PCDDs IN NATURALLY-FORMED AND MAN-MADE LAKE SEDIMENT CORES FROM SOUTHERN MISSISSIPPI, USA

C. Rappe[1], R. Andersson[1], K. Cooper[2], R. Bopp[3], H. Fiedler[4], F. Howell[5] and M. Bonner[6]

[1] Institute of Environmental Chemistry, Umeå University, SE 901 87 Umeå, Sweden
[2] Rutgers University, Cook College, New Brunswick, NJ 08903, USA
[3] Rensselaer Polytechnic Institute, Troy, NY 12180, USA
[4] University of Bayreuth, Ecological Chemistry and Geochemistry, D95440 Bayreuth, Germany
[5] University of Southern Mississippi, Department of Biological Sciences, Hattiesburg, MS 39404, USA
[6] Bonner Analytical Testing Co., Hattiesburg, MS 39402, USA

Introduction

From September 1995 to January 1996, we collected 15 sediment samples from lakes in southern Mississippi (1). Six of the 15 lakes were man-made, and we previously analyzed the cores from five of those lakes for PCDDs and PCDFs and dated the cores by reference to their respective dates of construction (2). Later, we used a ^{137}Cs method to date the cores from four of the nine naturally-formed lakes and analyzed the cores for PCDDs and PCDFs (3). In this study, we dated the cores from five of the remaining lakes using the same dating method and analyzed the cores for PCDDs and PCDFs. These results demonstrate that PCDDs and PCDFs were present in this part of Mississippi before anthropogenic sources, and the PCDD and PCDF patterns confirm our earlier findings of a significant natural formation of PCDDs in this area (1-4).

In earlier parts of our study, we reported a dominance of octaCDD, heptaCDDs and hexaCDDs in sediment cores from the man-made lakes and the naturally-formed lakes. In addition, these congeners also dominated river sediment and ox-bow lake sediments from the Leaf-Pascagoula River system in other parts of our study of PCDDs and PCDFs in southern Mississippi (4). Through an exhaustive methodology, we excluded all known anthropogenic sources as the source of these compounds and concluded to a reasonable degree of scientific certainty that a natural formation was the source of these compounds. This current study confirms the presence of PCDDs before anthropogenic sources and confirms our earlier conclusion of a natural formation of these compounds.

Experimental

We collected one lake sediment core each from Turkey Fork Reservoir, Plum Bluff Estates, Horseshoe Bend Lake, GP-Property and Big Lake in southern Mississippi. These lakes are used primarily for recreational purposes. All five lakes are situated in wetlands that are all surrounded by cypress and pine trees. None of these lakes has any known anthropogenic sources of PCDDs and PCDFs. The cores were collected using a split spoon coring device with a removable polycarbonate insert. Ten to fourteen strata (or layers) were identified in these cores, and the strata were numbered starting at the top of each core. Each strata was dated by a ^{137}Cs method.

We treated four strata from each lake with toluene, and performed clean-up and analyses for PCDDs and PCDFs as reported previously (1-4).

Results

Table 1 lists the lakes, the strata analyzed, the dates of the respective strata, and the Loss of Ignition (LOI) for each strata. Table 1 also reports for each strata (i) 2,3,7,8-tetraCDD concentrations on both an LOI and a dry matter (d.m.) basis; (ii) Σ heptaCDDs (LOI and d.m.); (iii) octaCDD concentrations (LOI and d.m.); (iv) I-TEQ, (d.m.); and, (v) the Σ PCDFs/Σ PCDFs (D/F ratio). Cores from three of the lakes could be dated to before the 1950s using ^{137}Cs.

2,3,7,8-TetraCDD was measured in 14 of the 20 strata. This is consistent with our earlier findings of 2,3,7,8-tetraCDD in 13 of 16 lake strata from this region (3).

OctaCDD was the dominant contributor to the I-TEQ in all strata, with concentrations ranging from 820 pg/g d.m. (Turkey Fork Reservoir, strata 8) to 25 000 pg/g d.m. (Plum Bluff, strata 12, and Big Lake, strata 5 and 12). The octaCDD concentrations based on LOI ranged from 4400 pg/g LOI (Horseshoe Bend Lake, strata 12) to
650 000 pg/g LOI (Plum Bluff, strata 8).

All strata had very high D/F ratios, (mean = 242, high = 1481). The octaCDD, heptaCDDs and hexaCDDs concentrations were extraordinarily high for lakes with no anthropogenic sources. These results are similar to our earlier analyses of cores from naturally-formed and man-made lakes in this area (1-4).

Conclusions

Pentachlorophenol (PCP) cannot be the source of the hexaCDDs found in these sediment cores. In PCP, the dominating hexa CDD peaks are 123679-/123689- and 123678-hexa CDD (5,6). However, in these cores the dominating peaks are 124679-/124689- (which is not found in, or is a minor contaminant of, PCP), and 123679-/123689- and 123789-hexaCDD, (which is found at very low levels in PCP). In addition, commercial PCP has a D/F ratio of 1-10 (5,6). As noted above, the mean D/F ratio for all sediment cores is 242.

Moreover aereal input of PCDDs and PCDFs in this region is very low (7). Therefore, aereal deposition cannot explain the high hexa-, hepta- and octaCDD values found in these sediment cores. Finally, there are no known anthropogenic sources of PCDDs and PCDFs to these lakes. This study confirms our earlier conclusion of a natural formation of hexa-, hepta- and octaCDD in this part of the United States.

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

References

1.C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, C. Lau and F. Howell. *Organohalogen Compds.* 32, 88-93 (1997).
2.C. Rappe, R. Andersson, K. Cooper, H. Fiedler, C. Lau, M. Bonner and F. Howell. *Organohalogen Compds.* 32, 18-22 (1997).
3.C. Rappe, S. Bergek, R. Andersson, K. Cooper, H. Fiedler, R. Bopp, F. Howell and M. Bonner.
4.*Organohalogen Compds.* 43, 111-116 (1999).
5.C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, F. Howell, S. E. Kulp and C. Lau. *Chemosphere.* 34, 1297-1314 (1997).
6.H. Hagenmaier and H. Brunner *Chemosphere.* 16, 1759-1764 (1987).
H. Hagenmaier. Cited in commission of the European Communities DC III. *Reference 4271.* April 1997.
7.H. Fiedler, C. Lau, K. Cooper, R. Andersson, M. Hjelt, C. Rappe, M. Bonner and F. Howell. *Organohalogen Compds.* 33, 123-127 (1997)

Table 1. Selected PCDDs (pg/g LOI, pg/g d.m.) I-TEQ, and D/F Ratio in Lake cores.

Lake	Strata	Date	% LOI	2378-TCDD LOI	2378-TCDD d.m.	Σ Hp CDDs LOI	Σ Hp CDD d.m.	OCDD LOI	OCDD d.m.	I-TEQ d.m.	D/F value
Turkey	2	Mid 60s	6.19	2.1	0.13	4400	270	82000	5100	8.4	39
Fork	4	1950s	1.79	ND	ND	4000	72	78000	1400	2.3	202
Reservoir	7	1950s	1.36	ND	ND	4400	55	65000	820	1.4	458
	9	well before 1950	1.37	4.2	0.058	6100	84	88000	1200	2.0	1139
Horseshoe	2	Mid 60s	10.6	8.6	0.91	14000	1500	210000	22000	38	69
Bend	5	Early 60s	11.2	ND	ND	13000	1400	150000	17000	34	57
Lake	9	1950s	10.8	3.1	0.31	14000	1400	200000	20000	33	1481
	13	Before 50s	81.1	ND	ND	360	290	4400	3600	8.5	94
G P	2	No	2.61	ND	ND	1700	45	36000	950	1.5	88
Property	5	indication	0.78	ND	ND	5200	41	110000	890	1.7	52
	8	of	1.15	24	0.28	11000	130	260000	3000	5.2	110
	11	sedimental diposition	1.40	14	0.20	18000	250	360000	5000	8.2	107
Big Lake	2	1970s	20.1	7.5	1.5	7000	1400	120000	24000	41	72
	5	1960s	12.0	8.3	1.0	28000	3300	210000	25000	55	31
	9	1950s	11.2	9.0	1.0	34000	3800	210000	23000	73	66
	13	Before 50s	9.7	12	1.2	55000	5300	260000	25000	90	340
Plum Bluff	2	Uniform	6.6	32	2.1	17000	1100	320000	21000	35	175
Estates	5	^{137}Cs	3.2	70	2.2	46000	1300	600000	19000	34	102
	8	Signal	9.7	55	1.8	34000	1100	650000	21000	35	89
	11		4.3	44	1.9	30000	1300	580000	25000	40	68