Assessing the Importance of Atmospheric Deposition of PCDD/Fs to the Great Lakes: Compositional Comparison of PCDD/F Sedimentary Accumulations

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Introduction

It is currently thought that air emissions from the combustion of wastes containing organochlorines contributes the major flux of PCDD/Fs to land and water [1]. If this is true, then atmospheric deposition should provide the major source of PCDD/F to the Great Lakes. In this paper we attempt to establish the validity of this assumption for three of the Great Lakes; Lakes Superior, Michigan, and Ontario.

Objectives

The objectives of the study were to determine the concentrations, accumulations and inventories of PCDDs and PCDFs in dated sediment cores from three of the Great Lakes and two remotely located "control lakes. We use a comparative approach to assess the relative importance of atmospheric deposition as a source of PCDD and PCDF to the lakes. The comparisons include: a) historical accumulation rates of ΣPCDD and ΣPCDF among cores, b) homolog compositions among cores, c) atmospheric deposition to core accumulation rates (by homolog), and d) accumulation rates in the control lakes to those in the Great Lakes (by homolog).

Methods

The details of the core locations and analytical methods are given in another publication [2]. Briefly, 10-50g wet sediment were extracted, interferences were removed using alumina/silica column chromatography, and PCDD/Fs were analyzed using GC/ECNCIMS. The sediment cores were dated using ^{210}Pb and accumulations and inventories were corrected for focusing.

Results

Historical accumulation rates of ΣPCDD and ΣPCDF among cores The surface accumulation rates (Figure 1) of both PCDD and PCDF are similar (by compound class) among the two Lake Superior cores and the control lake cores consistent with Lake Superior currently receiving PCDD and PCDF from remote air. During 1950-1970 the PCDF accumulation in the depositional core from Lake Superior is significantly greater than that in the controls suggesting

that there was a non-atmospheric source of PCDF to Lake Superior during that time. The PCDF accumulation in Lake Michigan is similar among all cores; about 2 x that of the PCDF accumulation in one of the controls (Siskiwit). This is consistent with either one dominant source of PCDF to the lake (atmospheric) or one or multiple sources well mixed throughout the lake. The PCDD accumulation in the northern portion of the lake is greater than in the southern portion. This suggests a non-atmospheric source of PCDD to the northern part of Lake Michigan since air concentrations of PCDD would be expected to decline in more remote regions [3]. The accumulation profiles of PCDF in Lake Ontario are similar among cores but the accumulation rates are 10-20 x those of the control lakes, Lake Superior, or the southern Lake Michigan cores. Either the air above Lake Ontario is much higher in PCDF concentration than that over southern Lake Michigan or significant non-atmospheric sources of PCDF are impacting Lake Ontario. The PCDD accumulations in Lake Ontario are also significantly greater than those in the other lakes and there is a gradient of increasing accumulation from the west to the east during the period of maximum accumulation. This is suggestive of at least one source of PCDD/F rich in PCDD entering the lake at a central or eastern location.

Homolog compositions among cores Principal component analysis (SPSS for Windows 7.0) was used to investigate for similarities among the concentration-independent homolog compositions of the cores. There are compositional differences among the lakes and between basins of the same lake (Figure 2). The differences suggest different source signals to the individual Great Lakes and to regions of the same Great Lake.

The compositions of the control lakes, LS-Basswood, and recent and early sections from the LS-NOAA3 (Figure 2d) are similar and similar to the composition of air particle samples [3], rain samples [4], and soil samples from remote and suburban locations of the Great Lakes basin and the continental US [5]. The homolog compositions of the Lake Michigan cores differ between the northern (Figure 2e) and southern (Figure 2f) zones and all differ from the control lake cores. Compared to the control lakes, the Lake Michigan cores are more similar to samples of total air or air vapor taken from remote and suburban areas [3,6,7] which does not exclude the atmosphere as a dominant source. However, the composition of the southern core differs from that of soils taken from southern Michigan [5]. Assuming that the soils received PCDD/Fs only from atmospheric sources, these differences indicate that either the source to southern Lake Michigan is not solely atmospheric or in-lake processes result in the sediments accumulating different proportions of PCDD/F homologs than soils. The homolog composition of LS-NOAA3 changes temporally (Figure 4g). From 1950 to 1973 it resembles the composition in the southern Lake Michigan core. This suggests that a major source(s) to Lake Superior from 1950 to 1973 was similar to the source(s) to southern Lake Michigan. In Lake Ontario, the western and central cores (Figure 4h and 4i, respectively) are similar but differ from the eastern core (Figure 4j). The in-lake difference suggests a non-atmospheric source entering in the central to eastern portion of the lake. Compared to the other cores, all three cores from Lake Ontario have a much more significant contribution from the higher PCDF homologs suggesting that Lake Ontario has been strongly impacted by non-atmospheric source(s) of PCDD/F.

Atmospheric deposition vs core accumulation rates As a group, the control lakes and Lake Superior have current accumulation rates that are similar by homolog and compound class to atmospheric deposition from remote locations (Table 1). The accumulation rates of PCDDs in Lake Michigan differ between the northern and southern basins but both could be

supported by deposition from remote to suburban air. The 4F and 5F accumulations in southern Lake Michigan are similar to atmospheric deposition from urban air but the accumulations of other homologs are much less than deposition from urban air. This suggests a non-atmospheric source rich in 4F and 5F to southern Lake Michigan. In Lake Ontario the PCDD accumulation rates are similar to atmospheric deposition from urban air but the 7F and 8F accumulation rates are higher than all but the source-impacted urban site. The PCDD accumulation in southern Lake Michigan, which has a population density similar to that around Lake Ontario, is only about 10 to 20% of that in Lake Ontario. From this we suggest that there must be significant non-atmospheric source(s) of PCDD/Fs to Lake Ontario.

Accumulation rates in the control lakes to those in the Great Lakes By ratioing the accumulation of PCDDs and PCDFs in the Great Lakes to that in the control lakes we can apportion the significance of atmospheric deposition from the background signal to each of the Great Lakes. Deposition from remote air can account for all the current accumulation of PCDD in Lake Superior and southern Lake Michigan. Only about 50% of the PCDD accumulation in northern Lake Michigan and ~15% in Lake Ontario can be attributed to the same source. All of the current PCDF in Lake Superior, ~30% in Lake Michigan, and < 5% in Lake Ontario can be attributed to the background signal.

Conclusions

We set out to test the hypothesis that atmospheric deposition was the dominant source of PCDDs and PCDFs to the Great Lakes. We could support the hypothesis for current sources to Lake Superior but not Lake Michigan or Lake Ontario. In Lake Michigan atmospheric deposition provides the major source of PCDDs to the southern part of the lake. However, there appears to be a non-atmospheric source rich in PCDFs that enters in the southern part and another source rich in PCDDs that enters in the northern portion of the lake. In Lake Ontario non-atmospheric sources appear to provide the major sources to the lake. The Niagara River probably provides a significant portion of the inputs but there also appears to be a source rich in PCDD that enters in the central or eastern portion of the lake. Historically Lake Superior received a non-atmospheric source rich in PCDF but currently it appears to be atmospherically driven.

References

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TABLE 1. Current focus-corrected accumulation rates of PCDD and PCDF in sediments and representative estimates of atmospheric deposition (wet + dry particle) from urban and remote locations. The fluxes are given on a homolog-specific and chemical class-specific basis. 5D-8D and 4F-8F represent the penta-octa chlorinated dioxins and tetra-octa chlorinated furans, respectively. PCDD is the total of all dioxin homologs and PCDF is the total of all furan homologs. The fluxes are in pg/cm^2 yr. The atmospheric depositions are calculated from concentrations in the given references and the homolog-specific total washout coefficients reported in [4] and dry deposition velocities reported in [3] and assume 100 cm/yr precipitation.

	5D	6D	7D	8D	PCDD	4F	5F	6F	7F	8F	PCDF	Ref.
Siskiwit (a)	0.8	0.8	5.2	15	22	1.5	1.4	1.2	1.0	0.7	5.7	
Outer (a)	mdl	mdl	mdl	5.2	5.2	mdl	mdl	mdl	mdl	mdl	mdl	
LS-Bass (a)	mdl	mdl	2.1	5.8	8.0	mdl	mdl	mdl	0.8	mdl	0.8	
LS-NOAA3 (a)	mdl	mdl	2.3	5.1	7.4	0.4	mdl	mdl	0.5	mdl	0.9	
LM-68k (a)	1.4	8.1	12	23	44	11	6.3	1.7	1.7	1.5	22	
LM-47s (a)	mdl	3.6	13	32	49	12	5.9	4.0	2.3	1.6	25	
LM-18 (a)	mdl	1.3	4.6	11	17	10	4.6	1.6	1.0	mdl	17	
LO-19 (a)	3.5	7.4	34	100	160	62	28	34	41	60	230	
LO-40a (a)	2.8	12	27	81	120	34	12	23	22	36	130	
LO-E30 (a)	37	13	40	130	220	23	23	29	40	58	170	
Trout Lake, WI (b)	0.1	1.1	2.6	3.1	6.9	0.5	0.5	0.5	0.3	0.2	2.0	3)
Walpole Island, Ontario (b)	-	-	6.4	13.1	19	-	-	-	-	-	-	8)
Bloomington, IN (c)	0.4	3.9	14	24	42	1.3	2.9	3.2	2.4	0.9	11	3)
Niagara Falls, NY (c)	0.2	1.9	14.4	38	54	2.8	2.8	3.9	4.1	2.4	16	9)
Windsor, Ontario (c)	-	10	21	41	72	2.6	2.1	3.0	2.7	4.4	15	8)
Indianapolis, IN (d)	4.6	18	28	32	83	7.5	21	23	8.7	2.5	63	3)
Bridgeport, CT (d)	4.3	23	34	72	130	11	14	18	13	7.1	61	7)
Niagara Falls, NY (e)	18	54	80	90	240	40	50	60	58	20	230	6)

(a) Sediment cores, this work. mdl indicates accumulation rates were below the method detection limit.

(b) Remote location. (c) Suburban location. (d) Urban location. (e) Source-impacted urban location.

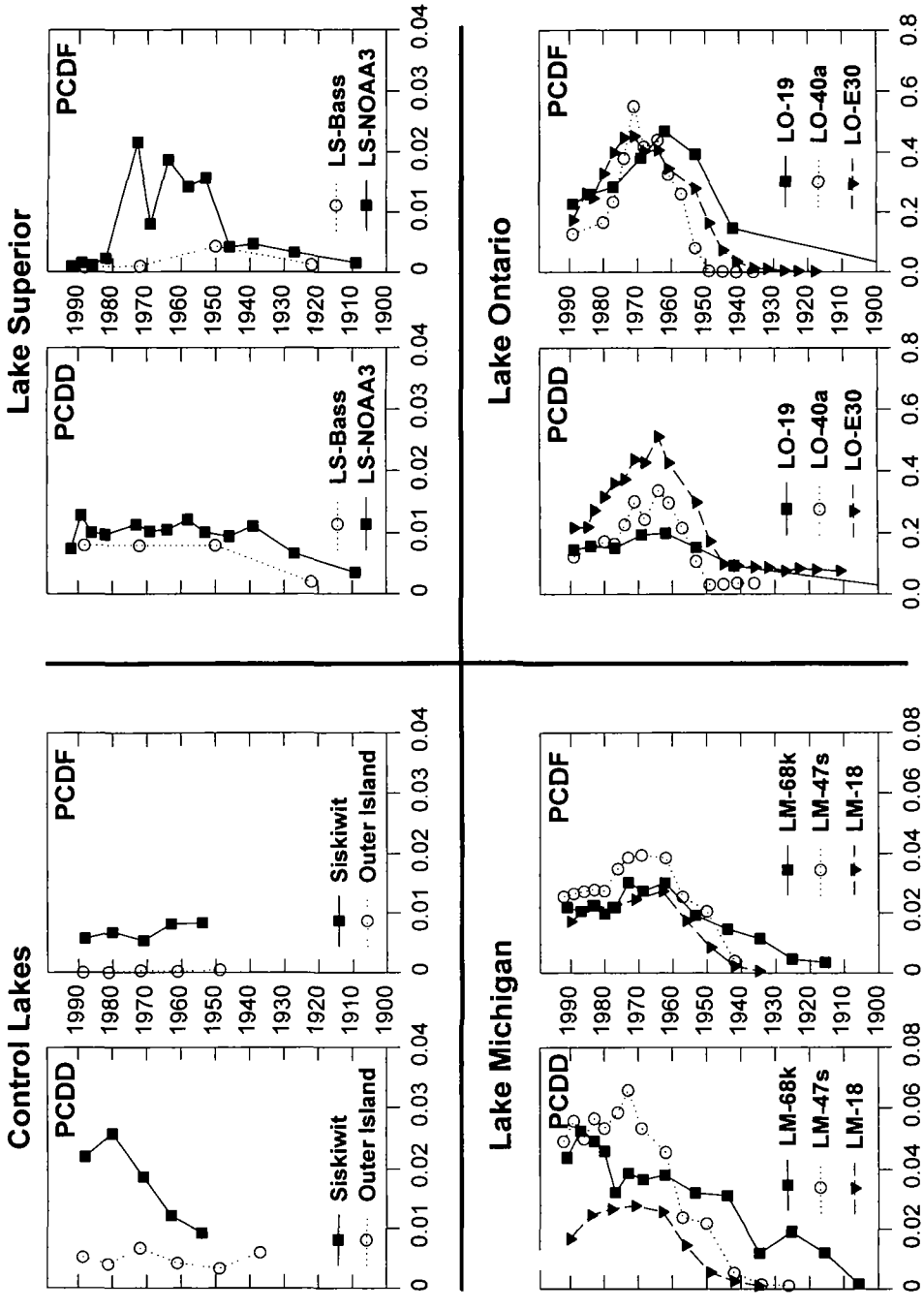

Figure 1. Hisorical accumulation (ng/cm^{2}yr) profiles of PCDD and PCDF in sediment cores

Figure 2. Principal Component Analysis Plot and the Homolog Compositions of the clusters
LO = Lake Ontario, LM = Lake Michigan, LS = Lake Superior