Development of the First Great Lakes Sediment Reference Materials for Chlorinated Dioxins and Furans.

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1. Objectives

The universal importance of analytical reference materials to help ensure accuracy in activities such as methods development, monitoring and research has been well emphasized. In general terms, intralaboratory quality control defines laboratory precision, interlaboratory round-robins determine between-lab comparability, but only through the use of certified reference materials, can one determine the degree of accuracy of any analytical process. The National Dioxin Interlaboratory QA Program, conducted by Environment Canada from 1988 to 1993, demonstrated the need for improvement in the accuracy of data obtained in dioxin/furan analyses of environmental samples. This paper describes the development of the first Great Lakes sediment reference materials for the determination of chlorinated dioxins and furans.

2. Approach

The naturally-contaminated sediment reference materials described in this paper were obtained from locations in the Great Lakes Basin. The procedures used for sample collection, freeze-drying, crushing, sieving and blending have been described in previous publications[1-5]. For each reference sediment, more than 5000 subsamples were bottled and stored at 4° C in the dark. In addition to the chlorinated dioxins and furans, other organic contaminants include 0.5 to 1 ppm total PCB, from 25-3500 ng/g PAHs, and from 20-300 ng/g chlorobenzenes.

Homogeneity of the subsamples was assessed using the ANOVA technique[6] on randomly selected bottles. Results statistically suggest the sample bottles are homogeneous for the analytes of interest. The integrity of the subsamples has now been monitored for more than 10 years by annual assessments of the stability of the PCB, chlorobenzene and PAH content. No signs of loss or degradation for these components in the reference materials have been observed in either reference sediment.

3. Results Obtained

Reference values for the seventeen 2,3,7,8-substituted dioxin and furan congeners were determined using a multi-laboratory, multi-method approach. To ensure the collection of reliable data, eleven qualified Canadian High Resolution Mass Spectrometry laboratories of known analytical competence were selected to analyze 10 replicates each of the two sediment reference materials, using their own in-house high resolution mass spectrometry methodologies and calibration standards. Over the next twelve months, some of the

participating laboratories analyzed the sediments as routine QC samples while others analyzed the replicate samples in two to four batches. A summary of the data is provided in Tables 1 and 2. The estimated uncertainties assume normal distribution of the data and are intended to correspond to 95% tolerance limits[6]. That is, the analytical results for 95% of subsamples should lie between the upper and lower limits given by the Mean ± 95% Tolerance Limit. The calculated means in Tables 1 and 2 include all data submitted and are considered to be preliminary reference values only. It is anticipated that as outliers are statistically rejected during the process of certifying the reference values, the 95% confidence interval will then narrow considerably, especially for the pentachloro- dioxin and furan congeners.

Stability of the samples with respect to the chlorinated dioxins and furans was assessed by comparing the current data with that obtained in the five National Dioxin Interlaboratory Studies from 1988 to the present. Because only homolgue total data was collected in these studies, the congener specific results could not be compared. Although the within-laboratory and between-laboratory precision has improved greatly over the past six to seven years, the comparability of the two sets of data appears to indicate that there is no problem with stability of the chlorinated dioxins and furans in the two sediments.

4. Conclusions

Two naturally-contaminated lake sediments were developed into reference materials for the 2,3,7,8-substituted congeners of dioxins and furans at pg/g levels. The reference values were derived from repetitive analysis by eleven Canadian HRMS laboratories using their own in-house methodologies and calibration standards. These values were further confirmed by several interlaboratory studies. The samples described above are suitable for long-term in-house or interlaboratory quality assurance applications. In addition, they will be valuable tools in the development and evaluation of analytical methods for dioxins and furans, as well as for the generation of accuracy statements in in-house and interlaboratory quality assurance activities.

5. References

1) Cheam, Venghuot and Alfred S.Y. Chau (1984). Analytical Reference Materials. Part IV. Development and Certification of the First Great Lakes Sediment Reference Material for Arsenic, Selenium and Mercury. Analyst 109, 775-779.
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6) Natrella, Mary Gibbons (1966). Experimental Statistics. NBS Handbook 91.

Table 1. Preliminary Reference Values for Dioxin / Furan Congener Data (pg/g) in Reference Sediment DX-1

Congener	Mean of Data	# of Data Points	Standard Deviation*	% Coefficient of Variation	95% Tolerance Interval**
2378-TCDD	259	115	28	11	62
total TCDD	404	115	92	23	204
12378-PeCDD	22	90	4	18	9
total PeCDD	226	105	71	32	159
123478-HxCDD	23	85	4	19	10
123678-HxCDD	77	102	13	17	30
123789-HxCDD	54	94	13	24	29
total HxCDD	638	113	165	26	365
1234678-HpCDD	637	113	97	15	214
total HpCDD	1222	114	228	19	504
OCDD	3905	115	465	12	1028
TOTAL PCDD	6507	105	694	11	1543
2378-TCDF	89	115	22	24	48
total TCDF	832	115	765	92	1692***
12378-PeCDF	41	102	12	30	27
23478-PeCDF	62	104	16	26	36
total PeCDF	836	111	388	46	861***
123478-HxCDF	714	96	138	19	309
123678-HxCDF	110	103	36	33	80
123789-HxCDF	31	44	24	79	59***
234678-HxCDF	58	88	19	33	44
total HxCDF	1830	115	408	22	901
1234678-HpCDF	2373	115	405	17	895
1234789-HpCDF	135	110	31	23	68
total HpCDF	3652	115	1020	28	2255
OCDF	7064	115	1190	17	2632
TOTAL PCDF	14322	111	2817	20	6242
TOTAL PCDD + PCDF	20970	105	3361	16	7478

* Standard deviation of the sample using (n-1) degrees of freedom.

** Two-sided tolerance limits such that there is 95% probability that 95% of the distribution of data will be included in the range defined as the Mean ± 95% Tolerance Limit.

*** The distribution implies less than 95% confidence. Any negative deviation is inadmissable.

Table 2. Preliminary Reference Values for Dioxin / Furan Congener Data (pg/g) in Reference Sediment DX-2

Congener	Mean of Data	# of Data Points	Standard Deviation*	% Coefficient of Variation	95% Tolerance Interval**
2378-TCDD	262	117	28	11	62
total TCDD	412	117	65	16	144
12378-PeCDD	28	96	7	25	15
total PeCDD	253	107	75	30	166
123478-HxCDD	27	96	12	43	26
123678-HxCDD	84	111	17	21	38
123789-HxCDD	60	102	14	23	32
total HxCDD	700	117	174	25	383
1234678-HpCDD	753	113	159	21	353
total HpCDD	1499	116	377	25	834
OCDD	4411	116	620	14	1372
TOTAL PCDD	7334	106	951	13	2115
2378-TCDF	136	117	30	22	67
total TCDF	906	117	362	40	799
12378-PeCDF		105	5	12	12
23478-PeCDF	82	104	20	25	45
total PeCDF	898	112	199	22	441
123478-HxCDF	825	103	201	24	448
123678-HxCDF	143	105	45	31	99
123789-HxCDF	39	67	25	65	58***
234678-HxCDF	68	90	23	33	51
total HxCDF	2100	117	407	19	896
1234678-HpCDF	2863	110	607	21	1347
1234789-HpCDF	146	111	38	26	85
total HpCDF	4040	117	863	21	1902
OCDF	7830	117	1490	19	3288
TOTAL PCDF	15846	112	2125	13	4714
TOTAL PCDD + PCDF	23269	106	2909	13	6472

* Standard deviation of the sample using (n-1) degrees of freedom.

** Two-sided tolerance limits such that there is 95% probability that 95% of the distribution of data will be included in the range defined as the Mean ± 95% Tolerance Limit.

*** The distribution implies less than 95% confidence. Any negative deviation is inadmissable.