Dioxin '97, Indianapolis, Indiana, USA

PCDDs and PCDFs in Lake Sediment Cores from Southern Mississippi, USA

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ABSTRACT

From September 1995 to January 1996, we collected core samples from five man-made lakes in southern Mississippi, USA. Each core was subdivided into either two or three sections based on visual inspection and we dated the cores by reference to the construction of each lake. Each stratum was analyzed for PCDDs and PCDFs. PCDDs were measured in all cores, although 2,3,7,8-Cl_4DD was not quantified in any. The total PCDDs ranged from 176 to 7 577 pg/g d.m., while the PCDFs ranged from non-detectable to 14.4 pg/g d.m. The PCDD and PCDF congener patterns are similar to the patterns we observed in most river sediments we analyzed from this region.

Key Words: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, man-made lakes, sediment cores, State of Mississippi, United States of America

1 INTRODUCTION

From September 1995 to January 1996, we collected sediment samples from 15 lakes in the southern part of the State of Mississippi. We report the results of that portion of this study elsewhere (1). Six of the 15 lakes were man-made, and during that collection we also collected core samples from five of those lakes. These results, presented here, would enable us to determine if PCDDs and PCDFs were present in this part of Mississippi before anthropogenic sources were present and to determine if different depositional layers (strata) exhibit similar PCDD and PCDF patterns. In addition, this study would assist in testing our earlier hypothesis that there is a natural formation of Cl_8DD in this area (2, 3). In earlier studies, we reported that sediments from the Leaf-Pascagoula River system and lake sediments from southern Mississippi generally were dominated by the Cl_8DD and Cl_7DD (1-4).

Sediment cores reflect the historical inputs from terrestrial and atmospheric sources (5). In addition, anthropogenic sources and activities can alter PCDD and PCDF levels. Kjeller *et al.* identified

PCDDs and PCDFs in a 110 year old core from the Baltic Sea (6). Jüttner *et al.* recently reported results of four lake sediment cores from the Black Forest in Germany (7). PCDDs and PCDFs were found in all cores back to the 18th and 19th centuries. In one of the lakes, there was a dominance of the Cl_8DD in the lower strata. In the other three lakes, PCDF concentrations exceeded PCDDs in some strata. Hagenmaier and Walczok reported sediment core concentrations from Lake Constance on the German-Swiss border, dating back approximately 100 years (8). In all three studies, the authors identified an increase of PCDDs and PCDFs in the post-1960 layers.

2 EXPERIMENTAL

Five cores were collected from man-made lakes predominantly used for recreational purposes and have no known anthropogenic PCDD/PCDF point source. Four of the lakes - Lake Bogue Homa, Lake Perry, Manor Creek Water Park, and Little Black Creek Water Park - are surrounded by mixed hardwood and pine forests. The fifth, Mallard Lake, is in the drainage area of a small residential community using septic systems. The Mississippi Department of Environmental Quality (MDEQ) has found fecal contamination in this lake. A general description of the five lakes and core strata are given in Table 1.

The sediment cores were collected using a split spoon coring device with a removable polycarbonate insert. The cores were wrapped in aluminum foil, labeled, placed in a plastic bag, and kept upright during transport to the local laboratory in Hattiesburg, MS, where they were frozen. After the collection was complete, all cores were unwrapped and visually inspected for stratification based on color and appearance. If three strata were identified, the layers were labeled A, B and C, from top to bottom. If only two strata could be identified, they were labeled A and B. The A stratum is the most recent and the bottom stratum (B or C) is the oldest. The samples were shipped on ice to the analytical laboratory in Umeå, Sweden. The determination of dry mass (d.m.) was done by heating the sample at 130°C overnight after the samples were dried in the hood. The organic content or loss of ignition (LOI) was determined by heating the sample at 500°C for 2 hours in an oven. All samples were extracted, fractionated and analyzed as previously described (9). Detection was performed on a VG70-250S double focusing mass spectrometer operating at a resolution of 8 000-10 000.

Table 1. Lake Sediment Cores Collected.

Lake and Location	General Description	Strata in Core
Lake Bogue Homa, Jones County	Constructed 1940; fishing and water sports; surrounded by forest	2 strata: A & B
Lake Perry, Perry County	Constructed 1960; fishing; located in the DeSoto National Forest	3 strata: A, B & C
Manor Creek Water Park, Wayne County	Constructed 1975; fishing & water skiing; surrounded by forest	3 strata: A, B & C
Little Black Creek Water Park, Lamar County	Constructed 1973; fishing; surrounded by forest	2 strata: A & B
Mallard Lake, George County	Constructed 1982; spring fed; fishing; residential community with septic systems	2 strata: A & B

3 RESULTS

We report the concentrations of all 2,3,7,8-substituted PCDD/PCDF congeners, the homologue sums, and the I-TEQ on a d.m. basis and give the dioxin/furan (D/F) ratio for each stratum in Table 2. 2,3,7,8-Cl_4DD was not quantified in any stratum and, generally, the 2,3,7,8-substituted PCDFs were not quantified in most strata or in very low concentrations in others. However, 2,3,7,8-substituted Cl_6DD through Cl_8DD were quantifiable in almost all strata. All lake strata were dominated by PCDDs and the D/F ratio ranged from 79 to 9 900. In fact, three of the twelve strata contained no quantifiable PCDFs and, thus, no D/F ratio could be calculated.

There was no observable trend for 2,3,7,8-substitued PCDDs, homologues, or I-TEQ that correlates to the age of the strata in each lake. For example, all these parameters are higher in the more recent stratum (A) than the older stratum (B) from Lake Bogue Homa. To the contrary, the B strata have higher concentrations for most of these parameters than the A strata from Little Black Creek Water Park and Mallard Lake. In the two lakes where three strata were identified, the middle stratum (B) is higher than the A and C strata for Manor Creek Water Park, but strata A and C are higher than stratum B in Lake Perry.

Figure 1 shows the Cl_6DD traces for the surface sediments and the two strata in the cores from Lake Bogue Homa (dating to 1940) and Mallard Lake (dating to 1982). The traces from all samples from Lake Bogue Homa contain 5-7 Cl_6DD peaks. This pattern is typical for all surface and core sediment samples in our study, with the exception of Lake Mallard, which has an anthropogenic input. In the trace from the Lake Mallard bottom strata, the first eluting isomer is dominating. The concentration of this isomer pair (1,2,4,6,7,9-/1,2,4,6,8,9) is almost ten times higher than in any other sample. See Table 1. In a PCA-plot of all lake sediments (not shown here) this core from Mallard Lake is an out-layer.

The organic content or LOI decreased in the lower strata in Lake Bogue Homa, Lake Perry and Mallard Lake. In other words, the LOI in these lakes decreased with the age of each stratum. In three strata from two lakes (Lake Perry B and C and Mallard Lake B) the LOI was less than 1%. The lower stratum (B) from Lake Bogue Homa decreased by a factor of 10 to 1.23%. The LOI-based Cl_8DD values in the bottom strata were 122 000 pg/g for Lake Bogue Homa, 550 000 pg/g for Lake Perry, and 920 000 pg/g for Mallard Lake.

4 DISCUSSION

The I-TEQs for the lake cores ranged from 0.38 to 9.52 pg/g d.m. None of the cores had quantifiable levels of 2,3,7,8-Cl_4DD. On the other hand, in our study of surface lake sediments, 2,3,7,8-Cl_4DD was quantified in 20 of 27 samples, including the Lake Bogue Homa, Lake Perry and Mallard Lake samples. In a 1992 MDEQ study of Leaf and Pascagoula river sediments, 14 of 22 samples had non-detectable concentrations of 2,3,7,8-Cl_4DD and the mean I-TEQ was 3.69 ng/kg d.m. (10). In our 1994 study of the river system from the same area as the lakes, the mean level in the river sediments was 10.6 ng I-TEQ/kg d.m. and the median concentration was 9.9 ng I-TEQ/kg d.m. (1-4). Certain samples in both the 1992 and 1994 studies were elevated by specific point source contamination (1, 3). The lakes with the lowest I-TEQs in this study were those most recently constructed, and have minimal anthropogenic sources in their water sheds.

Table 2. PCDD/PCDF (pg/g d.m.) in lake cores. Parentheses are LOQ for non-detects.

Description	Lake Bogue Homa		Lake Perry			Manor Creek Water Park			Little Black Creek		Mallard Lake	
Core Section	A	B	A	B	C	A	B	C	A	B	A	B
LOI%	12.67	1.23	4.48	0.97	0.82	3.49	8.13	5.38	4.49	6.46	1.22	0.6
2,3,7,8-Cl_4DD	(0.033)	(0.034)	(0.032)	(0.029)	(0.029)	(0.034)	(0.032)	(0.037)	(0.032)	(0.034)	(0.037)	(0.037)
ΣCl_4DD	0	0	0	0.39	1.8	0	0	0.25	0	0	0	30
1,2,3,7,8-Cl_5DD	0.1	(0.034)	0.18	0.041	(0.024)	(0.024)	0.15	0.14	(0.027)	(0.031)	(0.033)	0.13
ΣCl_5DD	2.2	0.1	4.9	2.8	19.0	0.11	2.2	1.4	2.0	1.7	0.72	92
1,2,3,4,7,8-Cl_6DD	0.43	0.1	0.49	0.096	0.16	(0.042)	0.22	0.11	(0.040)	(0.048)	(0.069)	0.31
1,2,3,6,7,8-Cl_6DD	1.2	0.25	1.7	0.44	1.1	0.2	0.64	0.27	(0.039)	(0.041)	0.36	0.86
1,2,3,7,8,9-Cl_6DD	3.5	2.1	5.9	3.0	7.0	0.28	2.0	1.6	0.78	0.89	2.1	10.0
ΣCl_6DD	24	10	46	34	92	2.4	13.0	8.2	3.9	5.0	22	750
1,2,3,4,6,7,8-Cl_7DD	87	50	130	62	140	16	38	29	11	15	52	150
ΣCl_7DD	180	110	300	150	310	32	69	67	17	27	140	320
Cl_8DD	3100	1500	7200	2700	4500	470	1400	970	150	260	1900	5500
2,3,7,8-Cl_4DF	0.12	(0.022)	0.18	(0.021)	(0.02)	(0.022)	0.045	(0.024)	(0.021)	(0.023)	0.087	(0.027)
ΣCl_4DF	0.12	0	0.18	0	0	0	0.075	0.22	0	0	0.087	0
1,2,3,7,8-Cl_5DF	0.3	(0.021)	0.061	0.022	(0.016)	(0.022)	0.038	(0.019)	(0.017)	(0.019)	(0.022)	(0.022)
2,3,4,7,8-Cl_5DF	0.078	(0.021)	0.039	(0.018)	(0.016)	(0.021)	0.24	(0.021)	(0.019)	(0.019)	(0.03)	(0.021)
ΣCl_5DF	1.8	0	0.52	0.024	0	0.11	1.10	0	0	0.025	0	0
1,2,3,4,7,8-Cl_6DF	0.11	(0.036)	(0.034)	(0.031)	(0.029)	(0.034)	0.13	(0.036)	(0.031)	(0.033)	(0.46)	(0.041)
1,2,3,6,7,8-Cl_6DF	(0.032)	(0.032)	(0.029)	(0.027)	(0.026)	(0.032)	0.042	(0.033)	(0.029)	(0.032)	(0.041)	(0.036)
1,2,3,7,8,9-Cl_6DF	(0.038)	(0.039)	(0.036)	(0.033)	(0.031)	(0.038)	(0.036)	(0.039)	(0.034)	(0.055)	(0.045)	(0.043)
2,3,4,6,7,8-Cl_6DF	(0.036)	(0.034)	(0.032)	(0.031)	(0.027)	(0.034)	(0.032)	(0.035)	(0.032)	(0.033)	(0.056)	(0.04)
ΣCl_6DF	1.8	0	0.43	0	0	0	1.1	0	0	0.34	0	0
1,2,3,4,6,7,8-Cl_7DF	3.0	(0.03)	0.67	0.24	(0.025)	1.4	1.5	(0.031)	0.36	1.6	0.33	(0.038)
1,2,3,4,7,8,9-Cl_7DF	(0.045)	(0.039)	(0.039)	(0.035)	(0.032)	(0.040)	(0.033)	(0.038)	(0.032)	(0.035)	(0.053)	(0.049)
ΣCl_7DF	5.90	0	1.1	0.27	0	2.5	2.5	0	0.39	2.2	0.66	0
Cl_8DF	4.8	(0.055)	2.3	(0.046)	(0.041)	2.0	0.94	(0.054)	(0.048)	1.1	0.45	(0.065)
I-TEQ (1/2 LOQ)	4.62	2.31	9.52	3.71	6.76	0.736	2.18	1.55	0.383	0.56	2.74	8.25
D/F Ratio	226	—	1690	9920	—	109	252	4860	454	79.1	1740	—

The D/F ratios for the sediment cores ranged from 79 to 9 900. The dominance of PCDDs in the surface sediments and the sediment cores in southern Mississippi is different than the data reported from the Great Lakes and Europe (5-7). Czuczwa and Hites reported data on sediment and sediment cores from the Great Lakes (5). No D/F values were reported, but a review of the published bar graphs indicates a D/F ratio in the range of 5 to 10 (except for 0.9 in Lake Ontario). Hagenmaier and Walczok reported D/F ratios in the range of 1.8 to 2.7 for the period 1963 - 1995 in cores from Lake Constance(8). Kjeller *et al.* reported a D/F range of 0.3 (in older strata) to 1.0 (in recent strata) in Baltic Sea cores (5).

Atmospheric deposition to these lakes is not a major contributor, due to low PCDD and PCDF levels from depositional sampling and high-volume air sampling (11) and the comparison with data from the Great Lakes and Europe. Also relevant is the 1 500 pg of Cl_8DD/g d.m. in the bottom stratum from Lake Bogue Homa. This stratum corresponds to the construction of this lake in 1940, the time commercial pentachlorophenol was introduced. It seems very unlikely that this new product was the source of PCDDs and PCDFs to this remote and new lake. This indicates an alternative source in southern Mississippi sediments (1).

In four of the five cores, the PCDF concentrations decreased significantly in the lower strata. A possible explanation could be a selective degradation of the PCDFs. Such a reaction has been reported by Öberg *et al.* in a study where sewage sludge was incubated for one week in the laboratory (12). In addition, the authors found enzymatic formation of Cl_7DD and Cl_8DD.

As a result, the data reported here support our earlier hypothesis that natural formation accounts for the high concentrations of Cl_8DD and Cl_7DD found in river sediments, dried-out oxbows, surface lake sediments and sediment cores in this part of the United States.

5 ACKNOWLEDGMENT

This project was sponsored by Georgia-Pacific Corporation, Atlanta, Georgia, USA.

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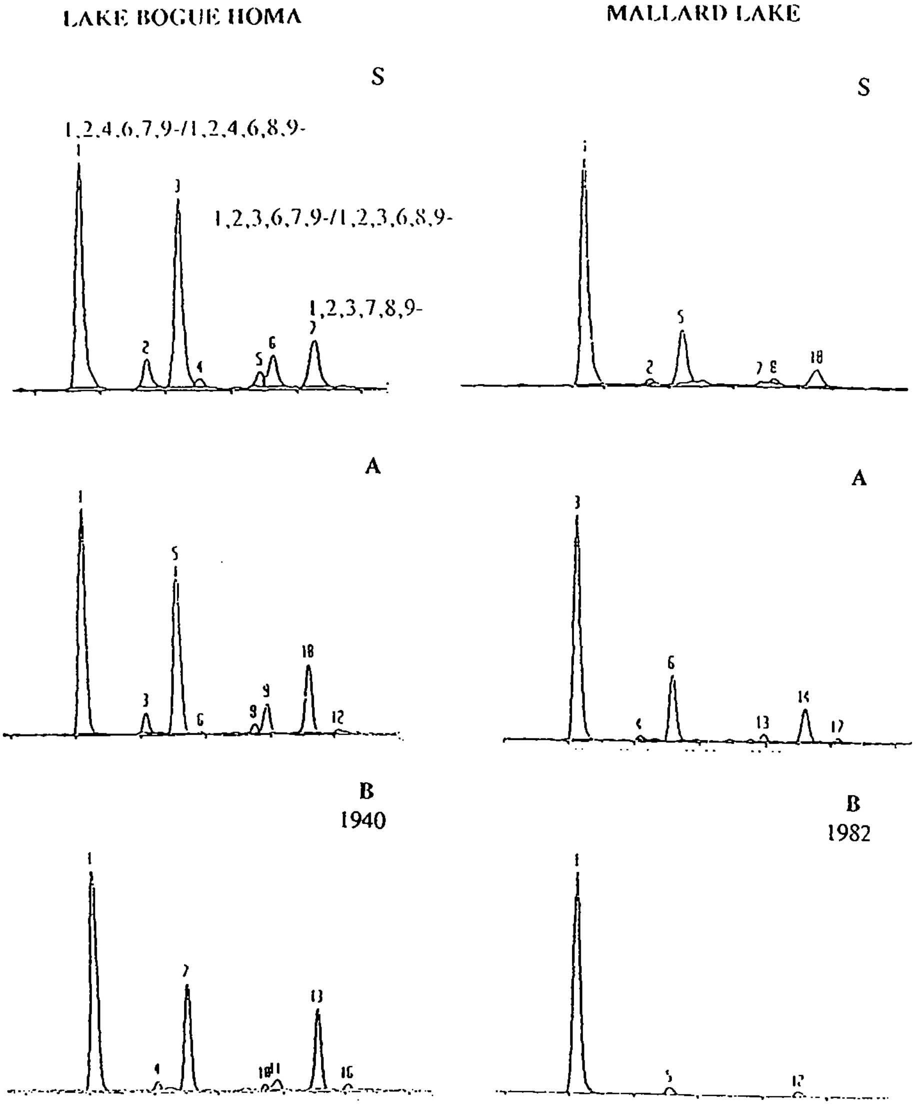

Figure 1. Hexa CDDs in sediment samples.
S: Surface sediment. A: Top stratum. B. Bottom stratum.