ENVIRONMENTAL LEVELS OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS IN SEWAGE SLUDGE COLLECTED ACROSS THE UNITED STATES

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Introduction

Sewage sludge, also known as biosolids, is highly beneficial when used for land application. Excellent nutrient availability makes sewage sludge good fertilizer, or as daily or final cover for a landfill. Approximately 60% of all sewage sludge produced in the year 1999 was used beneficially and that number is expected to grow to 70% by 2010.[1] Public wariness for land application of sewage sludge has been fueled by concerns over odor, spread of pathogens, and toxic chemicals. One such group of toxins is polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs).

We have conducted a study to analyze sewage sludge samples collected from publicly owned treatment works (POTWs) around the United States for PCDD/F and PCBs. The samples provided by the POTWs varied significantly in characteristics depending upon the type of material (Class A/B biosolids, or pretreatment process stream sampling) and treatment process. Processes varied between aerobic digestion/anaerobic digestion, dewatering techniques (e.g., heat treatment, vacuum filter press), and the addition of precipitating agents such as polymers.

In this study, we found that varying levels of PCDD/Fs were present in the samples and appeared to be independent of what treatment process was used. In this paper, we present and discuss the PCDD/F results for the sewage sludge samples.

Materials and Methods

All samples were prepared and analyzed according to isotope dilution quantitation specified in a Midwest Research Institute method based on requirements of US EPA Methods 8290[2] and 1613.[3]

Moisture content of the samples varied depending upon dewatering and/or drying procedures used by POTW. Percent solids measurements were then taken in order to obtain a 10-g dry weight aliquot for extraction. The biosolid samples and quality control (QC) samples (i.e., ongoing precision recovery, method blank, and LCS) were fortified with a mixture of ^{13}C-labeled PCDD/F internal quantitation standards (IQS) and then extracted by Soxhlet/Dean Starks for 21 hours with toluene.

Following sample extraction, extracts were fortified with ^{37}Cl-labeled 2,3,7,8-TCDD as a clean-up efficiency standard, partitioned against concentrated sulfuric acid followed by an open tubular neutral/acid silica gel column, and then processed through a Fluid Management Systems Power-Prep instrument. On the Power-Prep, the extracts were subjected to another neutral/acid/base silica gel column, an acid/base alumina column, and an AX-21 carbon column. Extracts were concentrated by nitrogen evaporation and fortified with a ^{13}C-labeled 1,2,3,4-TCDD/1,2,3,7,8,9-HxCDD recovery standard in tridecane, bringing the final volume to 10 µL.

The samples were analyzed by HRGC/HRMS using a Fisons AutoSpec Ultima triple focusing/triple sector high-resolution mass spectrometer interfaced to a Hewlett-Packard 5890 gas chromatograph. A DB-5MS gas chromatography column (60 meter, 0.25 mm ID, 0.25 μm film thickness) was used due to its ability to effectively separate 2,3,7,8-TCDF from its closest eluting isomers[4,5], as specified in USEPA Method 1613. Mass spectrometer acquisition was performed at 10,000 resolution in the selected ion monitoring mode (SIM).

A five-point initial calibration curve (I-CAL) for PCDD/PCDF was performed using a 0.5-200 pg/μL range for tetra-substituted isomers, 2.5-1000 pg/μL range for penta- through hepta-substituted isomers and 5-2000 pg/μL range for octa-substituted isomers. The I-CAL passed method criteria of less than 20% relative standard deviation (RSD) for all compounds. Continuing calibration was performed using the midpoint of the curve in the beginning and end of each 12-hr run. Each standard was within USEPA Method 1613 CAL-VER limits.

Results and Discussion

The 2,3,7,8-substituted PCDD/F results for sixteen samples taken from various POTWs around the United States are given in Table 1. The results have varying levels of 2,3,7,8-substituted PCDD/F and total PCDD/F (not presented here) congener patterns that appear to be relatively independent of the treatment process used and of the size of the POTW. The treatment processes used range from anaerobic/aerobic digestion, gravity thickening, $FeCl_3$ precipitation, and/or polymer addition. Filter press, centrifugation, composting, and/or dewatering, could follow these treatment processes.

One sample of interest is 1948, which has a significantly higher average concentration than the other samples. It is the only sample in the study from a facility that specified using lagoons for its microbial digestion processing. Possibly an open lagoon has a greater potential for pollutant deposition, particularly if it were near a combustion source. This is a point that should be investigated further.

We conclude from this work that there appears to be little correlation between amounts of PCDD/F in sewage sludge samples and the treatments used to produce the processed sludge. However additional investigation needs to be done with a larger sample set from each type of treatment, particularly from lagoons. This work is currently being done at Midwest Research Institute.

References

1. USEPA Municipal and Industrial Solid Waste Division, Office of Solid Waste, "Biosolids Generation, Use, and Disposal in the United States." September1999.
2. USEPA Method 1613, "Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B." Oct. 1994.
3. USEPA Method 8290, "Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography / High Resolution Mass Spectrometry (HRGC/HRMS), Revision 0." September 1994.
4. Abad, E., J. Caixach, J. Rivera, "Application of DB-5MS Gas Chromatography Column for the Complete Assignment of 2,3,7,8-Substituted Polychloro-dibenzo-*p*-dioxins and Polychlorodibenzofurans in Samples from Municipal Waste Incinerator Emissions." *Journal of Chromatography A*, v. 786, 1997.
5. Gruber, L., H. Santl, J. Seidl, "Confirmation of the DB-5MS Column and the Use in Routine Dioxin Analysis." *Organohalogen Compounds*, v. 23, 1995.

Table 1. Toxic PCDD/F Results in Sewage Sludge Collected from Various Municipalities Around the United States (pg/g dry wt.)

	Sample # and Treatment Processes								
PCDD/F Congener	1796 GT	1896 AN, POL	1897 AN	1915 AN	1917 AN	1948 AE, L	1983 AN	2064 AN	2112 AN, D
2,3,7,8-TCDF	1.84	1.95	2.59	2.96	1.39	9.78	2.77	0.540	2.15
2,3,7,8-TCDD	0.817	0.626	0.933	0.908	0.382	1.43	0.795	0.380	0.620
1,2,3,7,8-PeCDF	0.872	0.726	2.32	1.41	0.499	20.4	0.887	0.226	1.20
2,3,4,7,8-PeCDF	1.37	1.24	1.70	3.07	1.22	6.65	1.50	0.347	2.81
1,2,3,7,8-PeCDD	10	4.73	10.9	10.6	3.07	9.23	8.63	3.15	3.62
1,2,3,4,7,8-HxCDF	1.95	1.54	13.2	3.99	U (2.41)	47.3	2.63	0.483	2.97
1,2,3,6,7,8-HxCDF	1.96	1.41	3.03	2.84	U (1.97)	46.7	1.91	0.427	2.44
2,3,4,6,7,8-HxCDF	2.89	2.43	13.1	4.42	1.75	24.5	3.51	0.829	3.88
1,2,3,7,8,9-HxCDF	0.995	0.686	1.63	1.08	0.715	19.7	0.716	0.435	1.21
1,2,3,4,7,8-HxCDD	1.79	1.21	1.40	2.49	U (1.77)	4.72	1.89	0.611	3.11
1,2,3,6,7,8-HxCDD	5.58	4.67	5.16	9.94	7.26	14.9	6.72	1.34	9.95
1,2,3,7,8,9-HxCDD	3.06	2.31	2.03	4.23	86.3	8.38	3.18	0.700	6.08
1,2,3,4,6,7,8-HpCDF	55.7	65.4	113	83.9	61.7	246	101	17.1	49.4
1,2,3,4,7,8,9-HpCDF	U (1.97)	U (1.47)	U (24.6)	4.06	1.61	116	2.37	0.487	2.96
1,2,3,4,6,7,8-HpCDF	182	130	133	331	140	538	171	33.8	282
OCDF	172	239	1750	393	184	815	496	61.3	175
OCDD	1920	2050	1670	3770	1330	9810	4620	372	2580

Treatment Processes: GT = gravity thickening, AN = anaerobic digestion, POL = polymer treatment, L = lagooning, D = D.A.F.T.S. treatment, FC = $FeCl_3$ precipitation, AE = aerobic digestion

U - Undetected with either an estimated maximum possible concentration or a noise based detection limit given in brackets

Table 1 (cont.). Toxic PCDD/F Results in Sewage Sludge Collected from Various Municipalities Around the United States (pg/g dry wt.)

	Sample # and Treatment Process						
	2131	2132	2138	2147	2148	2151	2154
PCDD/F Congener	AN, FC, POL	AN	GT	AE	AE	AN, FC	AN
2,3,7,8-TCDF	0.692	0.342	U (0.0368)	0.728	2.14	2.68	2.52
2,3,7,8-TCDD	0.204	0.161	U (0.0244)	0.301	1.11	U (0.795)	1.00
1,2,3,7,8-PeCDF	0.445	0.296	U (0.107)	0.419	1.36	0.647	1.07
2,3,4,7,8-PeCDF	0.608	0.367	U (0.0668)	0.629	2.68	1.25	1.95
1,2,3,7,8-PeCDD	1.48	1.02	U (0.274)	3.19	12.1	7.21	8.55
1,2,3,4,7,8-HxCDF	0.765	2.41	U (0.0731)	0.828	4.42	1.56	2.98
1,2,3,6,7,8-HxCDF	0.739	0.809	0.146	0.844	2.69	1.47	1.99
2,3,4,6,7,8-HxCDF	1.04	0.745	0.144	1.45	4.85	2.92	3.00
1,2,3,7,8,9-HxCDF	U (0.611)	0.481	U (0.374)	0.703	1.12	0.679	0.903
1,2,3,4,7,8-HxCDD	0.733	U (0.352)	0.200	0.802	U (1.78)	U (1.68)	1.95
1,2,3,6,7,8-HxCDD	1.86	0.773	0.621	2.62	5.99	5.43	6.62
1,2,3,7,8,9-HxCDD	0.934	0.562	0.292	1.41	2.96	3.03	3.43
1,2,3,4,6,7,8-HpCDF	20.5	19.6	1.11	35.3	75.4	73.0	59.5
1,2,3,4,7,8,9-HpCDF	0.679	0.505	U (0.0288)	1.14	2.11	1.30	2.08
1,2,3,4,6,7,8-HpCDD	43.5	20.2	7.49	88.5	162	132	170
OCDF	63.7	56.1	1.97	128	201	248	193
OCDD	409	224	55.4	1150	1790	1370	1720

Treatment Processes: GT = gravity thickening, AN = anaerobic digestion, POL = polymer treatment, L = lagooning, D = D.A.F.T.S. treatment. FC = $FeCl_3$ precipitation, AE = aerobic digestion

U - Undetected with either an estimated maximum possible concentration or a noise based detection limit given in brackets