INTERLABORATORY EXERCISE FOR THE ANALYSIS OF PCDD/FS IN SAMPLES OF SEWAGE SLUDGE

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Introduction

With potential EU limit values for PCDD/Fs in sewage sludge being introduced in the future, a need to expand the dataset of PCDD/F concentrations in UK sewage sludge has been identified. There have been few studies on PCDD/Fs in UK sludge to date[1, 2] therefore it is anticipated that a large amount of monitoring work will be undertaken in the next few years. Sewage sludge is a very difficult matrix to analyse. Its composition is complex and highly variable and there are a great number of possible interfering compounds that must be removed before PCDD/F analysis can take place. It is therefore important to be certain of an acceptable degree of intra- and interlaboratory consistency in the results generated from such monitoring. The Environmental Science Department of Lancaster University was asked to coordinate an interlaboratory calibration exercise to ensure that laboratories wishing to participate in such monitoring work are able to meet required quality criteria.

Interlaboratory studies on PCDD/F analysis in the literature show a large amount of variation between laboratories. There have been a number of such exercises published in the literature in recent years on many different matrices. These include air, incinerator ash, standard solutions, paper industry waste, water, sediment, and sludge[3-7]. Such studies rarely examine the possible major sources of variation with a view to improving interlaboratory consistency. This study was designed to highlight the major sources of variation that may occur by including samples of sewage sludge at various stages of processing.

Materials and Methods

Six samples were sent to each participating laboratory comprised of the following: A wet digested sewage sludge sample (~400 g), dried digested sewage sludge (8 g), an extract of digested sewage sludge (5 ml), a cleaned digested sewage sludge extract (50 µl), dx2 certified reference sediment (4 g) and a standard solution of 17 2,3,7,8-PCDD/F congeners at known concentrations (50 µl). All the sewage sludge samples were prepared in the Lancaster University laboratory.

All the laboratories used HRGC-HRMS for analysis but were instructed to use their preferred methods for sample preparation and clean up, where appropriate. The sewage sludge samples were analysed and reported in duplicate to assess within-laboratory variability and to increase the statistical power of the exercise. Sub-samples of the same initial sludge were used throughout to remove uncertainty due to matrix effects and to facilitate statistical analysis. 15 litres of digested sewage sludge were collected from the digester holding tank at a UK

wastewater treatment works in 5 litre HDPE containers and stored at 4°C prior to preparation and distribution.

Results and Discussion

Seven UK laboratories agreed to participate in the exercise and five had returned a complete set of results by the deadline. Each laboratory reported the concentrations of the seventeen 2,3,7,8-substituted PCDD/Fs and the total homologue concentrations of the tetra to octa-PCDD/Fs.

	Wet Sludge	Dry Sludge	Extract	Clean Extract
2,3,7,8-TCDF	46	13	22	41
TCDF's	29	44	50	50
2,3,7,8-TCDD	28	46	23	27
TCDD's	124	77	44	42
1,2,3,7,8-PeCDF	79	34	33	40
2,3,4,7,8-PeCDF	51	50	48	59
PeCDF's	72	42	37	52
1,2,3,7,8-PeCDD	48	14	38	32
PeCDD's	70	48	36	35
1,2,3,4,7,8-HxCDF	25	23	36	40
1,2,3,6,7,8-HxCDF	29	42	36	43
2,3,4,6,7,8-HxCDF	49	49	51	73
1,2,3,7,8,9-HxCDF	*	13	20	*
HxCDF's	40	21	31	31
1,2,3,4,7,8-HxCDD	49	18	34	52
1,2,3,6,7,8-HxCDD	33	37	33	43
1,2,3,7,8,9-HxCDD	44	45	39	40
HxCDD's	32	25	26	29
1,2,3,4,6,7,8-HpCDF	23	15	15	17
1,2,3,4,7,8,9-HpCDF	40	16	58	49
HpCDF's	34	23	15	24
1,2,3,4,6,7,8-HpCDD	33	37	19	24
HpCDD's	31	32	18	22
OCDF	35	27	28	24
OCDD	29	23	7	17
WHO TEQ	41	36	31	28

Table 1. Relative standard deviations (RSDs) as a percentage of the mean (n=5) for the sewage sludge samples (* = not enough detected values to calculate RSD).

Table 1 shows the interlaboratory relative standard deviations as a percentage of the mean for the 17 2,3,7,8-substituted PCDD/F congeners, homologue group totals and the PCDD/F TEQ based on WHO TEF values, for each of the sewage sludge samples. No statistically significant difference between the interlaboratory variation of the various sludge samples could be detected. This suggests that no single step in the processing, extraction and clean up of sewage sludge is the major source of interlaboratory variation. The interlaboratory variation in this study is of a similar range to that of others in the literature and compares

favourably with a previous study done by Lindig on sewage sludge with RSDs in the range 17-89%[7]. The wet sludge variation reported here is a little higher than the Lindig study, but it should be pointed out that Lindig's samples were dried before distribution and no data has been rejected from this study, whereas Lindig eliminated outliers from his study.

Table 2 shows the median values of the reference sediment along with the reference value and 95% confidence range quoted in the certificate of analysis, and the median value of the standard solution alongside the actual concentration. The median of the reported values for the reference sediment are often close to the reference values and always within the 95% confidence limits. Relative standard deviations for the sediment range from 9-92%. This range compares well with a previous international round robin exercise on a sediment where a range of RSDs of 28-218% was reported[4].

	Reference Sediment				Standard Solution	
	Median	Ref Value	Max	Min	Median	Real Value
2,3,7,8-TCDF	76	134	195	73	2	2
TCDF's	809	975	1563	387		
2,3,7,8-TCDD	254	262	313	211	2	2
TCDD's	478	418	543	293		
1,2,3,7,8-PeCDF	42	46	56	36	9	10
2,3,4,7,8-PeCDF	104	88	116	60	10	10
PeCDF's	816	916	1267	565		
1,2,3,7,8-PeCDD	30	28	42	14	9	10
PeCDD's	270	253	411	95		
1,2,3,4,7,8-HxCDF	688	825	1173	477	10	10
1,2,3,6,7,8-HxCDF	130	153	214	92	9	10
2,3,4,6,7,8-HxCDF	72	70	117	23	9	10
1,2,3,7,8,9-HxCDF	41	36	81	-9	10	10
HxCDF's	1935	2111	2773	1449		
1,2,3,4,7,8-HxCDD	29	25	33	17	10	10
1,2,3,6,7,8-HxCDD	95	85	118	52	10	10
1,2,3,7,8,9-HxCDD	56	58	77	39	10	10
HxCDD's	857	739	957	521		
1,2,3,4,6,7,8-HpCDF	3025	3064	3809	2319	10	10
1,2,3,4,7,8,9-HpCDF	180	152	236	68	10	10
HpCDF's	3810	4068	5374	2762		
1,2,3,4,6,7,8-HpCDD	700	757	1077	437	10	10
HpCDD's	1415	1486	1962	1010		
OCDF	7167	7830	10917	4743	20	20
OCDD	4289	4402	5659	3145	20	20
WHO TEQ	499	516	669	362	23	25

Table 2. Median (n=5) of reported values for dx2 reference sediment, reference values and 95% confidence limit values (pg/g dw) and median (n=5) reported values for standard solution and real concentrations (pg/μl).

The laboratories show a good degree of precision as the reported medians are consistently close to, or the same as, the actual concentrations of the PCDD/Fs in the standard solution. The standard solution shows good comparability between laboratories with relative standard deviations from 15-41%. Laboratory 3 reported results that were biased slightly below the actual values. Laboratory 1 reported results consistently higher than the actual value. The weight of the sample was unchanged on delivery at laboratory 1 but solvent may have evaporated during storage at laboratory 1, causing increased concentration of the standard. If laboratory 1 is removed from the standard solution data the range of RSDs decreases to 5.5-25%. This range of variation compares well with that of a previous interlaboratory exercise on a standard solution, where a range of RSDs of 8-43% was reported[6].

In conclusion, the variation reported here is well within the range of previous exercises published in the literature and the participating laboratories may be considered competent in the analysis of PCDD/Fs in the matrices reported here.

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