SOURCES OF PCDD/PCDF CONTAMINATION IN LAKE CHAMPLAIN AND LAKE GEORGE, NEW YORK

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ABSTRACT

Principal components analysis showed that the congener profiles of PCDD/PCDF compounds were different in surface sediment samples from Lake Champlain as compared to Lake George. Higher lead levels were also found in the Lake George samples suggesting that emissions from power boats were responsible for the PCDD/PCDF contamination in this lake. In Lake Champlain most core and surface samples had high OCDD concentrations (3.5 to 18 ng/g) suggesting that past disposal practices for ash may be responsible for the contamination.

INTRODUCTION

Lakes George and Champlain are two large freshwater lakes in New York State. The general water flow is from north to south, and the northern end of Lake George is connected to the southern end of Lake Champlain via Ticonderoga Creek. The southern section of Lake George is a major recreational area, heavily utilized by power boats. To a large extent, these boats are equipped with 2-stroke outboard motors fueled by leaded gasoline. Consequently, during combustion the tetrachloro- and tetrabromoethane scavengers present in leaded gasoline could lead to contamination in the lake with polychlorinated- and polybrominated dibenzo-p-dioxins (PCDDs and PBDDs) and polychlorinated- and polybrominated dibenzofurans (PCDFs and PBDFs).

Power boats are not so prevalent on Lake Champlain. However, there was a kraft pulp and paper mill in operation near the mouth of Ticonderoga Creek until 1970 when it was replaced by a modern plant near Kirby Point, four miles north of the creek. It is known that the chlorine bleaching steps in the kraft process can result in the release of PCDD/PCDF compounds in waste streams from kraft pulp and paper mills (Clement et al., 1989). This study was undertaken to determine if PCDD/PCDF compounds had contaminated sediments in the southern sections of Lake Champlain and/or Lake George

EXPERIMENTAL

Surface sediment samples were collected at seven locations in the southern end of Lake

George using a Ponar grab sampler on June 7, 1989. On September 7, 1989, three core samples were taken in Lake Champlain near the mouth of Ticonderoga Creek and six surface samples at four locations covering an area from three miles north of Ticonderoga Creek to Elm Point, 15 miles north of Ticonderoga Creek. The core samples were taken with a hand-held corer consisting of lucite tubing (4 ft x 3" i.d.) attached to a one-way valve on a 10 ft metal handle.

On arrival at the laboratory, the samples were stored at 4°C. Prior to extraction, amples were dried overnight at 40°C. Soxhlet extraction, cleanup and analysis by capillary gas chromatography/low resolution mass spectrometry were accomplished by procedures described n the literature (O'Keefe et al., 1984). Each sample was spiked with eleven ^{13}C-labeled tandards.

Principal components analysis (PCA) was carried out using SIMCA-3X software (Principal ata Components, Columbia, MO 65201, USA) on an IBM-XT microcomputer.

ESULTS AND DISCUSSION

Data for the Lake George samples and a sediment sample from West Bearskin Lake, Minnesota re presented in Table 1. The separation of the Lake George data into two groups is supported

able 1. Concentrations (pg/g dry wt.) of PCDD/PCDF Compounds and Lead (μg/g dry wt.) in Surface Sediments from Lake George, New York and West Bearskin Lake, Minnesota[1].

	West Bearskin Lake	Lake George	
ompound(s)	(four replicates)	Low Level (three samples)	High Level (five samples)
3,7,8-TCDD	ND (4.9-16)	ND (7.6-13)	ND (4.5-14)
DDs	22, 7.2	ND (7.6-13)	ND (4.5-14)
DDs	ND (8.4-21)	ND (13-22)	ND (5.3-21)
CDDs	ND (8.4-30)	ND (17-26)	43 ± 22
CDDs	38 ± 8	34 ± 32	224 ± [illegible]
DD	270 ± 55	303 ± 150	1092 ± [illegible]
3,7,8-TCDF	ND (4.4-15)	ND (5.6-12)	20 ± 10
DFs	ND (4.4-15)	ND (5.6-12)	95 ± 39
DFs	5.5	ND (7.7-14)	84 ± 55
CDFs	5.1	ND (9.4-17)	78 ± 52
CDFs	14 ± 2.1	14 ± 13	108 ± 35
DF	19 ± 2.6	24 ± 8.9	112 ± 36
	16	52 ± 25	173 ± 33

hen three or more positive values were obtained, the results are expressed as the ave. s.d. Not detected (ND) values are expressed as a range.

PCA analysis which showed two distinct sample groups in an x/y plot. The three low-level mples were, in fact, grouped closely to the West Bearskin Lake sample suggesting that these liment samples are representative of background contamination in Eastern and Mid-western tes in the United States, characterized by the presence of hepta- and octaCDD/CDF compounds l trace or non-detectable levels of other PCDD/PCDF congeners. The other five Lake George samples contained higher concentrations of the hepta and octa congeners together with hexaCDDs and tetra- to hexaPCDFs. These samples also had higher lead concentrations. One possible explanation for the results is that emissions from power boats are contributing to PCDD/PCDF contamination in Lake George. In an investigation of automotive emissions, Bingham et al., 1989 found that the PCDD/PCDF congener pattern was dominated by lower chlorinated PCDF congeners (less than 5 chlorines). There are two factors which could explain the different pattern found in the present study. In the first place, the pattern could be altered by the combustion conditions of 2-stroke outboard motors as compared to 4-stroke automobile engines. In the second place, the lower chlorinated PCDD/PCDF compounds could be lost to the atmosphere as the exhaust gases are emitted just below the surface.

Results from Lake Champlain are shown in Table 2. The OCDD concentrations in the surface

Table 2. Concentrations (pg/g dry wt.) of PCDD/PCDF Compounds in Core and Surface Sediments from Lake Champlain, New York[1]

		Core Sediments[3]		
Compound	Surface Sediments (five samples)[2]	Core 1, Sections 1,3-6 Core 2, Sections 1-6 Core 3, Sections 2 and 4	Core 1, Section 2	Core 3, Section 3 Core 3, Sections 6-8
2,3,7,8-TCDD	ND	ND-24	14	ND
TCDDs	ND	ND-24	260	ND
PCDDs	ND	ND-39	3,300	ND
HxCDDs	74 ± 55	ND-760	24,000	ND
HpCDDs	376 ± 160	410-4,500	8,700	ND-750
OCDD	6,720 ± 1,748	3,100-18,000	5,500	940-4,400
2,3,7,8-TCDF	14-120	20-580	29	210-690
TCDFs	21-120	37-1,400	74	520-1,400
PCDFs	5.7 ± 5.2	ND-190	240	120-520
HxCDFs	26 ± 22	ND-850	9,200	0-130
HpCDFs	118 ± 66	190-2,500	41,000	0-29
OCDF	87 ± 70	87-690	11,000	0-230
Pb (µg/g)	33 ± 6.0			

[1]Results are expressed as the ave ± s.d. or as a range when there was wide dispersion in the data.

[2]Data were not included from a sample which contained only HpCDDs and OCDD at concentrations of 250 and 6300 pg/g respectively.

[3]The top two sections (1 and 2) of each core were 3 cm long. All other sections were 6 cm long. Core 3 was longer than Cores 1 or 2, and two additional sections were obtained from this core.

sediment samples were increased by a factor of seven compared to the high level Lake George samples. The penta- and, to a lesser extent, the hexaCDF concentrations were decreased relative to the same congener groups in the Lake George samples.

Core samples rather than surface samples were taken at the mouth of Ticonderoga Creek since an objective of this study was to determine the influence on PCDD/PCDF contamination of pulp and paper activities in the area from the 1880's to 1970. Low recoveries were obtained for hepta- and octaCDD/CDF internal standards in many of the core sections. In two cases, Sections 1 and 5 of Core 3, there were no signals for ^{13}C-OCDD, and data from these samples have been omitted from Table 2. However the core data do provide useful information on the possible sources of PCDD/PCDF contamination in the surface sediment samples which were all collected downstream (north) of the creek estuary.

All sections of Core 2, five sections of Core 1 and two sections of Core 3 had congener patterns which resembled the congener patterns in the surface sediment samples. Cores 1 and 2 were taken in an area where previous environmental monitoring studies have shown the presence of flyash and cinders in core samples (Wood, 1972). Flyash and, to a lesser extent, wood fibers appeared to be present in most of the Core 1 and Core 2 sections. The high OCDD concentrations in these samples are consistent with results from investigations on the PCDD/PCDF composition of flyash, especially coal flyash (Czuczwa and Hites, 1984) Core 3 in contrast had the appearance of a fine grained sediment. The upper three sections were a derk brown color and the lower sections were grey. While OCDD was the predominant congener in several of the upper sections of the core, the lower sections of the core had TCDF concentrations exceeding OCDD concentrations. High TCDF concentrations have been associated with effluents from pulp and paper mills using the bleached kraft process (Clement et al. 1989). This process was in use at the mill on Ticonderoga Creek when it was closed in 1970. It would appear that sediments contaminated with TCDFs from the plant have now been covered over by deposits from the areas where Cores 1 and 2 were collected.

Core 1, Section 2 had the highest PCDD/PCDF concentration and also a congener pattern which differed from the patterns in all the other core and surface sediment samples. The finding of high concentrations of hexaCDDs and heptaCDFs is consistent with an incineration source since a similar congener distribution has been described for PCDD/PCDF emissions from industrial and municipal waste incinerators (Czuczwa and Hites, 1985). Effluent from the sewage treatment plant at Ticonderoga could also be contributing to the PCDD/PCDF contamination.

In conclusion, the study results suggest that PCDDs and PCDFs from the Ticonderoga Creek area have contaminated downstream sediments in Lake Champlain. Additional sampling is being undertaken to determine if the new pulp and paper plant is contributing to the PCDD/PCDF contamination of the lake. The highest surface sediment TCDF concentration (120 pg/g) was found in a sample collected 0.5 miles downstream from the plant. However, effluent from the plants waste water treatment facility enters the lake 1.5 miles farther down stream from the point where this sample was collected.

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