PCDDs and PCDFs in Municipal Sewage Sludge and Effluent from the State of Mississippi, USA

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Abstract

During the summer 1995, we collected sewage sludge samples and effluent samples from 17 publicly owned treatment works (POTW) in the State of Mississippi, USA. In the sludge most PCDDs and PCDFs were detected, particularly hepta- and octaCDD. One plant had an octaCDD value exceeding 400 000 pg/g dry matter ("d.m.") sludge. Most effluent samples were below the detection limit of approximately 10 pg/L for tetra- through hexachlorinated congeners. One plant had an octaCDD value in the effluent of 2 500 pg/L. This plant is a potential point source to the Leaf River.

Key words: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, sewage sludge, sewage effluent, POTW, United States of America

1 INTRODUCTION

In 1984, Lamparski et al. (1) reported on the occurrence of PCDDs and PCDFs in sewage sludge samples from USA, including an archived 1933 sample from Milwaukee, WI. In all samples, they detected low concentrations of tetra- and hexachlorinated PCDDs and PCDFs (below 1 500 pg/g d.m.); much higher values were reported for heptaCDD (up to 9 700 pg/g d.m.) and for octaCDD (up to 60 000 pg/g d.m.). In 1985, Weerasinghe et al. (2) reported on two sewage sludge samples from the state of New York. In general, the concentrations in the sample from an urban area were 5-10 times higher than the concentrations in the sample from the rural area. The sample from the urban area contained 60 000 pg/g d.m. octaCDD.

In 1989, US EPA published the National Sewage Sludge Survey (3). In this study 239 sewage sludge samples from all over the US were analyzed for metals, pesticides, and organic pollutants, including PCDDs and PCDFs. Only one sample in this study was from the State of Mississippi. This sample,

2.2 Analytical

All sludge samples were dried in a gentle stream of air in the hood. Extraction of the sludge samples, clean-up of the extracts and the HRGC/HRMS analyses followed earlier described methods for sewage sludge and sediments (6-9).

All effluent samples were sucked through a series of polyurethane foam plugs, pre-washed by Soxhlet extraction using toluene for 24 hours. The foam plugs were fortified with a series of $^{13}C_{12}$-labelled PCDDs and PCDFs before filtration. Although a validation study showed good recoveries, some losses were observed for real samples and were determined to be the result of adsorbing on the glass surface. In order to minimize these losses, the glass equipment was washed with toluene. The toluene was subsequently used to extract the foam plugs in a Soxhlet extractor equipped with a Dean-Stark water collector for 18 hours. The clean-up of the concentrated extract was performed on the three column system as described earlier (6-9).

3 RESULTS

3.1 Sewage sludge

The analytical results of the 18 sewage sludge samples are given in Table 1. In addition to the higher chlorinated PCDDs and PCDFs, we report the value for the TEQ and the D/F ratio. Although the minimum and maximum values for hexa- through octaCDDs and CDFs varied by a factor of thousand or more, all the samples typically were dominated by octa- and heptaCDDs.

The highest concentrations of hepta- through octaCDDs and CDFs were found for the sample and blind duplicate sample from Picayune. The values for octaCDD were 480 000 pg/g d.m. and 420 000 pg/g d.m., respectively. Similarly, the respective values for the heptaCDDs were 250 000 and 210000 pg/g d.m. Finally, the TEQ-values were 1 270 and 1 240 pg/g d.m., respectively.

The lowest octaCDD value was from Leakesville (560 pg/g d.m.), and this sample also had the lowest TEQ (2.26 pg/g d.m).

3.2 Effluent

The results of the same parameters for the 18 effluent samples are given in Table 2. Most effluent samples were below the detection limit of approximately 10 pg/L for the tetra- through hexachlorinated congeners. The concentration variation for the effluent samples was smaller than for the sludge samples. For example, octaCDD values varied by a factor of 700 and TEQ by approximately 15. The highest hepta- and octaCDD values were detected in the effluent from the New Augusta POTW; the lowest values for these congeners were from the Pascagoula POTW. The New Augusta POTW had a value for heptaCDDs of 120 pg/L and an octaCDD value of 2 500 pg/L. The Pascagoula POTW had a heptaCDD concentration of 0.82 pg/L and an octaCDD concentration of 3.6 pg/L. The TEQs for New Augusta and Pascagoula were 3.84 and 0.264 pg/L, respectively.

from Corinth, MS, was reported to have a concentration of 2,3,7,8-tetraCDD of 116 pg/g d.m., the highest value for this congener in the study.

Hagenmaier et al. (4) published a study in 1990 where they reported concentrations of PCDDs and PCDFs from 43 sewage sludge samples suspected of containing high levels of dioxins from various parts of Germany. They reported a mean value of 202 pg TEQ/g d.m. (range: 28-1 560 pg TEQ/g d.m.) and values as high as 75 000 pg/g d.m. of heptaCDDs and 200 000 pg/g d.m. of octaCDD. In a later survey on German sewage sludges, Butzkamm-Erker and Mach (5) published an average of 50-60 pg TEQ/g d.m. In 1989, Rappe et al. (6) reported on two samples of sewage sludge from Sweden. One of the samples was from the city of Stockholm and the other from a rural area where the sewer system only received household effluents. The PCDD and PCDF concentrations, congener profiles and patterns were quite similar in the two samples, despite their different inputs. Both were dominated by the hepta- and octaCDD and both contained 15 000 - 20 000 pg/g d.m. of octaCDD. In 1994, Rappe et al. (7) reported on the analysis of 30 sewage sludge samples collected from urban and rural areas in Switzerland. In communities with only 100-150 persons, the octaCDD values were approximately 5 000 pg/g d.m. and these sludge samples had TEQ values of approximately 20 pg/g d.m. The highest octaCDD value (67 000 pg/g d.m.) was from a city with chemical industries; the TEQ value for this sample was 4 100 pg/g d.m.

2 EXPERIMENTAL

2.1 Sampling

We collected sewage sludge and effluent samples from 17 POTWs and one blind duplicate sludge sample and one blind duplicate effluent sample from one of the POTWs. The facilities are identified in Tables 1 and 2. In addition, one travel blank, one equipment blank, one solvent blank and one on site laboratory blank were analyzed.

Most sludge samples were collected from settling ponds using pre-cleaned stainless steel spoons. The lagoon sludge samples were collected using a Ponar sampler and/or a split spoon. Two liters of liquid sludge were collected using a composite sampler equipped with new pre-cleaned Teflon tubing and silicone pump tubing. All effluent samples were twenty-four hour composites and were collected using a US EPA approved automatic sampler equipped with new pre-cleaned Teflon tubing, new pre-cleaned Silicone pump tubing and pre-cleaned glass container that collected 165 mL per hour and a total volume of 4 L.

All sludge and effluent samples were placed on ice and shipped to the local laboratory. After acidification with sulfuric acid to a pH of approximately 2, all samples were coded and shipped in ice chests to the analytical laboratory.

Table 1: Concentrations in pg/g d.m. of higher chlorinated PCDDs, PCDFs, TEQ and D/F ratio for sewage sludge samples from the State of Mississippi.

Facility	Σ HxCDDs	Σ HxCDFs	Σ HpCDDs	Σ HpCDFs	OCDD	OCDF	TEQ	D/F Ratio
Waynesboro	85	34	920	180	7400	410	23.7	13.11
Meridian	10	20	1100	300	7400	410	27.6	11.18
Pascagoula	170	35	970	670	4300	170	26.4	5.873
W. Biloxi	280	15	370	530	2500	62	159	9.57
Gulfport	61	24	1500	390	10000	360	31	14.79
Laurel	22	12	160	32	2700	21	4.83	39.32
Brookhaven	130	110	1400	400	9300	230	36.7	13.95
Natchez	83	11	1000	320	6600	260	29.3	12.91
Picayune	17000	3700	250000	19000	480000	16000	1270	18.94
Picayune *	16000	2500	210000	19000	420000	17000	1240	16.54
Waveland	160	39	820	350	4300	120	19.7	9.523
Corinth	42	17	230	39	3300	36	7.4	36.6
New Augusta	21	5.3	140	13	1400	8.8	2.67	53.17
Beaumont	59	18	470	53	1900	42	6.18	20.11
Leakesville	16	8.2	92	13	560	26	2.26	13.54
McLain	39	0.16	140	3.5	2600	0.74	3.55	575
Hattiesburg South	170	65	1300	270	4400	180	33	10.61
Hattiesburg North	310	330	3600	920	27000	980	70.4	13.53

* Blind duplicate

Table 2: Concentrations in pg/L of higher chlorinated PCDDs, PCDFs, TEQ and D/F ratio for POTW effluents from the State of Mississippi.

Facility	Σ HxCDDs	Σ HxCDFs	Σ HpCDDs	Σ HpCDFs	OCDD	OCDF	TEQ	D/F Ratio
Waynesboro	ND	0.51	3.5	1.2	13	1.8	0.316	4.21
Meridian	1.3	ND	7.6	1.8	58	1.8	0.445	15.53
Pascagoula	ND	0.21	0.82	0.38	3.6	0.46	0.264	0.6642
W. Biloxi	ND	0.24	0.9	ND	4	ND	0.378	8.225
Gulfport	ND	0.22	2.3	0.22	9.9	0.78	0.371	6.402
Laurel	ND	ND	2.9	ND	38	ND	0.334	53.65
Brookhaven	0.85	1.8	3.2	1.6	28	1.7	0.796	3.671
Natchez	2.5	1.4	2.4	3.1	9.1	1.8	1.03	1.735
Picayune	6.5	0.8	38	2.5	120	2	0.715	23.56
Picayune *	6	ND	30	1.9	53	1.6	0.397	18.14
Waveland	ND	0.74	3	1.4	14	ND	2.4	0.4672
Corinth	0.77	0.17	2.7	0.55	18	0.9	0.276	11.9
New Augusta	21	4.2	120	3.3	2500	1.1	3.84	192.9
Beaumont	0.64	0.61	2.4	0.68	11	0.66	0.274	2.554
Leakesville	8.9	3.6	46	4.5	780	3.2	1.6	41.65
McLain	2.5	0.19	14	ND	200	ND	0.377	261.1
Hattiesburg South	1.2	0.89	4.5	1.6	29	0.77	0.32	7.6
Hattiesburg North	0.96	0.57	9.1	3.1	73	2.9	0.457	7.906

* Blind duplicate

4 DISCUSSION

4.1 Sewage Sludge

The sludge from the Picayune POTW had the highest concentrations of octa- and heptaCDDs, more than 50 times higher than the next highest. This plant receives industrial inputs, including effluents from wood treatment facilities which likely contain pentachlorophenol.

The 2,3,7,8-tetraCDD concentration in the sewage sludge from the Corinth POTW was reported in the US EPA Sewage Sludge Survey to be 116 pg/g d.m. and the TEQ exceeded 1 500 pg/g d.m. (3). These high values could not be confirmed in the present study. In fact, we found a concentration of only 0.3 pg/g d.m. for 2,3,7,8-tetraCDD and a TEQ of 7.4 in the sludge sample from Corinth. The PCDD and PCDF concentrations and profiles from the sludge sample collected in the present study from Corinth are very different from the earlier sample reported by EPA. The D/F-ratio (Table 1) was found to be 36.6; in the prior sample it was found to be 1.6 (3).

4.2 Effluent

A visual inspection of the POTW effluents revealed that some contained significant amounts of suspended particulates. The effluent from the New Augusta POTW was one of these and, consequently, this plant had the highest values for the higher chlorinated dioxins. Table 3 contains a comparison between this effluent and the median value for the 18 effluent samples included in this study. The octaCDD concentration in the New Augusta POTW effluent is 90 times higher than the median.

The New Augusta POTW discharges into the Leaf River between two sampling points (SE 505 and SE 506) where we collected sediment samples in an earlier study (9-11). A pulp mill is located between points SE 505 and SE 506 above the New Augusta POTW. In the earlier study we showed that the PCDDs and PCDFs associated with pulp bleaching (2,3,7,8-tetraCDD and 2,3,7,8-tetraCDF) are lower downstream the pulp mill than upstream, showing that the pulp mill is not a source to the Leaf River (9-11). Table 3 includes the PCDD and PCDF results from sediments SE 505 and SE 506 from the earlier study. A comparison with the composition of the POTW effluent in New Augusta shows the importance of this potential point source to the Leaf River.

Table 3: Concentrations of PCDDs and PCDFs in effluent from New Augusta POTW, median of all Mississippi POTW in this study and sediments SE 505 and SE 506 from Leaf River.

	Effluent POTW		Leaf River Sediments	
	New Augusta pg/L	Mississippi Median pg/L	SE 505 pg/g d.m.	SE 506 pg/g d.m.
2,3,7,8-TCDF	1.3	0.18	0.15	0.099
Σ TCDF	3.2	1.2	2	1.1
2,3,7,8-TCDD	ND (0.097)	ND (0.15)	0.36	0.38
Σ TCDD	8.1	1.2	6.6	11
Σ PeCDFs	1.9	0.34	4.8	2.2
Σ PeCDDs	15	0.45	18	32
Σ HxCDFs	4.2	0.51	15	5.5
Σ HxCDDs	21	0.85	110	210
Σ HpCDFs	3.3	1.4	40	9.8
Σ HpCDDs	120	3.2	510	790
OCDF	1.1	0.9	32	18
OCDD	2500	28	4800	13000

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