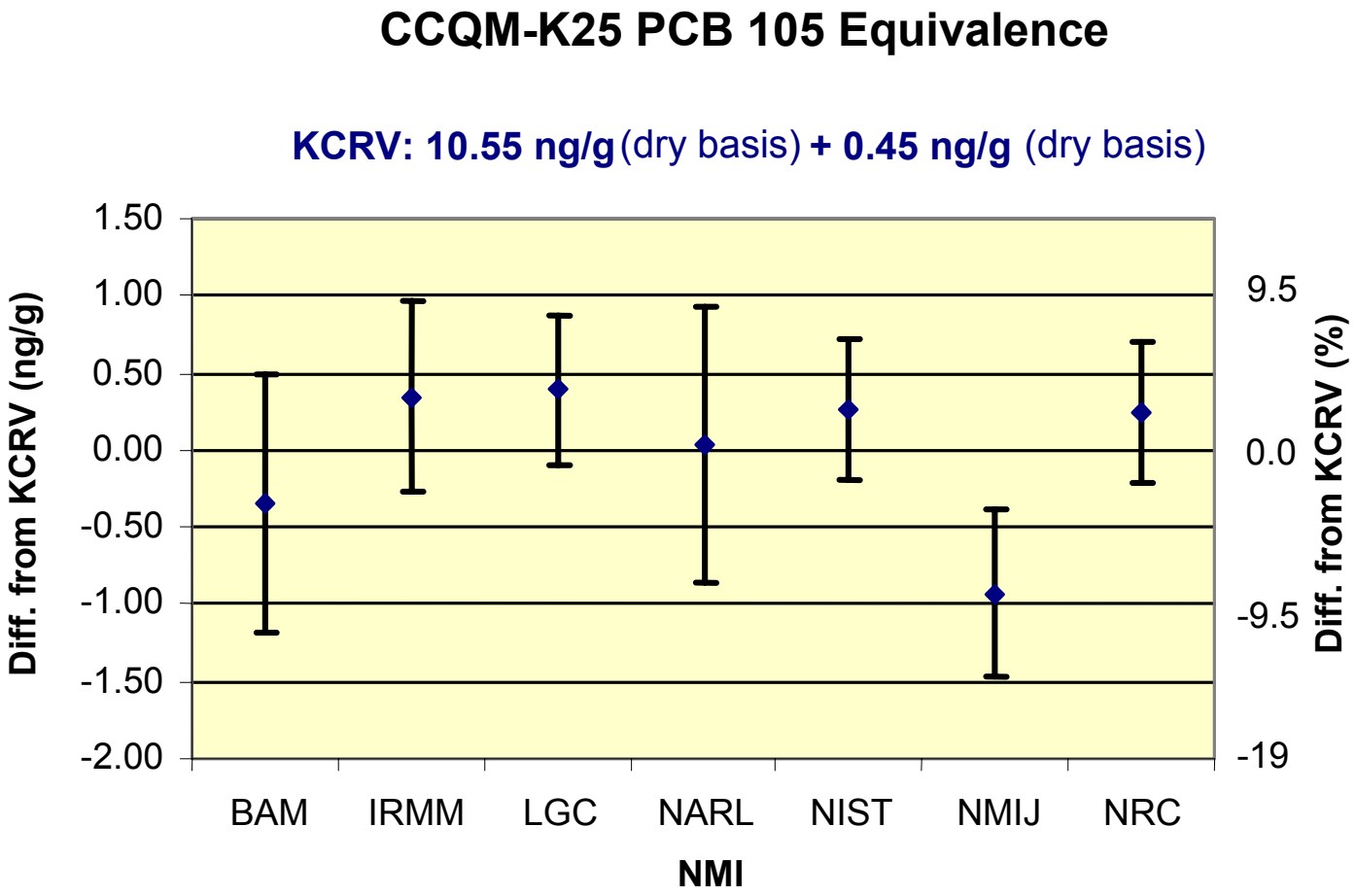
CCQM-K25: PCB Congeners in Sediment



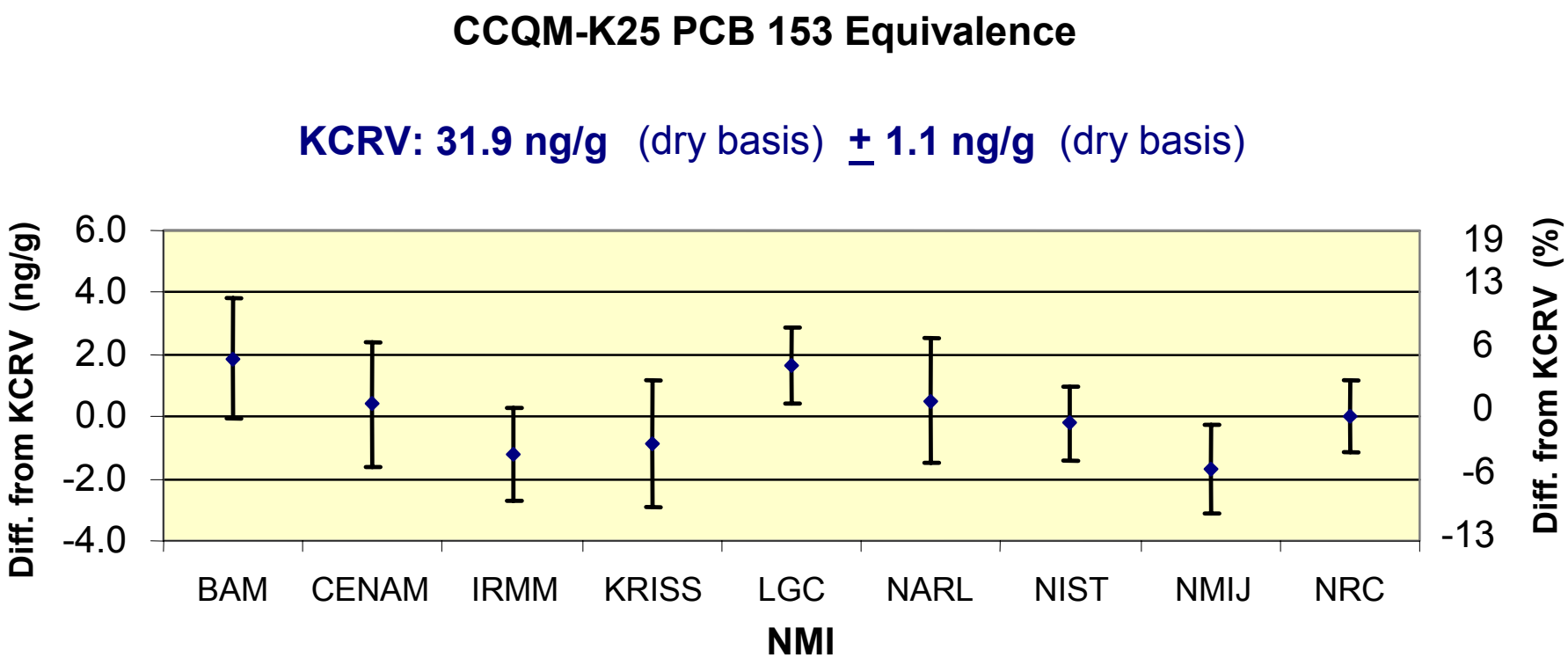
CCQM-K25: PCB Congeners in Sediment



CCQM-K25: PCB Congeners in Sediment



CCQM-K25: PCB Congeners in Sediment



CCQM-K25: PCB Congeners in Sediment

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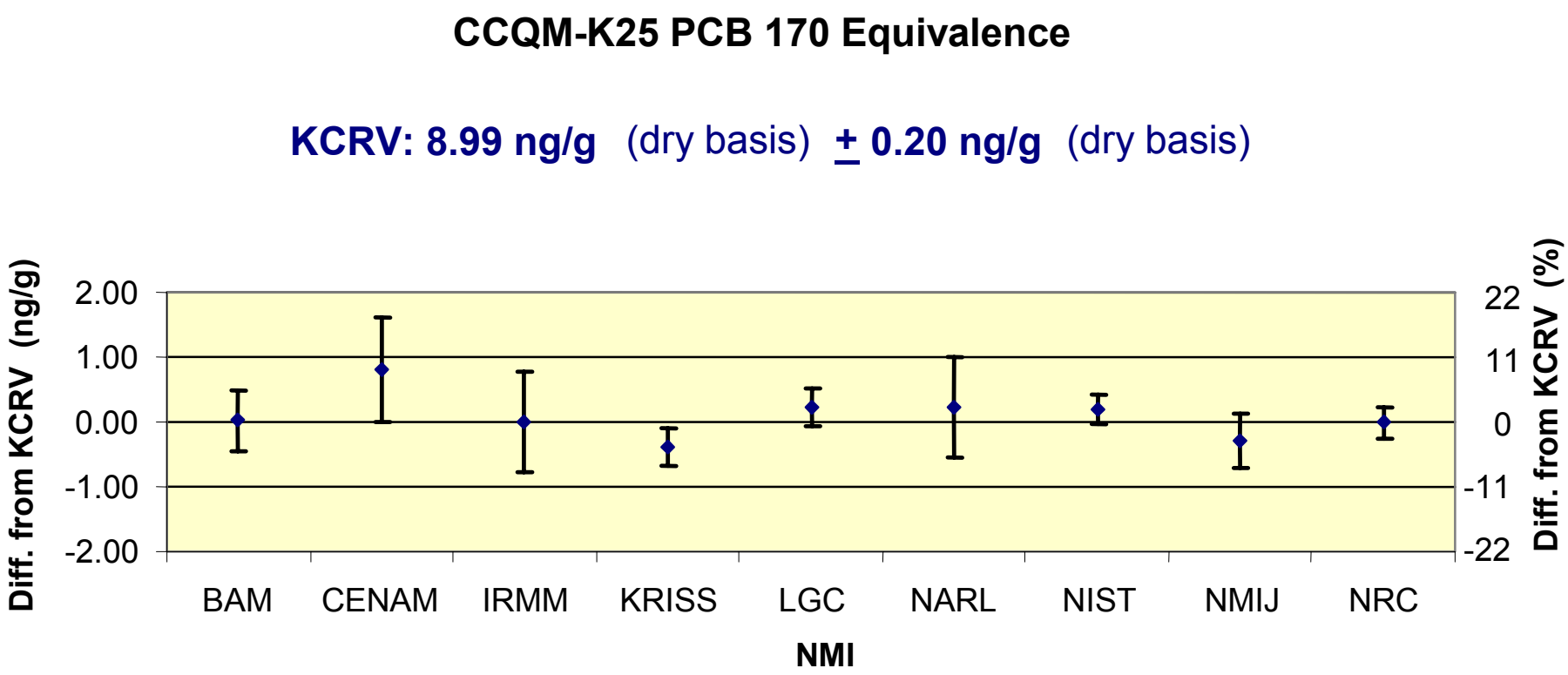

Appendix A

Determination of Source of Error for Results from BAM for CCQM-K25

Background

Initial evaluation of the results of the Key Comparison CCQM-K25, PCBs in Sediment, at the April 2002 Organic Working Group meeting, indicated that the results from all of the participants were in good agreement, with the exception of the BAM results for PCB 28 and PCB 101. A comparison of the CCQM-K25 KCRV and the BAM results is shown in Table 1. The results from BAM for PCB 28 and PCB 101 were high compared to the KCRV.

Table 1

PCB	CCQM-K25 KCRV ng/g dry basis	BAM results submitted March 2002 ng/g dry basis
28	33.64 ± 1.55	40.74 ± 1.06
101	30.44 ± 0.50	35.69 ± 1.95
105	10.55 ± 0.45	10.21 ± 0.76
153	31.90 ± 1.07	33.76 ± 1.70
170	8.99 ± 0.20	9.01 ± 0.43

To determine the source of error for the high values for PCB 28 and PCB 101 and to take proper corrective action in the laboratory, BAM investigated all of the analytical steps involved in the PCB measurements including:

1. potential errors in the concentrations of calibration solutions,
2. potential co-elution of PCB 28 and PCB 101 with other PCB congeners,
3. extraction, or
4. clean-up procedure.

1. First the PCB concentrations of the calibration solutions used for CCQM-K25 were compared with a new certified standard solution (USL-standard) and with a gravimetrically prepared solution from the certified neat PCB 28 and PCB 101 materials, and also against the isotopically-labeled internal standards. The stated concentrations of the calibration standards used for CCQM-K25 were confirmed by this procedure, and hence this potential source of error for the high values of PCB 28 and PCB 101 was excluded.

2. For the investigation of possible co-elution with other PCB congeners as a source of error, four different GC columns with different polarities were evaluated. One cleaned up extract used for the CCQM-K25 measurements was analyzed in duplicate on each of the four columns. The results of this investigation are shown in Table 2.

Table 2

PCB	CCQM-K25 KCRV ng/g dry basis	HT-8 50 m x 0.25 mm x .25µm ng/g dry basis	BP-10 50 m x 0.22 mm x 0.25 µm ng/g dry basis	HP-5 30 m x 0.25 mm x 0.25 µm ng/g dry basis	DB-17 MS 50 m x 0.25 mm x 0.25 µm ng/g dry basis
28	33.64	40.72	40.27	41.36	40.71
101	30.44	35.23	35.07	36.44	34.58

The results for each of the four columns were all similar to the original measurements, i.e., high compared to the KCRV. The results were the highest with HP-5 column (30 m length), which is not appropriate for the measurement of these PCB congeners because there is a co-elution of PCB 28 with PCB 31 and PCB 101 with PCB 90 and 84. All of the results from this investigation still indicated that there were significant differences compared to KCRV. It was therefore concluded that the errors must have arisen during the extraction or clean-up procedures.

3. A high value for PCB 28 and PCB 101 could indicate a potential loss of the two of the five isotopically-labeled internal standards from the solution added to the sediment prior to extraction. The loss of only two of the isotopically-labeled PCBs from the solution seemed improbable; however, the extraction could not be repeated because the sample material had been completely used in the original extractions.

4. For the investigation of the clean-up procedure as a possible source of error, the remaining portion of the original extracts of the CCQM-K25 sediment before clean-up, which had been stored under cold conditions, were reanalyzed after using different clean-up procedures. For analysis of the CCQM-K25 sediment, the extracts were clean up using a column with about 10 g of a self-prepared multiple-layer silica gel, which is our routine procedure for PCB analysis of matrices with high organic content. Most of the participants of CCQM-K25 used silica SPE cartridges after pre-treatment of the extract with pyrogenic copper. This same clean up method was used on the extracts and the results obtained are shown in the fourth column of Table 3 (10 independent analyses of the extracts), which are in good agreement with the KCRV for CCQM-K25. These results indicated that the multiple-layer silica gel column was the source of our high values for PCB 28 and PCB 101.

In the pilot study CCQM-P17, blank control of the whole procedure was carried out including the extraction and clean-up step where the multiple-layer silica gel column was rinsed with 30 mL of cyclohexane before the actual elution of the sample started, and at that time no PCB contamination was found in the blank. The mistake was to transfer these experimental conditions from the pilot study to the conditions of the key comparison. Based on the August 2002 investigations to determine the bias caused by the clean-up step, it was determined that the 30 mL of cyclohexane used to rinse the multiple-layer silica gel column was not sufficient to be free from PCB contamination. Only after rinsing with 60 mL of cyclohexane were no PCBs detected in the concentrated extract. The clean-up of the CCQM-K25 extracts was repeated with a multiple-layer silica gel column after rinsing the column with 60 mL of cyclohexane, and the results obtained are shown in column 5 of Table 3 (4 independent analyses of the extracts), which are in good agreement with the KCRV of CCQM-K25.

Table 3

PCB	CCQM-K25 KCRV ng/g dry basis	BAM results submitted March 2002 ng/g dry basis	Clean up silica SPE + copper ng/g dry basis	Clean up Multiple-level silica gel column (PCB free) ng/g dry basis
28	33.64 ± 1.55	40.74 ± 1.06	33.88 ± 1.05	33.79 ± 0.42
101	30.44 ± 0.50	35.69 ± 1.95	29.63 ± 1.70	29.84 ± 0.37
105	10.55 ± 0.45	10.21 ± 0.76	10.26 ± 0.33	10.36 ± 0.38
153	31.90 ± 1.07	33.76 ± 1.70	32.36 ± 1.08	30.47 ± 0.78
170	8.99 ± 0.20	9.01 ± 0.43	9.24 ± 0.60	9.16 ± 0.49

All the silica gel materials available in the laboratory were then systematically investigated. For this purpose 10 g of each material was extracted with 50 mL hexane and the extract was concentrated to 1 mL. In every material, independent of whether the materials were newly purchased or immediately removed from their containers, sealed, or already open, the typical PCB pattern was found. The PCB content from the material

used in CCQM is shown in column 4 of Table 4. For the plausibility check for the clean-up step that was determined to be the source of error for the BAM CCQM K-25 results, a case assessment was carried out to estimate how much the BAM CCQM-K25 results were affected by the contamination from the silica gel, under the assumption that 10 g of silica gel was used for the sample intake of about 2 g of sediment. It was not possible to keep all the conditions the same between the two measurements (CCQM-K25 measurements were performed in February 2002 and the PCB-contamination measurements were performed in August 2002). A conservative estimation of the contribution from the silica gel contamination would give the results shown in column 5 of Table 4.

Table 4

PCB	CCQM-K25 KCRV ng/g dry basis	BAM results submitted March 2002 ng/g dry basis	Content in 10 g silica gel ng(absolute)	Case assessment BAM-value – PCB from silica gel ng/g dry basis
28	33.64 ± 1.55	40.74 ± 1.06	9.08	36.09 ± 1.06
101	30.44 ± 0.50	35.69 ± 1.95	6.78	32.22 ± 1.95
105	10.55 ± 0.45	10.21 ± 0.76	0.28	10.07 ± 0.76
153	31.90 ± 1.07	33.76 ± 1.70	2.35	32.56 ± 1.70
170	8.99 ± 0.20	9.01 ± 0.43	0.38	8.82 ± 0.43

Conclusion

The outlier results from BAM in CCQM-K25 for PCB 28 and PCB 101 were a result of PCB contamination of the silica gel used for clean-up procedure. These measurements can be affected by this type of contamination, especially for measurements of PCBs at low ng/g levels.

Annex A

Description of the clean-up procedure with multiple-level silica gel column

The glass column was filled with quartz wool, 0.5 g Na_2SO_4, 0.5 g silica gel, 0.5 g silica gel/NaOH, 2 g silica gel; 2 g silica gel/H_2SO_4, 4 g silica gel/$AgNO_3$, 0.5 g Na_2SO_4 – rinsing with 30 mL up to 60 mL hexane. A 0.5 mL portion of the extract was transferred to the column, eluted with 70 mL cyclohexane and concentrated to 1 mL.