USEPA NATIONAL SEWAGE SLUDGE SURVEY RESULTS FOR POLYCHLORINATED DIBENZO-*P*-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

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ABSTRACT

Between July 1988 and March 1989, the United States Environmental Protection Agency conducted a survey of 181 of the over 15,000 publicly-owned sewage treatment works in the United States. The purpose of the survey was to collect data to support the development of regulations governing the disposal of sewage sludge under Section 405(d) of the Clean Water Act. Over 400 analytes were determined in samples from this survey, including the seventeen 2,3,7,8-substituted PCDDs and PCDFs. The results of this survey confirmed the ubiquitous nature of the most highly chlorinated PCDDs and PCDFs. OCDD, OCDF, and two HpCDD and HpCDF isomers were found in at least 80% of the samples from this survey, with no apparent relationship between concentrations of these compounds and treatment design, flow rate, storm runoff, or industrial input. 2,3,7,8-TCDD was found in less than 20% of all samples, at concentrations similar to those found by other investigators.

INTRODUCTION

In the twenty years since its inception, the United States Environmental Protection Agency (USEPA) has expended significant effort to improve the quality of surface waters in the United States. These efforts have been made in response to legislative requirements contained in the Clean Water Act (CWA) of 1972 and its amendments, and in response to various judicial consent decrees. The majority of these improvements have been realized through the implementation of treatment of wastewaters prior to their discharge into surface waters from industrial and municipal point sources, including publicly-owned treatment works (POTWs). While the "best available technology" (BAT) employed at these POTWs has reduced the impact of the discharges on the receiving waters, much of the improvement is due to the physical removal of suspended solids from the wastewater. Other improvements in water quality, particularly related to those compounds that are not associated with particulate materials (e.g. dissolved metals), have been due to reductions in inputs of these compounds to the POTWs. While aerobic and anaerobic digestion processes used in waste treatment reduce the amount of material discharged into the receiving waters, the treatment processes partition the materials removed from suspension into a solid phase or into the atmosphere. The solid phase materials form the sludge from the sewage treatment processes. Therefore, one effect of the treatment processes is to concentrate the "toxic pollutants" in the sludge.

At present, POTWs may utilize a variety of means to dispose of this sludge. The range of disposal practices includes: distribution and marketing of the sludge as a soil amendment; land application on non-agricultural lands; sludge-only landfills, termed "monofills"; mixed waste landfills; incineration; and even ocean disposal. Recognizing that such disposal practices represent potential inputs of toxic pollutants to the environment, Section 405(d) of the CWA requires the Agency to develop regulations governing the disposal and utilization of sewage sludge. As part of the development of such regulations, in 1988 the Agency began a large-scale sampling and analysis effort to assess the current levels of toxic pollutants in sewage sludge from POTWs. This sampling and analysis effort became known as the National Sewage Sludge Survey (NSSS).

Of the approximately 15,300 POTWs in the United States, 479 were chosen through a random stratified sampling design to receive questionnaires regarding their treatment processes, sludge disposal practices, types of inputs, and other associated data. Of the 462 POTWs that returned the questionnaire, 181 were chosen for sampling and analysis through the use of a second random design stratified by flow volume. Over 400 analytes were determined for each sample. The analytes included 57 volatile organics, 177 semivolatile organics, 31 organochlorine pesticides, 7 polychlorinated biphenyls as Aroclors, 36 organophosphorus pesticides, 4 phenoxy acid herbicides, 69 trace metals, 7 "classical" wet chemical water quality parameters, and 17 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs). This paper addresses the results of the analyses of the PCDDs and PCDFs.

SAMPLING AND ANALYSIS

Samples were taken at each of the 181 POTWs from the final sludge product or products disposed of by the plant. If no sludge left the facility, then that facility was not included in the 181 POTWs to be sampled, as the regulatory requirements of Section 405(d) address only off-site disposal practices. The designs of POTWs generally fall into three categories based on the physical characteristics of final sludge disposal product generated. The three final disposal products are digestor sludge (a liquid generally less than 1% solids), filter cake (a dewatered sludge from belt presses or centrifuges), and composted sludge (dried in open beds or mixed with leaves, wood chips, etc.).

Any plant that disposed of more than one type of sludge was sampled once for each sludge type. All samples were taken as grab samples at a point just before disposal. A total of 211 unique samples were taken from the 181 POTWs. Including a series of duplicate samples from some plants, a total of 240 samples were taken. The samples from the 181 plants were taken between July 1988 and March 1989. The distribution of solids contents of all 240 samples is shown in Table 1 below.

Table 1
Distribution of Percent Solids Data for NSSS Samples

No. Obs.	Mean	Median	Std. Dev.	Min.	Max.	Percentiles 25%	50%	75%
240	23.23	16.6	24.30	0.19	100	3.4	16.6	34.8

As can be seen from the mean and median values, the solids data are not normally distributed. Of the 240 samples, 75% had percent solids values less than 35%.

The analytical methods used in the NSSS for the PCDD/PCDF analyses underwent modifications during the course of the study. USEPA Method 1613 was under development during this study, and is discussed at length in another presentation at this meeting. The earliest sludge samples were analyzed using an early draft of Method 1613 (September 1988) loosely based on USEPA Method 8290. A significant modification to these procedures included the use of the Soxhlet-Dean Stark (SDS) extraction procedures developed by Dow Chemical (Lamparski and Nestrick, 1989). The use of the SDS for the extraction of sewage sludge was validated in a single laboratory, and then applied to all subsequent sludge samples with solids contents over 1% percent. Sludges samples with less than 1% solids were extracted as water samples. Later samples were analyzed using the procedures listed in the July 1989 draft of Method 1613, which included the SDS extraction procedure. All the analyses were performed by private laboratories under contract to the USEPA Industrial Technology Division (ITD).

ANALYTICAL RESULTS

Based on the distribution of solids shown in Table 1, the decision was made to evaluate the concentration data for PCDDs and PCDFs based on the wet weight of the samples. This use of wet weight concentrations resolved the apparent disparity among the concentration data. For instance, for samples with very low solids contents, 1% or less, the concentrations of any PCDDs and PCDFs that were detected appear inordinately high if expressed on a dry weight basis, and such reporting does not enhance comparisons of the concentrations of these analytes between samples. Dry weight concentrations would be useful in comparing data for samples taken from the same plant over a long period, but are not helpful when comparing "sludges" from different plants across the country that range from pourable liquids to solids collected off of a filter press or composted with leaves and wood chips.

The results of the analyses for the seventeen 2,3,7,8-substituted PCDDs and PCDFs are given in Table 2 below. These data cover the 211 unique samples from the survey, and do not include any duplicate samples at a given plant. The concentration data reflect only those analytes that were quantified in the samples: non-detects were eliminated from these calculations.

Table 2
Frequency of Occurrence and Concentrations of Detected Analytes for NSSS Samples
(all concentrations expressed in ng/Kg wet weight)

Analyte	No. Obs.	% Occur.	Mean Conc.	Median Conc.	Std. Dev.	Min. Conc.	Max. Conc.
2378-TCDD	37	17.5	3.39	0.18	13.06	0.01	78
2378-TCDF	125	59.2	4.67	0.78	12.86	0.01	132
12378-PeCDD	54	25.6	14.56	1.40	68.86	0.02	506
12378-PeCDF	57	27.0	10.13	1.05	46.40	0.02	351
23478-PeCDF	64	30.3	8.72	0.83	32.64	0.01	257
123478-HxCDD	55	26.1	20.22	1.20	92.08	0.02	678
123678-HxCDD	105	49.8	19.23	5.69	48.34	0.02	296
123789-HxCDD	83	39.3	29.33	1.85	118.6	0.03	1013
123478-HxCDF	89	42.2	31.44	1.43	167.0	0.01	1558
123678-HxCDF	65	30.8	11.14	0.69	48.15	0.01	382
123789-HxCDF	36	17.1	10.55	0.83	18.94	0.01	63
234678-HxCDF	62	29.4	15.59	0.81	89.89	0.01	709
1234678-HpCDD	209	99.1	350.73	51.57	1095	0.07	12114
1234678-HpCDF	172	81.5	98.10	12.40	477.5	0.05	5687
1234789-HpCDF	58	27.5	12.30	1.79	29.57	0.03	187
OCDD	211	100.0	3778.1	512.0	11584	0.57	107680
OCDF	178	84.4	258.63	35.86	759.1	0.04	5219

The concentration data are not normally distributed, but as with other environmental data, approximate a log-normal distribution with respect to a given analyte.

The relationship between PCDD/PCDF concentrations and percent solids was investigated as well. Statistical analysis (Pearson correlation) indicates that there is a strong positive correlation between the log of the concentration of each detected analyte and the log of the percent solids content of the sludge. As the solids content of the samples increase, the wet weight concentrations of detected PCDDs/PCDFs increase. This observation supports the assumption that the PCDDs/PCDFs are strongly associated with the particulate matter in an aqueous sample. Thus, when the sewage treatment process concentrates the solids to a greater degree, the amount of the PCDDs/PCDFs will increase as well.

Conversely, based on a Chi-squared test, there is no statistical relationship between the percent solids content of a sample and the likelihood of detecting a PCDD/PCDF. Using the data from this study, there is no relation between the simple presence or absence (detect vs non-detect) of an analyte and the solids content of the sample.

Because the differences in treatment processes and treatment plant designs have a significant effect on the residence time of materials entering a POTW, it was not possible to make synoptic measurements of the flow of influent to the treatment process that could be directly related to the sludge that was sampled. In fact, at some plants, sludge may accumulate for several months before disposal. However, daily average effluent flow data were collected from the records of each POTW that was sampled. Data are available for the domestic flow, the industrial flow, and in instances where the plant receives combined sanitary and storm water inputs, the daily average storm water flow. Attempts to correlate the detected concentration of a given analyte with any of these three effluent flows were inconclusive. There is no apparent relationship between flow rate and PCDD/PCDF concentration across the range of flow rates exhibited by these POTWs. Even when breaking the POTWs down into the four general flow groups used to stratify the sampling design, no relationship is apparent.

Further analyses of these data are underway, including attempts to relate the concentrations of the PCDDs/PCDFs to the concentrations of other of the 400 analytes and possible relationships to contributions from specific industrial sources. However, as can be seen from the data in Table 2, PCDDs and PCDFs are frequently detected in sludge samples in this study. Two dioxin compounds, OCDD and 1,2,3,4,6,7,8-HpCDD are ubiquitous in these samples, while two furans, OCDF and 1,2,3,4,6,7,8-HpCDF, were found in over 80% of all samples. The concentrations of these compounds varied greatly among the plants, with seven orders of magnitude between the lowest and highest concentrations. The more toxic tetrachlorinated and pentachlorinated compounds were found less frequently, and at generally lower concentrations. These initial findings support those of Lamparski *et al.* (1984) and Rappe *et al.* (1988), who detected PCDDs/PCDFs in sewage sludges from Milwaukee, Wisconsin, and two sites in Sweden.

Attempts are underway to use pattern recognition techniques to classify the PCDD/PCDF results for the POTWs in this survey. The development of patterns of occurrence may assist in identifying the sources of these compounds to POTWs. At this time, the lack of correlations with industrial inputs to those POTWs that receive industrial waste, and the lack of distinction between plants from rural and urban areas indicates that at least some portion of the PCDD/PCDF input to sewage treatment processes is contributed by domestic sources.

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