

## A Time-Trends Study of the Occurrences and Levels of CDDs, CDFs and Dioxin-like PCBs in Sediment Cores From 11 Geographically Distributed Lakes in the United States

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### 1. Introduction

Polychlorinated dibenzo-p-dioxins (CDDs), polychlorinated dibenzofurans (CDFs) and certain non- and mono-ortho substituted polychlorinated biphenyls (cp-PCBs) are a general class of chlorinated aromatic compounds that are considered as dioxin-like. The term 'dioxin-like' refers to compounds having basic similarities in molecular structure, chemical properties, environmental persistence, bioaccumulation potential, mechanisms of toxic actions, and these are displayed in Table 1<sup>1,2,3,4</sup>. Because these chemicals are highly toxic, are resistant to physical, chemical and biological degradation and transformation processes, are highly lipophilic and bioaccumulate into ecological and agricultural food chains, attention has been directed to the identification of anthropogenic source activities with the objective of reducing the overall environmental burden. In this regard, certain fundamental questions arise as to environmental trends over time in terms of environmental concentrations and fluxes to environmental sinks. When did these chemicals initially appear in the general environment and are they related to anthropogenic activities? What has been the chronology of environmental burden from the recent time to decades in the past in terms of environmental concentrations and fluxes to the sink? Is there evidence of any trends in environmental burden with time?

To address these fundamental questions, the United States Environmental Protection Agency (USEPA) in collaboration with the United States Department of Energy (USDOE) has completed a time-trends study of the occurrences and levels of CDDs, CDFs and cp-PCBs in the U.S. environment using dateable sediment deposits obtained from 11 freshwater lakes geographically distributed in the United States. The objective of the USEPA/USDOE study was to determine the chronology of the deposition of dioxin-like compounds in the United States over the past 200 years.

### 2. Methods

The USDOE maintains an archive of sediment core samples from 64 lakes and reservoirs. Three primary conditions were applied in identifying 11 lakes, to include: 1/ remoteness from specific anthropogenic source activity, e.g., >10 km from the shoreline; 2/ geographical coverage

of the continental U.S.; and 3/ existence of adequate dating records. Table 2 gives descriptive information on the location and dating of sediment cores of each lake. The identification number of each lake in Table 2 corresponds to the relative geographical position in the United States, i.e., NE=Northeast; SE=Southeast; RM=Rocky Mountains; W=Western; A=Alaskan/Arctic.

Sediment corings were collected using a 21 cm diameter sphincter launched from a boat and drilled into the lake sediment. Cores up to 1 m length were extruded and sectioned in 2-10 cm lengths. The samples were placed in precleaned glass jars and stored in a cool dark facility until required for analysis. Radiometric techniques, together with counting laminations, were applied to date the sediment cores. Both atmospherically deposited (excess)  $^{210}\text{Pb}$  and radiation fallout  $^{137}\text{Cs}$  were used as tracers to determine the sedimentation rates in the cores, and, subsequently, to date distinct core sections. Each sediment core was counted by gamma spectrometry from the surface section down to the section which no longer contained  $^{137}\text{Cs}$  or excess  $^{210}\text{Pb}$ . Temporal resolution may vary by an order of magnitude with these methods, but typically the values ranged from 5 to 10 years<sup>5</sup>. The dating corresponded to ca. 10 year intervals from the most recent layer at the time of sampling, back in time, in some cases several hundred years (see Table 2). This resulted in 77 samples from 11 lakes (10 lakes from the continental U.S., and 1 lake in the Arctic region of Alaska). The samples were maintained at a temperature of 4°C, and shipped to an analytical laboratory for chemical analysis of dioxin-like compounds.

### 3. Laboratory methods

Table 1 lists the target CDDs, CDFs and cp-PCB analytes for laboratory analysis in this study. USEPA method 1613B was generally followed using isotope dilution HRGC/HRMS<sup>6</sup>. Samples were homogenized. Ten - 20 g aliquot (dry weight) of each sample was mixed with 50 - 100 g clean quartz sand, and fortified with 100 to 600 pg/ $\mu\text{L}$   $^{13}\text{C}$ -labeled CDD, CDF, and cp-PCB isomer according to method 1613B, the exception being the addition of 6 labeled isomers of PCBs (IUPAC # 77, 105, 118, 126, 156, 169). The aliquot was Soxhlet extracted with 400 mL toluene for 21 hours. The extract was eluted through a 6-g acidified silica gel/1-g neutral silica gel column followed by 90 mL hexane. The combined extract was eluted through a neutral alumina column. The target analytes were collected in a 20 mL fraction of 60% dichloromethane/hexane. The fraction was further cleaned up on a 8% AX-21/Celite 545 column. Analysis was conducted using a VG70-250S at a minimum resolution of 10,000. A 60 m DB-5MS GC columns was used, providing a 25% valley resolution between 2,3,7,8-TCDD and all other TCDD isomers. Isomer concentration levels were calculated by isotope dilution. Detection limits were based on the low calibration standard as expressed in pg/g and based on a 10- $\mu\text{L}$  final extract volume and the dry weight of the sample. When isomers were not detected, the chromatogram was examined for quantifying responses above 2.5 time the noise level. The ion ratio criterion used to identify qualifying responses was  $\pm 20\%$  of the theoretical. A relative standard deviation of  $<20\%$  from the mean relative response factor was met for all analytes in the initial calibration. The mean recoveries of the internal labeled standards ranged from 48% to 89% for CDDs and CDFs, and from 42% to 106% for the cp-PCBs.

### 4. Results

Several general observations about CDD, CDF and cp-PCB concentrations, profiles, ratios of concentration to baseline levels are made based on the analysis of the sediment core samples to the 11 U.S. lakes as follows. For purposes of comparison with other studies of this nature, the results are described as concentrations in the sediments. However, another related term is flux, which represents the aggregate delivery of contaminant concentration per m<sup>2</sup> of lake sediment per year, corrected for the sediment accumulation rate.

i. *Generally, CDD and CDF concentrations begin to rise in the 1930s and 1940s, and*

- begin to decline in some lakes in the 1960s and 1970s. Figure 1 is an example lake.
- ii. Generally, total CDD concentrations are higher than the total CDF concentrations.
    - CDD/CDF ratios are usually  $> 1$  (0.5 - 42).
    - CDD concentrations range from  $10 \text{ pg g}^{-1}$  to  $2,806 \text{ pg g}^{-1}$  in the 10 continental U.S lakes.
    - CDD concentrations range from  $1.4 \text{ pg g}^{-1}$  to  $3.8 \text{ pg g}^{-1}$  in the Alaskan lake.
    - CDF concentrations range from  $1.8 \text{ pg g}^{-1}$  to  $922 \text{ pg g}^{-1}$  in the 10 continental lakes.
    - CDF concentrations range from  $1.7 \text{ pg g}^{-1}$  to  $5.4 \text{ pg g}^{-1}$  in the Alaskan lake.
  - iii. The order of magnitude changes in CDD and CDF concentrations over time range from  $< 1$  to about 2 orders of magnitude for the ten continental lakes and  $< 3$  fold change occurs in the Alaskan Arctic lake.
  - iv. Concentrations of CDDs and CDFs increase as the location of the sites move from West to East across the continental U.S. along the approximately similar latitude.
  - v. OCDD usually dominates; CDFs are more variable, but TCDF and OCDF frequently dominate in total concentration.
  - vi. The 2,3,7,8-substituted congeners accounted for 47% to over 90% of the total CDD/CDF concentrations for the 11 lakes evaluated. TEQ concentrations ranged from  $0.1 \text{ pg g}^{-1}$  to  $15.6 \text{ pg g}^{-1}$ .
  - vii. Generally, most cp-PCBs were detected only in the post 1930 time period. Increases were observed from the 1930s to the 1960s; declines occur only in the most recent dating periods.
    - Cp-PCB concentrations range from non-detected up to  $3,700 \text{ pg g}^{-1}$ .
  - viii. In general, concentrations of PCB-118 had the highest concentration of all the PCBs, often accounting for more than half the total cp-PCBs analyzed. PCB-169 and PCB-126 usually account for the lowest percentage of total cp-PCBs. These PCB proportions appear to be relatively consistent over all lakes and time periods.

## 5. Statistical analysis of results

The statistical analysis was directed at observing whether there were significant differences in concentrations of dioxin-like compounds between two relative time scales: pre- and post- 1930. The initial analysis of temporal variability in the data was done using a t-test on five lakes having sufficient dating history to permit this aggregation by time-period. Results of the t-test shows that there were significant differences between the two time periods for four out of the five lakes across most CDD, CDF and cp-PCB compounds. These significant differences reflects more than a 10-fold increase in concentration in the post-1930s as compared to pre-1930 period. A series of regression analyses were performed. The results showed that for the pre-1930s, the concentrations of total CDD/F in sediment cores did not differ significantly over time for three of the four lakes with adequate data. This indicates that significant increases did not occur prior to the 1930s. For the four lakes having adequate data (NE4, RM12, W14, W15), the pre-1930 slopes of concentration ranged from -0.05 to 1.4, and the post-1930 slopes ranged from 2.9 to 20.7. The consistency with which all slopes increased from before 1930 to after 1930 strongly indicates that concentrations are increasing with time. This finding is further supported by the post-1930s concentration slopes of the other 6 lakes (NE4, NE11, SE2, SE4, RM7, RM11) which ranged from 6.1 to 61.9. The consistency of the positive, upward slope of post-1930s concentration across all lakes is a striking observation, and strongly supports a hypothesis that dioxin-like compounds increased with time beginning with the 1930s. An interesting exception to these observed relationships is that the post-1930s total CDD/F slope for the Alaskan/Arctic lake was only 0.005, indicating very slow increases in the concentrations in these sediments over time (e.g., very little change occurred).

## 6. Conclusions

This study is the most extensive evaluation to date of the chronology of deposition of dioxin-like compounds in sediments of freshwater lakes geographically distributed in the U.S. Data indicate that CDD, CDF and cp-PCB inputs to U.S. lakes have increased over time, with significant increases occurring only after the 1930s. This is consistent with the findings of other researchers involving North American and Swiss lakes<sup>7,8,9,10,11,12</sup>. In general, a minimum of an order of magnitude increase in concentration occurred from the pre- to post-1930s time frame. With few exceptions, this observation was consistent for all of the 2,3,7,8-substituted CDD/CDF congeners, CDD/CDF homologue groups and cp-PCBs. The observed temporal trends were consistent across lakes (except the Alaskan/Arctic lake), especially for lakes within the same geographic region (e.g. east, west, north, south, and central regions). For some lakes, a downward trend appeared to exist for the most recent time periods, but this observation was based on qualitative analyses only. The point of inflection for this downward trend varied across lakes, but for CDDs/Fs it appeared to occur between the 1960s and 1970s, and for cp-PCBs it appeared to occur between 1950s and 1970s. Further studies that include sediment core samples from more recent time periods are needed to confirm this observation with quantitative analyses. The data also indicate that CDD, CDF and cp-PCB profiles are similar across all time periods and across all lakes.

## 7. Tables and Figures

Table 1. Dioxin-like compounds subject to analyses in the sediment cores

CDD	CDF	PCB Type		PCB (IUPAC#)
2,3,7,8-TCDD	2,3,7,8-TCDF	non-ortho	✓	(77) 3,3',4,4'-TeCB
1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDF		✓	(126)3,3',4,4',5-PeCB
1,2,3,4,7,8-HxCDD	2,3,4,7,8-PeCDF		✓	(169)3,3',4,4',5,5'-HxCB
1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDF	mono-ortho	✓	(105)2,3,3',4,4'-PeCB
1,2,3,7,8,9-HxCDD	1,2,3,6,7,8-HxCDF			(114)2,3,4,4',5-PeCB
1,2,3,4,6,7,8-HpCDD	1,2,3,7,8,9-HxCDF		✓	(118)2,3',4,4',5-PeCB
1,2,3,4,6,7,8,9-OCDD	2,3,4,6,7,8-HxCDF			(123)2',3,4,4',5-PeCB
	1,2,3,4,6,7,8-HpCDF		✓	(156)2,3,3',4,4',5-HxCB
	1,2,3,4,7,8,9-HpCDF		✓	(157)2,3,3',4,4',5'-HxCB
	1,2,3,4,6,7,8,9-OCDF	di-ortho		(167)2,3',4,4',5,5'-HxCB
				(189)2,3',3',4,4',5,5'-HpCB
				(170)2,2',3,3',4,4',5-HpCB
				(180)2,2',3,4,4',5,5'-HpCB
Total TetraCDD	Total TetraCDF			
Total PentaCDD	Total PentaCDF			
Total HexaCDD	Total HexaCDF			
Total CDD	Total CDF			

Note: ✓ indicates PCBs analyzed in the sediment core samples.

## 8. References

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Table 2. Descriptive information on selected sites of sediment core study

ID number	Site	Relative location	No. Samples	range (years)
NE-4	Canandaigua Lake	Finger lake, NY	12	1728 - 1991
NE-5	Skaneateles Lake	Finger lake, NY	8	1914 - 1991
NE-11	Sacandaga Res.	Johnstown, NY	5	1929 - 1983
SE-2	Santeetlah Res.	Robbinsville, NC	5	1935 - 1983
SE-4	Blue Ridge Res.	Blue Ridge, GA	5	1934 - 1983
RM-7	Deer Creek	Heber City, UT	4	1946 - 1982
RM-11	Echo Lake	Coalsville, UT	4	1941 - 1982
RM-12	Panguitch Lake	Panguitch, UT	10	1882 - 1985
W-14	Ozette Lake	Olympic Penn, WA	11	1720 - 1985
W-15	Beaver Lake	Olympic Penn, WA	9	1884 - 1985
A-4	Chandler Lake	North Slope, AK	4	1117 - 1993

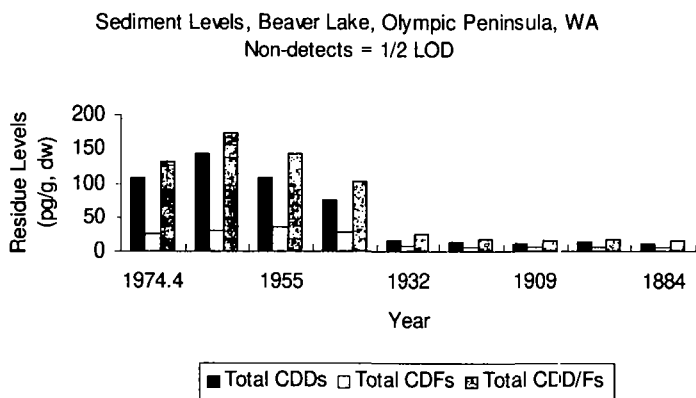


Figure 1.  
Example of time-trends of CDDs, CDFs, and total CDDs/Fs: Lake W-15