POLYCHLORINATED DIBENZO-p-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) IN SEWAGE SLUDGES FROM RURAL AND URBAN/INDUSTRIAL WASTEWATER TREATMENT PLANTS (WWTPs)

Thomas O. Tiernan, John H. Garrett, Joseph G. Solch, Garrett F. VanNess, Daniel J. Wagel and Farai Rukunda, Brehm Laboratory, Wright State University, Dayton, Ohio 45435, USA

Abstract

The concentrations of PCDDs and PCDFs present in sewage sludge from rural wastewater treatment plants (WWTPs) which receive little or no waste from industrial sources were found to be significantly lower than the levels of these compounds in sludge from urban WWTPs which receive industrial waste input. Also, the mean levels of PCDDs/PCDFs in both types of sludge samples surveyed in this study were significantly lower than the mean levels which were reported by the U.S. EPA from the 1988 National Sewage Sludge Survey. The 2,3,7,8-substituted PCDDs/PCDFs isomer profiles of the sludge samples suggest that pentachlorophenol sources may account for much of the higher chlorinated congeners in these samples.

Introduction

Some five million metric tons of dry sewage sludge is generated by wastewater treatment plants (WWTPs) in the U.S. annually. Approximately 30% of this sludge is applied to agricultural lands for soil conditioning and fertilization. Extensive studies conducted by the U.S. EPA in 1988, in which sludges from some 175 WWTPs were surveyed, showed that all of the 2,3,7,8-substituted PCDDs/PCDFs were detectable in these wastes, including 2,3,7,8-TCDD in some of the samples, and that the concentrations of these varied enormously.[1] Other studies of sewage sludges conducted in Germany,[2] Sweden,[3] and England[4] resulted in similar observations. These findings have prompted concerns about the use of PCDDs/PCDFs-containing sewage sludge for agricultural purposes, because of the possibility that this could introduce these toxic compounds into the food chain.

Following the 1988 U.S. EPA sewage sludge survey, several states in the U.S. implemented sludge monitoring programs to assay WWTP sludges for PCDDs/PCDFs. The study reported here is a limited survey which was aimed in part at determining whether or not levels of PCDDs/PCDFs occurring in sewage sludges from rural WWTPs receiving minimal industrial waste are significantly different than the levels in urban WWTPs which typically receive both household and industrial wastes. Since higher chlorinated PCDDs/PCDFs detected in sewage sludges analyzed in previous studies have been tentatively associated with pentachlorophenol (PCP) sources, the present study has focused on the patterns of the PCDDs/PCDFs congeners in the sludges as indicators of potential environmental sources.

Experimental

Sewage sludge samples, generally containing relatively low percent solids, were obtained

directly from WWTPs located in both rural and urban areas. The dry weights of these sludges were determined, and the samples were analyzed for both total congener groups and 2,3,7,8-substituted isomers of the PCDDs/PCDFs using U.S. EPA Method 1613.

Results and Discussion

Table 1 summarizes the concentrations of the 2,3,7,8-substituted PCDDs/PCDFs, expressed as Toxic Equivalents (I-TEQs), which were measured in the sludge samples analyzed here. Sludge samples A through C originated from rural WWTPs while sludge samples D through J were obtained from urban WWTPs impacted with industrial sources. As can be seen from the data in Table 1, the total TEQs of PCDDs/PCDFs detected in the rural sludges are substantially lower than those detected in the urban sludges. However, the total TEQs measured for these two groups of sludges are reasonably consistent within each group. While these data show considerable variability in the 2,3,7,8-substituted congeners for the various sludge samples in a given group, the major isomeric components in most of sludges are hexa-, hepta- and octa-CDDS and CDFs.

In Table 2, the levels of the 2,3,7,8-substituted PCDDs/PCDFs found in the sludge samples analyzed here are compared with the mean and median concentrations reported by the U.S. EPA from the 1988 National Sewage Sludge study. Clearly, the levels detected in the present study are substantially lower than the mean and median levels reported by the U.S. EPA. It cannot be determined from the limited study reported here whether this difference reflects a general decline in PCDDs/PCDFs in sewage sludges in the U.S. over the past decade, or whether the lower levels observed here simply reflect the characteristics of the particular sets of WWTPs which were surveyed here.

In Table 3, the contribution of the individual 2,3,7,8-substituted PCDDs/PCDFs congeners detected in the sludges analyzed here to the mean total TEQs for these samples are shown. These are compared with corresponding data from the U.S. EPA study (here the median concentrations were used since the means vary so widely), from a more recent study conducted in England and with contributions to the total TEQ from the 2,3,7,8-substituted isomers which were found in a commercial pentachlorophenol (PCP) product. As can be seen from these results, there is considerable agreement between the several studies in terms of the isomers which yield major contributions to the total TEQs, and in terms of the relative contributions of dioxins as compared to furans. In addition, as observed, these same isomers are major contributors to the total TEQ of the PCP product. While this supports the conclusions of previous studies which indicate that PCP sources are likely responsible for most of the higher chlorinated PCDDs/PCDFs in sewage sludges, the observation of more substantial concentrations of lower chlorinated congeners in the sludges, including 2,3,7,8-TCDD, indicates that other sources, probably including atmospheric deposition from incineration processes, also impact these sludges.

Literature Cited

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TABLE 1
2,3,7,8-SUBSTITUTED PCDDs/PCDFs MEASURED IN SEWAGE SLUDGE
FROM RURAL AND URBAN/INDUSTRIAL WASTE WATER TREATMENT PLANTS EXPRESSED AS TOXIC EQUIVALENTS (I-TEQ)

Toxic Equivalent Concentration (I-TEQ) for Each 2,3,7,8-substituted Isomer (picograms per gram of sample or parts per trillion)[a]

Sample Number[b]	TEF	Sludge A	Sludge B	Sludge C	Sludge D	Sludge E	Sludge F	Sludge G	Sludge H	Sludge I	Sludge J
2378 TCDF	0.10	ND (0.0138)	0.053	0.568	0.228	0.349	0.238	0.199	0.378	0.33	0.170
2378 TCDD	1.00	ND (0.233)	0.473	ND (0.237)	ND (0.215)	ND (0.130)	ND (0.428)	1.44	ND (0.188)	1.10	4.38
12378 PeCDF	0.05	ND (0.0035)	ND (0.0074)	ND (0.0097)	0.0399	0.0834	0.0759	0.0531	0.103	0.309	0.0635
23478 PeCDF	0.50	ND (0.0405)	ND (0.0942)	ND (0.073)	ND (0.262)	0.768	1.47	0.937	0.992	2.17	1.39
12378 PeCDD	0.50	ND (0.0395)	ND (0.118)	ND (0.062)	1.22	0.964	1.17	1.33	1.46	2.19	2.17
123478 HxCDF	0.10	ND (0.0107)	ND (0.0227)	ND (0.0143)	0.368	0.289	0.615	0.322	0.703	1.77	0.800
123678 HxCDF	0.10	0.0280	ND (0.0186)	ND (0.0251)	0.214	0.373	0.325	0.167	0.394	0.691	0.368
234678 HxCDF	0.10	ND (0.0181	ND (0.0287)	ND (0.0161)	0.243	0.239	0.542	0.439	0.358	0.655	0.394
123789 HxCDF	0.10	ND (0.0135)	ND (0.0247)	ND (0.0189)	ND (0.0213)	ND (0.0207)	ND (0.064)	ND (0.0417)	ND (0.0153)	ND (0.141)	ND (0.0711)
123478 HxCDD	0.10	ND (0.0160)	ND (0.0589)	ND (0.0209)	0.178	0.499	0.381	0.418	0.342	0.413	ND (0.0574)
123678 HxCDD	0.10	0.0390	ND (0.0486)	ND (0.0214)	3.17	2.34	1.03	3.74	3.42	0.887	ND (0.0476)
123789 HxCDD	0.10	0.0416	ND (0.0514)	ND (0.0283)	1.38	0.961	0.866	1.38	1.35	0.866	1.06
1234678 HpCDF	0.010	ND (0.0077)	ND (0.0096)	ND (0.0090)	0.302	0.313	0.411	0.278	0.505	0.791	0.724
1234789 HpCDF	0.010	ND (0.0017)	ND (0.0051)	ND (0.0075)	0.0291	0.0279	0.0443	ND (0.0088)	ND (0.0186)	0.135	0.0677
1234678 HpCDD	0.010	0.0715	0.157	0.115	2.36	3.36	1.90	3.60	3.58	2.28	2.80
OCDF	0.001	0.0016	ND (0.0011)	0.0073	0.0754	0.0569	0.118	0.0231	0.0709	0.155	0.197
OCDD	0.001	0.0679	0.119	0.295	1.31	1.58	3.13	2.07	2.68	3.11	5.11
TOTAL I-TEQ[c]		0.65	1.29	1.31	11.6	12.4	12.9	16.5	16.5	18.0	19.9

a. The TEQ shown is obtained by multiplying the measured concentration of each isomer by the Toxic Equivalents Factor (TEF). In cases where an isomer is not detected (ND), the TEQ which is reported beside the ND notation is obtained by multiplying one-half the detection limit by the TEF.
b. Sludge samples A through C are from rural WWTPs; sludge samples D through J are from urban/industrial WWTPs.
c. This is the sum of the TEQs for all 2,3,7,8-substituted isomers.

TABLE 2

COMPARISON OF 2,3,7,8-SUBSTITUTED PCDDs/PCDFs IN SEWAGE SLUDGE AS MEASURED IN THE U.S EPA's NATIONAL SEWAGE SLUDGE SURVEY (1988) WITH RESULTS OF PRESENT STUDY

Congener	Concentrations in ng/kg, dry weight or ppt			
	Mean (U.S. EPA)[a]	Median (U.S. EPA)[a]	Present Study - Rural WWTP	Present Study - Urban/Industrial WWTP
2378-TCDD	7.3	4.4	0.32	1.1
12378-PeCDD	16	6.5	0.15	3.0
123478-HxCDD	27	13	0.32	3.3
123678-HxCDD	43	19	0.36	21
123789-HXCDD	39	19	0.41	11
1234678-HpCDD	1,290	400	11	284
OCDD	16,530	3,500	161	2,713
2378-TCDF	12	8.0	2.1	3.2
12378-PeCDF	16	6.5	0.13	2.1
23478-PeCDF	17	6.5	0.14	2.3
123478-HxCDF	54	18	0.32	7.0
123678-HxCDF	24	12	0.24	3.6
123789-HxCDF	26	11	0.42	4.1
234678-HxCDF	26	13	0.38	1.1
1234678-HpCDF	241	66	1.7	48
1234789-HpCDF	30	13	0.95	4.7
OCDF	1,100	170	9.9	100
Total TEQ	83	31	1.2	15

a. Rubin, A.; White, C. National Sewage Sludge Data Base, U.S. Environmental Protection Agency (USEPA), Office of Science and Technology, Health and Ecological Criteria Division, Sludge Risk Assessment Branch, 1992.

TABLE 3

CONTRIBUTION OF INDIVIDUAL 2,3,7,8-SUBSTITUTED CONGENERS TO TOTAL TOXIC EQUIVALENTS (TEQ) OF PCDDs/PCDFs PRESENT IN SEWAGE SLUDGE AND IN A PENTACHLOROPHENOL PRODUCT

Congener	Percent of Total TEQ				
	USEPA, 1988 Median	Sewart et al, 1995 Mean	Present Study - Mean Rural WWTP	Present Study - Mean Urban/Industrial WWTP	PCP Product
2378 TCDD	14	3.1	27	7.3	0.056
12378 PeCDD	10	2.7	6.3	9.7	0.044
123478 HxCDD	4.2	0.6	2.8	2.1	0.011
123678 HxCDD	6.1	3.9	3.1	14	13
123789 HxCDD	6.1	1.6	3.5	7.3	0.34
1234678 HPCDD	13	27	9.9	18	35
OCDD	11	24	14	18	13
Total PCDD	65	63	67	76	61
2378 TCDF	2.6	5.8	18	1.8	0.011
12378 PeCDF	1.0	12	0.59	0.68	0.013
23478 PeCDF	11	1.8	6.0	7.4	0.088
123478 HxCDF	5.8	3.4	1.4	4.5	3.4
123678 HxCDF	3.9	0.10	2.1	2.4	1.3
234678 HxCDF	3.5	3.9	1.8	2.7	0.89
123789 HxCDF	4.2	3.8	1.6	0.35	0.79
1234678 HpCDF	2.1	5.1	0.76	3.1	27
1234789 HpCDF	0.42	0.18	0.41	0.31	1.0
OCDF	0.55	0.89	0.29	0.65	4.1
Total PCDF	35	37	33	24	39

a. Rubin, A.: White, C. National Sewage Sludge Survey Data Base, USEPA, 1992.
b. Swart, A.; Harrad, S. J.; McLacklan, M. S.; Jones, K. C. *Chemosphere* 1995, 30, 51-67.