PCDDs and PCDFs in Lake Sediments from a Rural Area in the USA

C. Rappe[1], R. Andersson[1], M. Bonner[2], K. Cooper[3], H. Fiedler[4], C. Lau[4], and F. Howell[5]

[1] Institute of Environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden
[2] Bonner Analytical Testing Co., Hattiesburg, MS 39402, USA
[3] Rutgers University, Cook College, New Brunswick, NJ 08903, USA
[4] University of Bayreuth, Ecological Chemistry and Geochemistry, D-95440 Bayreuth, Germany
[5] University of Southern Mississippi, Department of Biological Sciences, Hattiesburg, MS 39406, USA

ABSTRACT

From September 1995 to January 1996, we collected and analyzed 27 sediment samples from 15 lakes in the southern part of the State of Mississippi, USA. The samples included four blind double samples. All samples were dominated by octaCDD and heptaCDDs. 2,3,7,8-TetraCDD was quantified in 20 of the samples, with the highest concentration based on dry matter being 1.0 pg/g and the highest concentration based on LOI being 15.0 pg/g. Other PCDDs and PCDFs were quantified and the TEQ-values in these lake sediments ranged from 2 pg/g d.m. to 63.7 pg/g d.m. The most plausible source of the octaCDD is natural formation because (a) these lakes are in areas not impacted by any industrial sources of PCDDs and PCDFs; (b) the PCDD and PCDF concentrations and ratios detected do not resemble other known anthropogenic sources or technical products; and (c) aerial deposition in this region is low.

Key words: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, heptaCDDs, octaCDD, 2,3,7,8-tetraCDD, lake sediments, dry matter, loss of ignition, natural formation, State of Mississippi

1 INTRODUCTION

In earlier publications we reported that sediments in the Leaf-Pascagoula River system in southern Mississippi contain high levels of octa- and heptaCDDs (1-3). Where the waters of this river system pass through national forests, the concentrations of these congeners increased significantly. Because no anthropogenic source could be identified, we could not exclude a natural formation of octa- and heptaCDDs in this environment. We also previously analyzed sediment from a remote lake (Bogue Homa) (26 000 pg octaCDD/g d.m. or 230 000 pg octaCDD/g LOI (SE 301)) and include those results in this study (Table 1 and Ref. 3). Most of the river samples had a dioxin to furan (D/F) ratio greater than 100. In addition, most of the samples collected from dried-out oxbows in our prior soil study from this same area, had high octa- and heptaCDDs concentrations and high D/F ratios (> 100) (3).

In this study, we report the results of lake sediments collected in the same area of Mississippi and confirm our earlier hypothesis that there is a natural formation of octa- and heptaCDDs in this region.

2 SAMPLING

From September 1995 to January 1996, we collected 27 lake sediment samples from 15 lakes in eight counties in southern Mississippi (Figure 1), including samples from Lake Bogue Homa which we first analyzed in 1994. Deep lake sediments and, when possible, sedimentation area sediments were collected from each lake. All the lakes are in pristine areas without any known industrial sources of PCDDs and PCDFs. The samples included four blind double samples collected at the same time at the same location (Table 1).

3 ANALYTICAL

The samples were air-dried in glass jars for several weeks. The dried sediment samples were crushed in a steel blender (Waring MC-2) and sieved; only the fraction < 2 mm was analyzed. The organic content or loss of ignition (LOI) was determined by heating the sample at 500°C for 2 hours in an oven. After addition of $^{13}C_{12}$-labeled compounds, extraction of the sediment samples was performed in a Soxhlet extractor equipped with a Dean Stark collector with 150 mL of toluene for at least 12 h. The clean-up, fractionation, and detection of PCDDs and PCDFs were performed as previously described (3).

4 RESULTS

For highly lipophilic compounds such as PCDDs and PCDFs, which are formed on or bound to organic particles, it is preferable to normalize the results based on the organic content of the sample as determined by LOI. Our results here are reported on an LOI basis; the octaCDD and TEQ values also are given on a dry matter (d.m.) basis. Table 1 provides PCDD and PCDF results of the 27 sediment samples from this study and the single lake sediment (SE 301) from the earlier study (3) as follows: (i) 2,3,7,8-tetraCDD, Σ HpCDDs, octaCDD, Σ PCDDs, Σ PCDFs and TEQ based on LOI; (ii) octaCDD and TEQ based on d.m.; and, (iii) the D/F ratio (Σ PCDD/Σ PCDF).

The recovery of the $^{13}C_{12}$-labeled compounds in all cases ranged from 60-110%. There was good agreement between the two sediments from Lake Bogue Homa that were collected and analyzed more than one year apart and for all blind double samples analyzed in the current study (Table 1).

2,3,7,8-TetraCDD was identified in 20 of the 27 lake sediments from the current study and in the prior sample from Lake Bogue Homa, but no sample was greater than 15 pg/g LOI or 1 pg/g d.m. (Table 1). The results for TEQ ranged from 19.6 to 895 pg/g LOI and from 1.98 to 63.8 pg/g d.m. All samples were dominated by the PCDDs, especially the octa- and heptaCDDs. The D/F ratio ranged from 19 to 764 and 22 of the 28 samples, including the prior Lake Bogue Homa sample, had a D/F ratio greater than 100. The octaCDD values ranged from 1 400 to 43 000 pg/g d.m. with a median value of 7 700 pg/g d.m. and from 11 000 to 640 000 pg/g LOI with a median value of 87 000 pg/g LOI. The Σ heptaCDDs values ranged from 63 to 2 000 pg/g d.m. with a median value of 430 pg/g d.m., and from 620 to 30 000 pg/g LOI with a median value of 4 200 pg/g LOI.

5 DISCUSSION

Several earlier studies report PCDD and PCDF levels from lake sediments in North America and Europe. While we report PCDD and PCDF concentrations on a dry matter and an LOI basis, these earlier studies only report these values on a dry matter basis. Nonetheless, a comparison of our results with the results from these earlier studies is useful. In particular, such a comparison supports our conclusion of the natural formation of octaCDD.

Koistinen *et al.* reported sediment data from 18 lakes in central Finland (4). For octaCDD, most lakes were below the detection limit of 50 pg/g d.m. Using improved analytical technology, the highest reported value was 42 pg/g d.m. -- approximately 200 times lower than the median value found in our study. Czuczwa and Hites reported PCDD and PCDF levels from various lake sediments in the United States (5). The concentrations of octaCDD in the Great Lakes ranged from 780 pg/g d.m. (Lake Michigan) to 4 800 pg/g d.m. (Lake Ontario). Lake Siskiwit on Isle Royal in Lake Superior, which receives only aerial PCDD and PCDF deposition, had an octaCDD value of 560 pg/g d.m. -- approximately 15 times lower than the median value in our study. O'Keefe *et al.* reported PCDD and PCDF values from lake sediments in Minnesota and New York (USA) (6). The concentrations of octaCDD in these samples ranged from 270 pg/g d.m. to 1 100 pg /g d.m. -- significantly below the lowest value for the southern Mississippi samples.

In our study, the highest value of octaCDD on a LOI basis was 640 000 pg/g LOI in the sample from Aldrich Lake. This lake is a cypress swamp oxbow, occasionally flooded by the Leaf River. The highest concentration of octaCDD on a d.m. basis was 43 000 ng/kg in Big Lake. The octaCDD concentration in this pristine lake was 75-80 times higher than that reported from Lake Siskiwit (560 ng/kg) (5).

As part of our study of PCDDs and PCDFs in southern Mississippi, we measured air concentrations by high-volume samplers and aerial deposition by Bergerhoff samplers. In addition, we measured PCDD and PCDF levels on pine needles which reflect both air concentrations (by extracting the gaseous portion out of the air by the waxy layer) and aerial deposition (by collecting the dust particles accumulated on the needles) (7, 8). Because aerial deposition is low and, therefore, not a significant contributor of PCDDs and PCDFs in this area, the PCDD and PCDF concentrations in the lake sediments are not signficantly attributable to atmospheric deposition. It also is highly unlikely that there is a local point source of the very high octaCDD concentrations in the lakes in this pristine area. These levels are much higher than any earlier reported value for lake sediments.

In our studies of PCDDs and PCDFs in the State of Mississippi, we confirmed that sewage sludge is a known source of octaCDD (9-16) by analyzing sludge from 17 publicly-owned treatment works (POTW) (17, 18). Only the sludges from the Picayune POTW had a higher octaCDD value than the sediments from Big Lake, Parkers Lake, Horseshoe Bend Lake, Aldrich Lake, and Lake Bogue Homa on an LOI basis and Big Lake and Horseshoe Bend Lake on a d.m. basis. In other words, the lake sediments from these pristine areas had higher octaCDD values than sludge from 16 of 17 POTWs in the same area. Finally, we are not aware of any technical product exhibiting the dominance of PCDD (a D/F ratio greater than 100) that we consistently observe in our study. For example, recently, Versar reported the D/F ratio for commercial pentachlorophenol to be in the range of 0.59 to 7.36 (mean value 3.54, median value 3.70), the only known commercial product also dominated by octaCDD and heptaCDD (19).

(mean value 3.54, median value 3.70), the only known commercial product also dominated by octaCDD and heptaCDD (19).

We also collected and analyzed sediment cores from 5 of the 15 lakes sampled in this study and report those results elsewhere (20). The data reported here and in our sediment core study (20) support our earlier hypothesis that natural formation accounts for the high concentrations of octa- and heptaCDDs found in river sediments, in dried-out oxbows and in lake sediments in this part of the United States.

6 ACKNOWLEDGMENT

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

7 REFERENCES

1. C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler and F. Howell, *Organohalogen Compounds*, **24**, 273-280 (1995)
2. Fiedler, C. Lau, K. Cooper, R. Andersson, S.-E. Kulp, C. Rappe, F. Howell, M. Bonner, *Organohalogen Compounds*, **24**, 349-352 (1995)
3. C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, F. Howell, S.-E. Kulp, C. Lau, *Chemosphere,* **34**, 1297-1314 (1997)
4. J. Koistinen, J. Paasivirta, J. Särkkä, *Chemosphere*, **21**, 1371-1379 (1990)
5. J. Czuczwa, R. Hites, *Environ. Sci. Technol.*, **20**, 195-200 (1986)
6. P. O'Keefe, R. Smith, S. Connor, K. Aldous, H. Valente, R. Donnelly, *Arch. Environ. Contam. Toxicol.*, **27**, 357-366 (1994)
7. H. Fiedler, C. Lau, K. Cooper, R. Andersson, M. Hjelt,, C. Rappe, M. Bonner, F. Howell, Manuscript submitted to Dioxin '97
8. Fiedler, C. Lau, K. Cooper, R. Andersson, S.-E. Kulp, C. Rappe, F. Howell, M. Bonner, *Organohalogen Compounds*, **24**, 285-292 (1995)
9. L. Lamparski, T.J. Nestrick, V.A. Stenger, *Chemosphere*, **13**, 361-365 (1984)
10. N.G.A. Weerasinghe, M.L. Gross, D.J. Lisk, *Chemosphere*, **14**, 557-564 (1985)
11. US EPA National Sewage Sludge Survey, PB 90-107491 (1989)
12. W.A. Telliard, H.B. McCarty, J.R. King, J.B. Hoffman, *Organohalogen Compounds,* **2**, 307-311 (1990)
13. H. Hagenmaier, H. Brunner, W. Knapp, U. Weberruss, Forschungsbericht 103 03 305, UBA-FB-89-068, Berlin (1990)
14. R. Butzkamm-Erker and R.E. Mach, *Korrespondenz Abwasser* **37**, 161-163 (1990)
15. C. Rappe, L.-O. Kjeller, R. Andersson, *Chemosphere*, **19**, 13-20 (1989)
16. C. Rappe, R. Andersson, G. Karlaganis, R. Bonjour, *Organohalogen Compounds*, **20**, 79-84 (1994)
17. C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, F. Howell, C. Lau, *Organohalogen Compounds*, **28**, 105-110 (1996)
18. C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, F. Howell, Manuscript submitted to *Chemosphere*
19. Versar, Inc., Springfield, VA 22151, USA. *Dioxin Reservoir Sources.* A Background Paper, July 15, 1996
20. K. Cooper, C. Rappe, R. Andersson, H. Fiedler, C. Lau, M. Bonner, F. Howell, Manuscript submitted to Dioxin '97

TABLE 1: Results from analyses of sediment samples from southern Mississippi, USA
D = Deep Lake; S = Sedimentation Area

Lake	% LOI	2,3,7,8 TetraCDD LOI	ΣHpCDD LOI	OctaCDD LOI	OctaCDD d.m.	ΣPCDD LOI	ΣPCDF LOI	TEQ LOI	TEQ d.m.	D/F ratio
Lake Bogue Homa (D)	8.44	ND(1.1)	18000	260000	22000	279411	930	355	30.0	301
Lake Bogue Homa (D)*	7.78	1.3	20000	290000	22000	309049	1090	397	30.9	284
Lake Bogue Homa (D)**	11.25	2.4	11000	230000	26000	244857	846	296	33.3	290
Lake Bogue Homa (S)	41.18	ND(0.27)	1200	26000	11000	26884	184	37.8	15.6	147
Lake Bogue Homa (S)*	33.28	0.77	1300	29000	9500	30084	206	42.8	14.2	146
Lake Perry (D)	6.41	2.7	4600	120000	7700	124776	449	163	10.5	278
Lake Perry (S)	15.78	0.75	4200	140000	22000	143145	187	172	27.2	764
Kitrell Sand and Gravel Lake (D)	3.42	ND(2.5)	2600	83000	2800	85782	242	108	3.69	354
Manor Creek Water Park (D)	10.40	ND(0.27)	2400	20000	2100	23016	1229	51.9	5.44	19
Manor Creek Water Park (S)	9.52	0.29	870	17000	1600	18182	331	32.5	3.10	55
Little Black Creek Water Park (D)	8.50	ND(0.31)	2400	31000	2600	33687	898	62.7	5.33	38
Little Black Creek Water Park (S)	15.30	ND(0.15)	1100	11000	1700	12325	314	27.5	4.21	39
Turkey Fork Reservoir (D)	8.55	0.58	4200	87000	7400	91549	459	124	10.6	199
Turkey Fork Reservoir (S)	9.75	0.44	3800	85000	8300	89316	1706	124	12.1	52
Mallard Lake (D)	2.35	8.8	12000	180000	4300	196985	415	273	6.43	474
Aldrich Lake (D)	2.59	6.4	30000	640000	17000	675313	959	895	23.2	704
Horseshoe Bend Lake (D)	8.26	6.7	15000	360000	30000	381987	2639	507	41.9	145
Horseshoe Bend Lake (D)*	9.47	5.3	13000	360000	34000	378437	2821	490	46.4	134
Horseshoe Bend Lake (S)	8.41	6.1	9500	270000	22000	278236	1933	375	31.6	144
Horseshoe Bend Lake (S)*	9.72	4.6	9200	250000	25000	265451	2101	354	34.5	126
G-P Property (D)	1.72	3.6	3600	81000	1400	85551	135	115	1.98	634
Big Lake (D)	8.47	12	24000	510000	43000	535712	6060	752	63.7	88
Big Lake (S)	15.03	6.0	12000	260000	39000	274023	2045	378	56.8	134
Plum Bluff Estates (D)	10.85	ND(0.62)	620	14000	1500	14598	26	19.6	2.13	573
Parkers Lake (D)	6.19	8.4	14000	230000	14000	250413	2193	419	25.9	114
Parkers Lake (S)	5.05	15	17000	400000	20000	421737	2183	641	32.4	193
Sandy Branch (D)	12.69	0.48	1900	25000	3200	27299	1052	50.2	6.37	26
Atkinson Creek (D)	4.88	3.5	2800	74000	3600	77166	158	108	5.26	488

*blind double sample
**sample SE 301, reference 3.

FIGURE 1: Lake sediment sampling locations, southern Mississippi, USA.