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

C. Rappe[1], S. Bergek[1], R. Andersson[1], K. Cooper[2], H. Fiedler[3], R. Bopp[4], F. Howell[5], 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] University of Bayreuth, Ecological Chemistry and Geochemistry, 95440 Bayreuth, Germany
[4] Rensselaer, Troy, NY 12186, USA
[5] University of Southern Mississippi, Department of Biological Sciences, Hattiesburg, MS 39404, USA
[6] Bonner Analytical Testing Co., Hattiesburg, MS 39402, USA

Abstract

From September 1995 to January 1996, we collected sediment samples from four naturally-formed lakes in southern Mississippi, USA with no known anthropogenic source(s) of PCDDs and PCDFs. Each sample was subdivided into at least ten strata (2 cm discs) or cores, and all cores were dated by ^{137}Cs and four cores from each lake were analyzed for PCDDs and PCDFs. The PCDDs dominated all cores, with dioxin-furan ratios ("D/F ratio") ranging from 49-3736 and a mean D/F ratio of 994. The PCDD patterns were similar to the patterns we previously observed in many other samples from this area, which indicated a natural formation of dioxins.

Key words: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, lakes, sediment cores, State of Mississippi, United States of America, natural formation.

Introdution

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 reported the PCDD and PCDF concentrations in the cores from five of those lakes and dated the cores from these lakes by reference to their respective dates of construction (2). In this study we used a ^{137}Cs method to date the cores from four naturally-formed lakes 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 were present and the PCDD and PCDF patterns confirm our earlier findings of a significant natural formation of PCDDs in the area.

Sediment cores reflect the historic input of PCDDs and PCDFs from terrestrial and anthropogenic sources (1-5). In addition, anthropogenic sources and activity can change the PCDD and PCDF concentrations. Jüttner et al. recently reported that PCDDs and PCDFs were found in four lakes from the Black Forest in Germany dating back to the 18th and the 19th centuries (4). In one lake octaCDD significantly dominated the lowest strata. In the other three lakes, PCDFs concentrations exceeded PCDD concentrations in some strata. Hagenmaier and Walczok reported a dominance of octa- and heptaCDDs in a sediment core from Lake Constance on the German-Swiss border dating back approximately 100 years (5). In these two studies the authors identified a significant increase of PCDDs and PCDFs in the post-1960 years (4,5).

In earlier parts of our extensive study of PCDDs and PCDFs in southern Mississippi, we reported a dominance of octaCDD, heptaCDDs and hexaCDDs in sediment cores from man-made lakes, in river sediments and in ox-bow lakes from the Leaf-Pascagoula River system. This data demonstrates a natural formation of these compounds in southern Mississippi. This study demonstrates the presence of PCDDs and PCDFs before anthropogenic sources and confirms the natural formation of these compounds in this area (1-3).

Experimental

We collected one core sample each from Kitrell Sand and Gravel Lake, Aldrich Lake, Sandy Branch Lake and Atkinson Creek Lake in southern Mississippi. These lakes were naturally-formed and are used primarily for recreational purposes. All four lakes are situated in wetlands that are all surrounded by cypress and pine trees. They have no known anthropogenic sources of PCDDs and PCDFs. The sediment cores were collected using a split spoon coring device with a removable polycarbonate insert. Twelve strata (or layers) were identified in the cores from Kitrell Sand and Gravel, Aldrich, and Atkinson Lakes. Fourteen strata were identified in the core from Sandy Branch Lake. 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 solvent, and performed clean-up and analyses of PCDDs and PCDFs as reported previously (1-3).

Results

Table 1 reports the (i) 2,3,7,8-tetraCDD concentrations; (ii) Σ HeptaCDDs; (iii) octaCDD concentrations; and (iv) I-TEQ, on both loss of ignition (LOI) and a dry matter (d.m.) basis, for four strata from each of the four naturally-formed lake cores. Table 1 also includes the Σ PCDDs/Σ PCDFs (D/F ratio) for each strata. Cores from all lakes could be dated using ^{137}Cs to approximately the mid-1960, and the oldest cores were determined to be from the 1940s-1950s. Finally, Table 1 includes the results for these same parameters from our earlier man-made lake study (2).

2,3,7,8-TetraCDD was measured in 13 of the 16 strata for which we report results. In contrast, 2,3,7,8-tetraCDD was not measured in any strata from any of the man-made lake sediment cores we analyzed.

OctaCDD was the dominant isomer in terms of contribution to the I-TEQ in all strata from the four naturally-formed lakes, with concentrations ranging from 220 pg/g d.m. (Sandy Branch Lake strata # 2) to 30 000 pg/g d.m. (Aldrich Lake strata # 8). The octa CDD concentrations based on LOI ranged from 27 000 pg/g LOI (Sandy Branch Lake strata # 2) to 940 000 pg/g LOI (Aldrich Lake strata # 11).

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

Lake	Strata	Date	%LOI	2,3,7,8-TCDD LOI	2,3,7,8-TCDD d.m.	∑HpCDD LOI	OCDD LOI	OCDD d.m.	TEQ LOI	TEQ d.m.	D/F Ratio
Kitrell Sand and Gravel Lake*	2	1990s	13.12	0.99	0.13	2400	76000	10000	102	13.4	455
	5	Late 1970s	3.51	5.1	0.18	16000	310000	11000	564	19.8	2215
	8	Early 1960s	3.40	4.4	0.15	12000	280000	9400	406	13.8	2475
	11	1954	14.69	0.68	0.10	2200	52000	7700	76.2	11.2	889
Aldrich Lake*	2	1990s***	0.23	21	0.049	29000	340000	790	691	1.59	622
	5	Late 1970s	4.19	13	0.55	29000	430000	18000	773	32.4	59
	8	Mid 1960s	6.35	13	0.84	28000	470000	30000	795	50.5	251
	11	Early 1950s	2.87	22	0.62	49000	940000	27000	1400	40.1	775
Sandy Branch*	2	1990s	0.83	ND(5.8)	ND(0.048)	1700	27000	220	49.8	0.413	94
	6	Late 1970s	4.87	1.4	0.068	2500	55000	2700	86.0	4.19	86
	10	Mid 1960s	0.92	ND(6.0)	ND(0.055)	2800	40000	370	82.3	0.757	49
	14	1950s	5.07	ND(0.95)	ND(0.048)	4100	150000	7600	190	9.61	1134
Atkinson Creek*	2	1990s	2.82	4.3	0.12	2600	120000	3500	169	4.77	1630
	5	1980s	0.81	14	0.11	14000	440000	3600	590	4.78	3736
	8	1970s	2.19	6.8	0.15	9600	300000	6500	413	9.04	913
	11	1960s	2.05	12	0.24	18000	410000	8400	629	12.9	514
Lake Bogue Homa**	A		12.67	ND(0.26)	ND(0.033)	1400	24000	3100	36.5	4.62	226
	B	1940s	1.23	ND(2.8)	ND(0.034)	8900	120000	1500	188	2.31	----
Lake Perry**	A		4.48	ND(0.71)	ND(0.032)	6700	160000	7200	213	9.52	1690
	B		0.97	ND(3.0)	ND(0.029)	15000	280000	2700	382	3.71	9920
	C	1960s	0.82	ND(3.5)	ND(0.029)	38000	550000	4500	824	6.76	----
Manor Creek Water Park**	A		3.49	ND(0.97)	ND(0.034)	920	13000	470	21.1	0.736	109
	B		8.13	ND(0.39)	ND(0.032)	850	17000	1400	26.8	2.18	252
	C	1975	5.38	ND(0.69)	ND(0.037)	1200	18000	970	28.8	1.55	4860
Little Black Creek**	A		4.49	ND(0.71)	ND(0.032)	380	3300	150	8.53	0.383	454
	B	1973	6.46	ND(0.53)	ND(0.034)	420	4000	260	8.67	0.560	79
Mallard Lake**	A		1.22	ND(3.0)	ND(0.037)	11000	160000	1900	225	2.74	1740
	B	1982	0.60	ND(6.2)	ND(0.037)	53000	920000	5500	1380	8.25	----

* Naturally-formed Lakes
** Man-made Lakes, see Ref 2
*** No detectable ^{137}Cs concentration

In Aldrich Lake, Sandy Branch Lake and Atkinson Creek the octa CDD concentrations increase with the age of the strata both on an LOI and on a d.m basis. In Kitrell Sand and Gravel Lake the octa CDD LOI values in all strata are quite high and no trend is observable.

All strata from the naturally-formed lake cores had high D/F ratios, with ranges from 49 (Sandy Branch Lake strata # 10) to 3736 (Atkinson Creek Lake strata # 5). The octa CDD, hepta CDDs and hexa CDDs concentrations were extraordinarily high for lakes with no anthropogenic sources. These results are similar to those from our earlier analyses of cores from man-made lakes, see Table 1 and ref. 2.

Conclusions

Pentachlorophenol (PCP) cannot be the source of the hexaCDDs found in these sediments. In PCP, the dominating hexa CDD peaks are 123679-/123689- and 123678-hexa CDD (6,7). However, in the cores from the naturally-formed lakes 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).

Previously, we reported that the aereal input of PCDDs and PCDFs in this region is very low and, therefore, cannot explain the high hepta- and octaCDD values found in this and earlier studies (8). Notwithstanding that there are no known anthropogenic point sources to these four naturally-formed lakes, the PCDD levels, particularly the octa-, hepta-, and hexa CDDs, are remarkably high, especially when compared with levels from other US lakes that have known anthropogenic sources of these compounds. This study confirms our earlier conclusion of a natural formation of hexa-, hepta- and octaCDD in this part of the United States.

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