**2010 Project Abstract**
For the Period Ending June 30, 2012

**PROJECT TITLE:** Evaluation of Dioxins in Minnesota Lakes
**PROJECT MANAGER:** William Arnold
**AFFILIATION:** University of Minnesota, Department of Civil Engineering
**MAILING ADDRESS:** 500 Pillsbury Drive SE
**CITY/STATE/ZIP:** Minneapolis, MN 55455
**PHONE:** 612-625-8582
**E-MAIL:** arnol032@umn.edu
**WEBSITE:**
**FUNDING SOURCE:** Environment and Natural Resources Trust Fund
**LEGAL CITATION:** M.L. 2010, Chp. 362, Sec. 2, Subd. 5f

**APPROPRIATION AMOUNT: $264,000**

**<u>Overall Project Outcome and Results</u>**

Triclosan is an antimicrobial agent in many consumer products such as liquid handsoaps, bar soaps, dishwashing liquid, deodorants, anti-gingivitis toothpaste, and acne creams. Because it is washed down the drain through the normal course of use, triclosan is commonly detected in wastewater effluent. During water and wastewater disinfection with chlorine, triclosan can be transformed to a series of chlorinated triclosan derivatives. When discharged into surface waters, triclosan and its derivatives react in sunlight to form a series of four polychlorinated dibenzo-*p*-dioxins. Dioxins are persistent organic pollutants that are toxic, carcinogenic, and endocrine disrupting. Thus, dioxins pose a risk to the health of aquatic species and their predators (including humans). To evaluate the historical and current exposure of surface waters to triclosan, chlorinated triclosan derivatives, and their derived dioxins, sediment cores were collected from wastewater-impacted Minnesota lakes. Following radiometric dating, triclosan and chlorinated triclosan derivatives were extracted from core sections and quantified. Dioxins were extracted from the same core sections and also quantified. The concentrations and temporal trends of triclosan, chlorinated triclosan derivatives, and their dioxins in aquatic sediments were found to be a function of historical wastewater treatment operations and lake system scale. Cores collected from large-scale riverine systems with many wastewater sources recorded increasing concentrations of triclosan, chlorinated triclosan derivatives, and their derived dioxins since the patent of triclosan in 1964. The trends were directly attributed to increased triclosan use, local improvements in treatment, and changes in wastewater disinfection practices. Concentrations of triclosan, chlorinated triclosan derivatives, and their dioxins were higher in small-scale systems, reflecting a greater degree of wastewater impact. In a lake receiving no wastewater influent, no triclosan was detected. Low levels of the four triclosan-derived dioxins were found in northern wastewater-impacted Minnesota lakes prior to the introduction of triclosan as well as in the lake with no wastewater input. The background levels of these dioxins were attributed to a secondary, region-specific source. Nonetheless, it is clear that triclosan is the major source of these dioxins after 1960. The contribution of the triclosan-derived dioxins to the total dioxin pool in terms of mass was determined for each sediment core. In heavily impacted systems, the dioxin contribution from triclosan and chlorinated triclosan derivatives accounted for up to 60% of total dioxin mass in recent sediment. Thus, the discharge of triclosan and chlorinated triclosan derivatives may pose a threat to wastewater-impacted lakes. The findings of this work suggest that additional treatment of wastewater to remove triclosan, additional regulation of triclosan use, or dissemination of information regarding the prevalence of triclosan in consumer products may be necessary. Full results are presented in the M.S. Thesis of Cale T. Anger submitted with this report.

**<u>Project Results Use and Dissemination</u>**

This project led to the production of the M.S. Thesis of Cale T. Anger, *Quantification of Triclosan, Chlorinated Triclosan Derivatives, and their Dioxin Photoproducts in Lacustrine Sediment Cores.* The thesis received the Distinguished Master's Thesis Award from the University of Minnesota, recognizing it as the best thesis at the U of MN for 2011-2012. A manuscript with the same title has been submitted the peer reviewed journal *Enviornmental Science & Technology*. The results of the work have been presented at the American Chemical Society National Meeting, the St. Croix River Research Rendevous, the Itasca Water Legacy Project lecture series, and the Mississippi River Forum. Two more presentations at the American Society of Limnology and Oceangraphy and the IWA Micropol and Ecohazard conferences are planned. We anticipate press coverage of the findings upon publication of the peer-reviewed article.

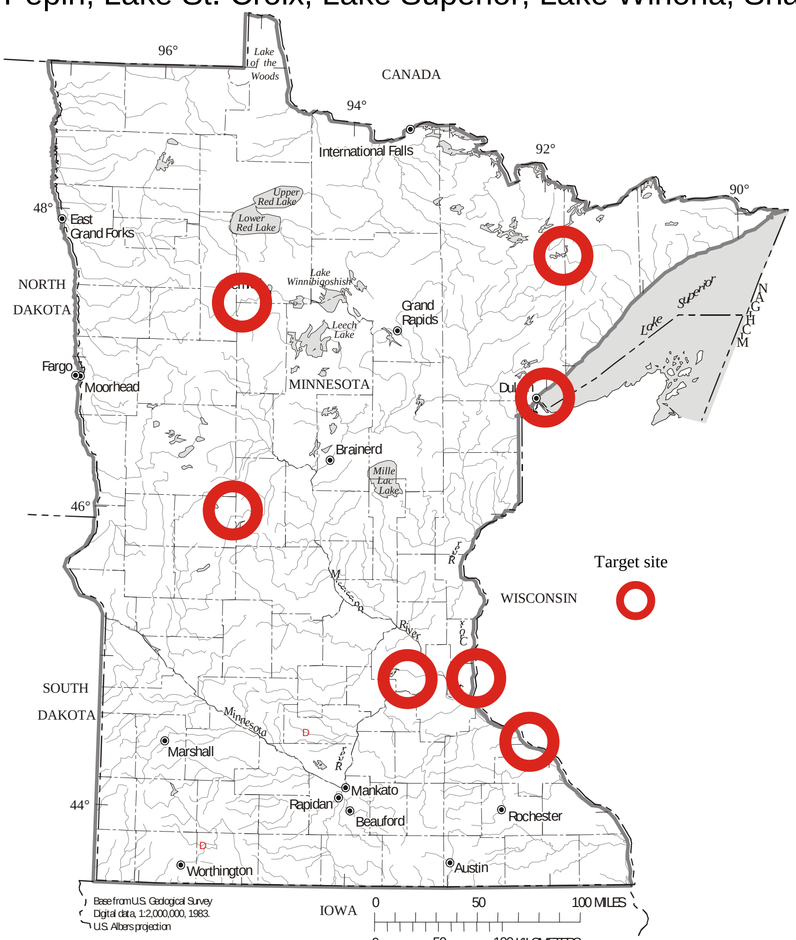
# Environment and Natural Resources Trust Fund (ENRTF) 2010 Work Program

**Date of Report:** December 11, 2012
**Final Report**
**Date of Work Program Approval:**
**Project Completion Date:** June 30, 2012

## I. PROJECT TITLE: Evaluation of Dioxins in Minnesota Lakes


**Project Manager**: William A. Arnold
**Affiliation:** University of Minnesota, Department of Civil Engineering
**Mailing Address:** 500 Pillsbury Drive SE
**City / State / Zip :** Minneapolis, MN 55455
**Telephone Number:** 612-625-8582
**E-mail Address:** arnol032@umn.edu
**FAX Number:** 612-626-7750
**Web Page address:** not applicable


**Location:** University of Minnesota, Hennepin County, Minneapolis, 55455 and St. Croix Watershed Research Station, Washington County, Marine on St. Croix, 55047. Lake Pepin, Lake St. Croix, Lake Superior, Lake Winona, Shagawa Lake, and Lake Itasca.



| | | |
|---|---|---|
| **Total ENRTF Project Budget:** | **ENRTF Appropriation** | **$ 264,000** |
| | **Minus Amount Spent:** | **$ 264,000** |
| | **Equal Balance:** | **$ 0** |

**Legal Citation: M.L. 2010, Chp. 362, Sec. 2, Subd. 5f**

**Appropriation Language:**
$264,000 is from the trust fund to the Board of Regents of the University of Minnesota to examine the concentration of dioxins in lake sediment and options to improve water quality in lakes.

## II. and III. FINAL PROJECT SUMMARY

Triclosan is an antimicrobial agent commonly detected in wastewater effluent. During water and wastewater disinfection with chlorine, triclosan can be transformed to a series of chlorinated triclosan derivatives. When discharged into surface waters, triclosan and its derivatives react in sunlight to form a series of four polychlorinated dibenzo-*p*-dioxins. To evaluate the historical and current exposure of surface waters to triclosan, chlorinated triclosan derivatives, and their derived dioxins, sediment cores were collected from wastewater-impacted Minnesota lakes. Following radiometric dating, triclosan and chlorinated triclosan derivatives were extracted from core sections and quantified. Dioxins were extracted from the same core sections and also quantified. The concentrations and temporal trends of triclosan, chlorinated triclosan derivatives, and their dioxins in aquatic sediments were found to be a function of historical wastewater treatment operations and lake system scale. Cores collected from large-scale riverine systems with many wastewater sources recorded increasing concentrations of triclosan, chlorinated triclosan derivatives, and their derived dioxins since the patent of triclosan in 1964. The trends were directly attributed to increased triclosan use, local improvements in treatment, and changes in wastewater disinfection practices. Concentrations of triclosan, chlorinated triclosan derivatives, and their dioxins were higher in small-scale systems, reflecting a greater degree of wastewater impact. In a lake receiving no wastewater influent, no triclosan was detected. Low levels of the four triclosan-derived dioxins were found in northern wastewater-impacted Minnesota lakes prior to the introduction of triclosan as well as in the lake with no wastewater input. The background levels of these dioxins were attributed to a secondary, region-specific source. Nonetheless, it is clear that triclosan is the major source of these dioxins after 1960. The contribution of the triclosan-derived dioxins to the total dioxin pool in terms of mass was determined for each sediment core. In heavily impacted systems, the dioxin contribution from triclosan and chlorinated triclosan derivatives accounted for up to 60% of total dioxin mass in recent sediment. Thus, the discharge of triclosan and chlorinated triclosan derivatives may pose a threat to wastewater-impacted lakes. The findings of this work suggest that additional treatment of wastewater to remove triclosan, additional regulation of triclosan use, or dissemination regarding the prevalence of triclosan in consumer products may be necessary. Full results are presented in the M.S. Thesis of Cale T. Anger submitted with this report.

## IV. OUTLINE OF PROJECT RESULTS*:*

**RESULT 1:** *Core collection and dating*

**Description:** Duplicate sediment cores will be taken from five lakes impacted by wastewater effluents (and thus triclosan) and one control site. The impacted sites to be sampled are Lake Pepin, Lake St. Croix, Lake Superior near the entrance to the Duluth Harbor, Lake Winona near Alexandria, and Shagawa Lake near Ely. The control site will be either Lake Itasca or a lake in the Boundary Waters Canoe Area that is not impacted by wastewater or triclosan. The control site will allow determination of background dioxin levels. Fresh sediment cores are needed to minimize any losses of the dioxins during storage/handling. The cores will be collected by a piston or box-type corer from a small boat. Cores will be dated as a function of depth using lead-210 and cesium-137 methods, and the organic matter content will be determined as a function of depth. Sediment deposition rates as a function of time will be calculated based on the dating results. By knowing the year in which sediments were deposited and the rates of sediment deposition, it will be possible to calculate the mass of triclosan and dioxins delivered to the sediment over time after conducting the analyses outlined in Result 2.

**Summary Budget Information for Result 1:** **ENRTF Budget: $ 94,000**
**Amount Spent: $ 90,483**
**Balance: $ 3,517**

| Deliverable/Outcome | Completion Date | Budget |
|---|---|---|
| **1.** Core collection | February 2011 | $ 18,000 |
| **2.** Core dating and determination of sediment deposition rates | August 2011 | $ 76,000 |

**Result Completion Date:** September 2011

**Result Status as of** (January 2011): Cores have been collected from Lake Pepin, Lake St. Croix, Lake Superior/Duluth Harbor, and Lake Winona. The measurements of organic matter and water content on these cores are complete. As expected, water contents and organic matter contents are greater at shallow depths. Dating for the Lake Pepin core is complete and dating is in progress on the other three cores.

**Result Status as of** (July 2011)**:** Cores have been collect from Lake Shagwa near Ely and Little Wilson Lake (control site) in the Superior National forest. The measurements of organic matter and water content on all cores are complete. For all cores (except Little Wilson Lake) there is a clear change in organic content that gives a marker as to when European settlement occurred. Dating of the cores from Lake Pepin, Lake St. Croix, Lake Superior/Duluth Harbor, and Lake Winona is complete. Dating for the last two cores is underway. Determination of deposition rates will be calculated for all cores when dating is complete.

**Result Status as of** (January 2012)**:** Preliminary dating for Lake Shagwa and Little Wilson is complete, and the data are being refined.

**Final Report Summary:** All cores have been dated and sediment fluxes determined as a function of time using appropriate focusing factors. The water and organic contents of each section were also determined. These results were used in Result 2 to evaluate the temporal trends in triclosan and dioxin concentrations and fluxes. These tasks came in slightly under budget, but the residual funds were used in completing Result 2.

**RESULT 2:** *Measurement of triclosan and dioxins in sediment cores*

**Description:** The collected sediment cores will be sliced into sections (each with a mass of 5-30 grams) as a function of depth. Each sample will be split with one being extracted for triclosan (and, if possible, triclosan derivatives) and the other for dioxins. Samples to be analyzed for triclosan will be extracted using the requested accelerated solvent extraction system. The extracts will be cleaned using solid-phase extraction and silica gel and then triclosan concentrations will be determined using liquid chromatography-tandem mass spectrometry. Samples for dioxin analysis will be extracted using the Soxhlet method, cleaned up, and analyzed using high resolution gas chromatography-high resolution mass spectrometry. Appropriate surrogate and internal standards will be used to ensure data accuracy and reproducibility. The triclosan and dioxin concentrations and loads (mass and mass per area) will be determined as a function of time. We will also analyze for all di- to octa-chlorinated dioxins in the sediment cores. Analyzing for all dioxins (not just those that are triclosan derived) will provide additional valuable information about the relative sources (e.g., atmospheric deposition versus wastewater) of dioxins to Minnesota waters.

**Summary Budget Information for Result 2:** **ENRTF Budget: $ 170,000**
**Amount Spent: $ 173,517**
**Balance: $ -3,517**

| **Deliverable/Outcome** | **Completion Date** | **Budget** |
|---|---|---|
| 1. Determine triclosan concentrations | January 2012 | $ 75,000 |
| 2. Measure triclosan derived and total dioxins in the sediment core | March 2012 | $ 75,000 |
| 3. Calculate current and historical contribution of triclosan to dioxin loads using calculated dates of samples and deposition rates | June 2012 | $ 10,000 |
| 4. Data synthesis, reporting, and recommendations | June 2012 | $ 10,000 |

**Result Completion Date:** July 2012

**Result Status as of** (January 2011): The triclosan extraction method using the purchased accelerated solvent extractor is being optimized. Chromatography methods for triclosan have been verified. Dioxin standards have been purchased and when they arrive, standards will be made and the analyses will begin.

**Result Status as of** (July 2011)**:** Based on the dating results of Lake Pepin, Lake St. Croix, Lake Superior/Duluth Harbor, and Lake Winona cores, the core samples were combined and/or subsampled such that sufficient mass was available for both triclosan and dioxin analysis for a given time interval. Samples for dioxin analysis were delivered to Pace Analytical for the Lake Pepin and Lake St. Croix cores in May and processing of the samples is ongoing. Additional samples will be delivered shortly. The triclosan extraction method has been developed. The percent recovery is currently being determined, and the processing of the Lake Pepin and Lake St. Croix cores is underway.

**Result Status as of** (January 2012)**:** Dioxin profiles in Lake Pepin and Lake St. Croix are complete. Triclosan analyses in these cores is also complete. The trends show increasing concentrations of triclosan and the dioxins derived from triclosan with time. Samples for Lake Winona and Duluth Harbor are currently being extracted for triclosan analysis. The samples for dioxin analysis in Lake Winona and Duluth Harbor have been delivered to Pace Analytical, and are currently being processed. Samples for Lake Superior, Lake Shagwa, and Little Lake Wilson have been prepared for processing and extractions/analyses will begin shortly.

**Final Report Summary:** All triclosan and dioxin analyses are complete. The extraction method developed allowed measurement in lake sediments of triclosan and the chlorinated triclosan derivatives that are produced when triclosan is exposed to chlorine during disinfection. In Little Wilson Lake which receives no wastewater input, no triclosan or chlorinated triclosan derivatives were detected. In all other lakes (Lake Pepin, Lake St. Croix, Lake Winona, Lake Shagawa, Duluth Harbor, and Lake Superior) triclosan was detected starting in ~1960 with increasing concentrations to present day. This parallels trends in triclosan usage. The exception was East Lake Gemini where concentrations started off high and decrease with time. This is attributed to upgrades in the wastewater treatment plant since the lake was formed in 1967. The highest concentrations observed are 10-20 ng/g sediment, except for Lake Winona, which had concentrations ~10-fold higher. Lake Superior concentrations are on the order of 1 ng/g due to dilution in the large lake. The trends of chlorinated triclosan derivatives parallel those of triclosan, with peak concentrations ranging from 300-2000 pg/g sediment. Interestingly, effects of disinfection practices are seen in the chlorinated triclosan derivative data. At sites where wastewater chlorination was discontinued (Lake St. Croix) or reduced (Duluth Harbor), chlorinated triclosan derivative levels decrease after the change was made. In the six sites clearly impacted by wastewater (Lake Pepin, Lake St. Croix, Lake Winona, East Lake Gemini, Lake Shagwa, and Duluth Harbor), the levels of the four dioxin congeners derived from triclosan and chlorinated triclosan derivatives in the sediment cores parallel the trends of triclosan since 1960. This suggests that these dioxins are derived from the photolysis of triclosan and its derivatives, and that discharge of triclosan is leading to accumulation of these four dioxins in Minnesota lakes. In terms of mass, these four triclosan-derived dioxins account for 6% (Lake St. Croix) to 60% (Lake Winona, East Lake Gemini) of the total dioxin mass in the most recent sediments. In contrast to the triclosan-derived dioxins, the dioxins derived produced from incineration sources have been decreasing since the 1970s. An exception is Lake Winona, where all dioxin levels are still increasing, suggesting a local source of higher chlorinated dioxins that merits further investigation. The four triclosan-derived dioxins are observed at low levels prior to the introduction of triclosan to the market in Lake Shagwa, Duluth Harbor, Lake Superior, and Little Wilson Lake. This suggests that there is an atmospheric source of these specific dioxins to northern Minnesota lakes separate from the inputs related to triclosan. The level of these dioxins increases, however, upon the introduction of triclosan, and triclosan is the dominant source of these four dioxins after 1960.

## V. TOTAL ENRTF PROJECT BUDGET:

**Personnel**: $150,000. Project manager Dr. William Arnold will be paid for 10% of his annual effort to the project (during summer months). He will be responsible for project coordination, assisting with core sampling and extractions, and project reporting. Two graduate students will be employed by the project. Each will devote 43.75% of their time during their academic year and 50% during one summer to the project. For graduate students, 50% time is full employment. The students will date and extract the sediment cores and conduct the analyses for triclosan.
**Contracts:** $ 37,000. Dr. Daniel Engstrom (Science Museum of Minnesota & Adjunct Professor of Geology, University of Minnesota) will have responsibility for collecting and dating the sediment cores. He will devote 4% of his time to the project ($12,000). The remaining $25,000 is analytical costs associated with sediment dating.
**Equipment/Tools/Supplies**: $ 35,000 Accelerated Solvent Extractor
**Acquisition (Fee Title or Permanent Easements):** $ 0
**Travel:** $ 3,000 for in-state travel. Mileage, hotel, meal charges for trips to collect sediment samples
**Additional Budget Items:** $ 39,000. The funds will be used to purchase necessary chemicals, solvents, standards, extraction cartridges, and other laboratory supplies necessary to extract and quantify triclosan and the dioxins in the core samples ($14,000). The remaining $25,000 is to pay for extraction of dioxins and time on the instruments used for the analysis of triclosan and dioxins and for instrument maintenance and repairs ($700 as of January 9, 2012).

**TOTAL ENRTF PROJECT BUDGET: $ 264,000**

**Explanation of Capital Expenditures Greater Than $3,500:**
A sum of $35,000 is budgeted for the purchase of a accelerated solvent extraction system. This essential piece of equipment is needed to extract triclsoan and its derivatives from sediment core samples. It allows extractions to be done in 2 hours per sample (versus 2-4 days with traditional methods). Given the number of samples to processed for triclosan, this efficiency is needed. In the future the equipment would be used for extraction of a variety of endocrine disrupting compounds and pharmaceuticals from sediments, soils, and sludges for analysis. This equipment is currently not available at the University of Minnesota.

## VI. PROJECT STRATEGY:

**A. Project Partners:** Dr. Daniel Engstrom (Science Museum of Minnesota & Adjunct Professor of Geology, University of Minnesota) will have responsibility for collecting and dating the sediment cores (contract of $37,000). Charles Sueper (Pace Analytical Laboratories) will assist with dioxin extractions and analyses.

**B. Project Impact and Long-term Strategy:** Triclosan is of questionable effectiveness as an antibacterial compound and the formation of dioxins is an undesirable outcome of its use. We will provide the data necessary for a voluntary or a regulatory solution.

**C. Other Funds Proposed to be Spent during the Project Period:** Dr. Arnold will contribute 2% unpaid effort to the project.

**D. Spending HIstory:** None.

**VII. DISSEMINATION**: Information will be disseminated and archived via reports to LCCMR, peer-reviewed publications, and presentations at conferences. Sediment samples will be stored and/or freeze-dried for potential future analyses. Extracts will also be labeled and archived (frozen) for potential future analyses. Products include the M.S. Thesis of Cale Anger, presentations at two national and one international conference (travel funded by other sources), and a manuscript submitted to the journal *Environmental Science and Technology*. Dr. Arnold has also spoken at the Mississippi River forum about triclosan in Lake Pepin.

**VIII. REPORTING REQUIREMENTS:** Periodic work program progress reports will be submitted not later than January 2011, July 2011, and January 2012. A final work program report and associated products will be submitted between June 30 and August 1, 2012 as requested by the LCCMR.

Attachment A: Budget Detail for 2010 Projects - **Summary and a Budget page for each partner (if applicable)**

**Project Title:** Evaluation of Dioxins in Minnesota Lakes

**Project Manager Name:** William Arnold

**Trust Fund Appropriation: $** 264,000

| 2010 Trust Fund Budget | Result 1 Budget: | Amount Spent (date) | Balance 12/31/2011 | Result 2 Budget: | Amount Spent (date) | Balance 12/31/2011 | TOTAL BUDGET | TOTAL BALANCE |
|---|---|---|---|---|---|---|---|---|
| | *Core collection and dating* | | | *Measurement of triclosan and dioxins in sediment cores* | | | | |
| **BUDGET ITEM** | | | | | | | | |
| **PERSONNEL: wages and benefits** | | | | | | | | |
| William Arnold (10%, summer salary per year, fringe benefit rate 32.3%) | 10,272 | 8,255 | 2,017 | 27,860 | 25,760 | 2,100 | 38,132 | 4,117 |
| Graduate Student 1 (43.75% time, tuition $14.25 per hour salaried, health insurance 17.56%, summer FICA 7.44%) | 28,982 | 28,982 | 0 | 26,952 | 26,952 | 0 | 55,934 | 0 |
| Graduate Student 2(43.75% time, tuition $14.25 per hour salaried, health insurance 17.56%, summer FICA 7.44%) | 16,246 | 16,246 | 0 | 39,688 | 50,763 | -11,075 | 55,934 | -11,075 |
| **Contracts** | | | 0 | | | 0 | | |
| **Professional/technical** Science Museum of Minnesota, Dr. Daniel Engstrom, Sediment Coring and Dating | 37,000 | 37,000 | 0 | | | 0 | 37,000 | 0 |
| **Capital equipment over $3,500** (Accelerated Solvent Extraction System) | | | 0 | 35,000 | 35,000 | 0 | 35,000 | 0 |
| **Supplies** (Laboratory supplies) | | | 0 | 14,000 | 13,206 | 794 | 14,000 | 794 |
| **Travel expenses in Minnesota** | 1,500 | | 1,500 | 1,500 | 1,025 | 475 | 3,000 | 1,975 |
| **Other** (Instrument time/analytical fees - and instrument repairs as of January 9, 2012) | | | 0 | 25,000 | 20,811 | 4,189 | 25,000 | 4,189 |
| **COLUMN TOTAL** | **$94,000** | **$90,483** | **$3,517** | **$170,000** | **$173,517** | **-$3,517** | **$264,000** | **$0** |

Environmental Science & Technology

Article

pubs.acs.org/est

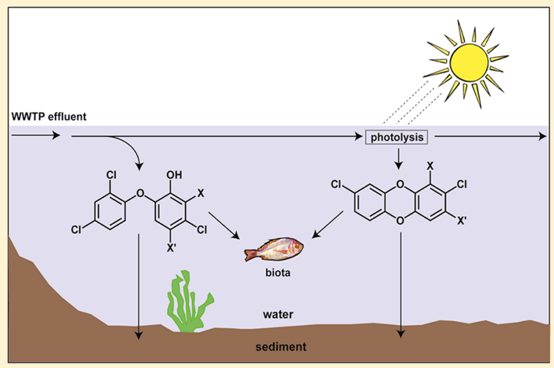
# Quantification of Triclosan, Chlorinated Triclosan Derivatives, and their Dioxin Photoproducts in Lacustrine Sediment Cores

Cale T. Anger,[†] Charles Sueper,[‡] Dylan J. Blumentritt,[§] Kristopher McNeill,[∥] Daniel R. Engstrom,[⊥] and William A. Arnold[†,*]

[†]Department of Civil Engineering, University of Minnesota, 500 Pillsbury Drive SE, Minneapolis, Minnesota 55455, United States
[‡]Pace Analytical Services Inc., 1700 Elm Street, Minneapolis, Minnesota 55414, United States
[§]Department of Earth Sciences, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, Minnesota 55455, United States
[∥]Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zurich, 8092 Zurich, Switzerland
[⊥]St. Croix Watershed Research Station, Science Museum of Minnesota, 16910 152nd Street North Marine on St. Croix, Minnesota 55047, United States

*Supporting Information*

**ABSTRACT:** When discharged into surface waters via wastewater effluents, triclosan, the antimicrobial agent in handsoaps, and chlorinated triclosan derivatives (CTDs, formed during disinfection with chlorine) react photochemically to form polychlorinated dibenzo-*p*-dioxins. To evaluate the historical exposure of waters to these compounds, the levels of triclosan, CTDs, and their derived dioxins were determined in sediment cores collected from wastewater-impacted Minnesota lakes. The accumulation rates and temporal trends of triclosan, CTDs, and dioxins in aquatic sediments were found to be a function of historical wastewater treatment operations and lake system scale. Cores collected from large-scale riverine systems with many wastewater sources recorded increasing concentrations of triclosan, CTDs, and their derived dioxins since the patent of triclosan in 1964. In small-scale lakes with a single wastewater source, the trends were directly attributed to increased triclosan use, local improvements in treatment, and changes in wastewater disinfection since the 1960s. In the lake with no wastewater input, no triclosan or CTDs were detected. Overall, concentrations of triclosan, CTDs, and their dioxins were higher in small-scale systems, reflecting a greater degree of wastewater impact. In cores collected in northern MN, the four dioxins derived from triclosan are present prior to the patent of triclosan, suggesting a secondary source. It is clear, however, that triclosan and CTDs are the dominant source of these congeners after 1965 in systems impacted by wastewater.




## ■ INTRODUCTION

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is a common antimicrobial found in a wide array of personal care products.[1−7] Up to 96% of triclosan is washed down the drain during normal use, leading to concentrations on the order of 1−10 $\mu$g/L in wastewater treatment plant (WWTP) influent.[7−14] Although WWTPs with conventional activated sludge treatment typically remove >90% of triclosan through sorption or biodegradation, triclosan persists through treatment and into surface waters.[8,15] Effluent concentrations ranging from 10 to 600 ng/L, and as high as 2.7 $\mu$g/L, have been reported.[7,9−11,13,14,16−19] Based on an estimated per capita usage of 3−5 mg/day, loading rates to U.S. surface waters are on the order of 10−20 t/year.[6,20]

During the disinfection of water and wastewater with free-chlorine, triclosan is chemically transformed into chlorinated triclosan derivatives (CTDs).[21−24] Electrophilic addition of chlorine yields 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol (4-Cl-TCS), 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol (6-Cl-TCS), and 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol (4,6-Cl-TCS). After chlorination of the wastewater, the remaining triclosan and formed CTDs are discharged into surface waters.[10]

Triclosan concentrations in waters from riverine and lacustrine systems impacted by WWTPs typically range from 1 to 200 ng/L.[3,7,12,14,15,17,25,26] In arid regions, where wastewater effluent may dominate stream flows, triclosan contamination may be more severe. During the 2001 dry season, 70% of the Sacramento-San Joaquin River flow was comprised of wastewater, leading to a maximum triclosan concentration of 734 ng/L in raw drinking water.[27] Triclosan was also detected in sediments both upstream and downstream of WWTPs in Minnesota, confirming the widespread occurrence and persistence of triclosan in surface waters.[28] Concentrations ranging from

**Received:** November 6, 2012
**Revised:** January 11, 2013
**Accepted:** January 15, 2013

0.4 to 85 ng/g were found in the top 10 cm of sediments near WWTPs, with the highest concentrations found in lacustrine systems.[28]

In surface waters, direct photolysis is the primary mechanism by which triclosan and CTDs are photochemically transformed.[29−31] Triclosan and CTDs undergo a photochemical cyclization reaction, with triclosan forming 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD)[29−33] and 4-Cl-TCS, 6-Cl-TCS, and 4,6-Cl-TCS yielding 2,3,7-trichlorodibenzo-*p*-dioxin (2,3,7-TriCDD), 1,2,8-trichlorodibenzo-*p*-dioxin (1,2,8-TriCDD), and 1,2,3,8-tetrachlorodibenzo-*p*-dioxin (1,2,3,8-TCDD), respectively.[29] Because polychlorodibenzo-*p*-dioxins (PCDDs) are a class of compounds known to be toxic and carcinogenic,[34] their production from triclosan and CTDs is of clear concern.

Triclosan, CTDs, and their photochemically produced PCDDs have the potential to persist in sediments. Buth et al.[35] investigated two sediment cores from a depositional zone along the Mississippi River. Dated sediment cores provided evidence of rising triclosan usage since the 1960s. The concentrations of 2,8-DCDD, 1,2,8- and 2,3,7-TriCDD, and 1,2,3,8-TCDD correlated with triclosan. Cantwell et al.[5] investigated four urbanized estuaries along the U.S. Atlantic coast. Spatial and temporal trends of triclosan in these cores reflected increased consumer usage and improvements in wastewater treatment processes over the last 40 years. Singer et al.[7] reported similar depositional trends when conducting a triclosan mass balance in Lake Greifensee, Switzerland, and a study by Miller et al.[36] found that triclosan levels directly parallel heavy metal concentrations in estuarine sediment near a WWTP, suggesting both arise from the wastewater discharge.

Sediment cores provide a useful proxy for evaluating the exposure of an aquatic ecosystem to triclosan, CTDs, and their PCDDs over time. The aim of this study was to investigate the depositional trends of triclosan, CTDs, and their derived PCDDs in sediment cores from an array of wastewater-impacted Minnesota lakes. Cores were collected in large- and small-scale aquatic systems with varying degrees of wastewater impact. The lakes chosen are impacted by urban or rural populations of different sizes, and the wastewater treatment plants use different disinfection techniques (chlorine or UV). Changes in historical treatment practices at relevant WWTPs were probed to evaluate influences on trends in the sediment record.

## ■ EXPERIMENTAL SECTION

Chemical sources and purities as well as details regarding preparation of solutions are provided in the Supporting Information (SI). To prevent analyte cross-contamination and carryover in the laboratory, a specific set of cleaning procedures was required for glassware, tools, and instrumentation, which are also provided in the SI.

**Sediment Core Collection.** Sediment cores were collected from eight sites in Minnesota. The collection dates, a map of the lake locations, details about the lakes and their watersheds, and global positioning system coordinates for the points of core collection are provided in the SI. Four of the sites (Lake Pepin, Lake St. Croix, Duluth Harbor, and Lake Superior) have large watersheds and multiple wastewater inputs. Lake Winona, Lake Shagawa, and East Lake Gemini are small lakes receiving direct inputs of wastewater effluent. Little Wilson Lake has no wastewater input and little anthropogenic contact.

All sediment cores, with the exception of Lake Superior, were collected using a piston corer equipped with a polycarbonate barrel and operated by Mg-alloy drive rods from the water surface. The Lake Superior core was collected on the R/V *Blue Heron* using an Ocean Instruments Multicorer. Upon collection, cores were extruded vertically and sectioned at designated intervals. Down-core smearing was removed from the outer circumference of each interval to prevent analyte drawdown in the core. Except for the Lake Pepin core, sections were transferred to glass jars, homogenized, and subsampled for radiometric dating. Jars were then covered with foil, cooled to 4 °C, and frozen within 24 h of collection.

Prior to radiometric dating or analyte extraction, loss-on-ignition analysis was performed on each sediment core section.[37,38] Briefly, core intervals were homogenized and subsampled into crucibles. Subsamples were sequentially dried for 12 h at 105 °C, 4 h at 550 °C, and 2 h at 1000 °C to determine sample water content, organic percent, and carbonate percent, respectively.

**Radiometric Dating.** Sediment cores were dated using lead-210 ($^{210}$Pb) and cesium-137 ($^{137}$Cs) methods, as described in recent literature.[39,40] Total $^{210}$Pb in the core profile (measured via quantification of $^{210}$Po) was used to determine radiometric dates and sedimentation rates through the constant rate of supply model.[39] To supplement $^{210}$Pb dating, $^{137}$Cs activity was measured in 6−10 stratigraphic intervals in some cores using gamma spectrometry.[40] The Lake Pepin core was dated by conducting whole-core magnetic susceptibility measurements using a Geotek LTD multisensory core logger. The susceptibility profile was matched to those from recently dated cores in the same depositional area of the lake.[40]

**Extraction and Analysis.** *Triclosan and CTDs.* Wet samples, corresponding to 10 g dry weight from each core interval, were freeze-dried for 3−5 days. Each dried sample was spiked with $^{13}C_{12}$-triclosan (500 ng in 1 mL of acetonitrile) as an isotope-dilution surrogate for triclosan and CTD recovery. For each core, a method blank (freeze-dried Ottawa sand) was spiked with $^{13}C_{12}$-triclosan and processed to ensure there was no analyte contamination. Spiked samples were covered with foil and allowed to equilibrate for 12 h prior to extraction.

Samples were extracted on a Dionex model 350 accelerated solvent extractor (ASE) as described in the SI. Due to a wide range of organic content in the collected sediment cores, two separate cleanup methods for the ASE extracts using solid phase extraction and/or silica gel were developed based on those in Buth et al.[35] Details are in the SI.

Sediment core extracts were analyzed on an Agilent 1100 capillary HPLC equipped with a Finnigan TSQ Quantum Discovery MAX MS-Q$^3$ tandem mass spectrometer. Details regarding chromatographic separation, selected reaction monitoring transitions, analyte quantification, and quality assurance/quality control measures are in the SI. Also described in the SI is the preconditioning procedure for the ion transfer tube that was necessary to obtain maximum sensitivity.

*Dioxins and Furans.* Between 7 and 12 g (dry weight) of each core interval was analyzed for PCDD/F congeners. East Lake Gemini was an exception, where between 1 and 2 g was processed. For all cores, samples were spiked with nineteen $^{13}C_{12}$-labeled di- through octa-CDD/F isomers as isotope-dilution surrogates and analyzed using an expanded version of U.S. EPA Method 1613B.[41] The extraction and high-resolution gas chromatography-high-resolution mass spectrometry (HRGC-HRMS) analysis are described in the SI.

## ■ RESULTS AND DISCUSSION

**Analytical Method Performance.** The method for triclosan and CTD quantification effectively separated the analytes of interest. SI Figures S4 and S5 are example chromatograms from a representative standard and Lake Pepin sediment extract, respectively. For each sediment core, trace amounts of triclosan were detected in method and instrument blanks. Reported triclosan sediment concentrations were at least 10 times greater than those observed in the blanks. Blank subtraction was not performed on these results. CTDs were not detected in procedural blanks, and all reported CTD concentrations were required to be above the lowest point in their respective calibration curves. The raw analyte signal-to-noise ratio was always >10 for any reported triclosan or CTD concentration. Using these criteria, limits of quantification (LOQs) ranging from 0.36 to 0.9 ng/g dry weight (triclosan) and from 60 to 70 pg/g dry weight (CTDs) were achieved. In all cases, the CTDs eluted later than $^{13}C_{12}$-triclosan and triclosan due to their higher hydrophobicity. Calibration curves were linear, with $R^2$ values ≥0.98 for each analyte.

Due to the wide range of sediment matrices in this study, the absolute recovery of $^{13}C_{12}$-triclosan varied significantly (SI Table S5). Higher recoveries were observed in cores with low organic content, where matrix effects/ion suppression effects were less severe. Recovery of triclosan, relative to the $^{13}C_{12}$-triclosan surrogate, was ∼100% for all matrices (SI Table S6). Relative CTD recovery, however, generally decreased with increased matrix complexity. This pattern may be attributed to increased matrix suppression at CTD retention times or a disproportional loss of CTDs relative to $^{13}C_{12}$-triclosan and triclosan during sample extraction and cleanup.

The absolute recovery of the $^{13}C_{12}$−PCDD/F surrogates ranged from 20−116% in sediment extracts, within the target range specified in Method 1613B (SI Table S7). Moreover, the relative recovery of nineteen native PCDD/F isomers in sand spikes ranged from 74 to 129%. Spike and recovery experiments were performed in duplicate on all sediment matrices, with the exception of East Lake Gemini. Relative recovery of native PCDD/F isomers ranged from 72 to 126% with relative percent differences ranging from 0 to 17.5% for individual analytes between duplicate matrix spikes (SI Table S8). One recovery outlier was observed in the Little Lake Wilson core, where 2,8-DCDD exhibited a maximum relative recovery of 238%. Note that while lower extraction efficiencies lead to higher uncertainty, the overall trends for a specific analyte/core are not compromised.

For all cores, trace amounts of specific di- through octa-CDD/F isomers were detected in method blanks, most of which were well below calibration ranges. All reported PCDD/F concentrations were >10 times the levels in these blanks.

**Triclosan, CTDs, and Their PCDDs in MN Lakes.** Figure 1 shows the temporal trend of the accumulation rates (ng or pg $cm^{-2}$ $y^{-1}$ corrected for sediment focusing; see SI) for triclosan, CTDs, and their photochemically derived PCDDs for the eight lakes. The same data are presented on a concentration basis (ng or pg per g dry sediment) in SI Figure S6. Accumulation rates in Figure 1 are corrected for sediment focusing to determine analyte loading on a whole-lake basis.

In all but one core, the first appearance of triclosan matches well to its introduction into the environment in the mid-1960s, confirming the $^{210}Pb$ dating, at least for the last half-century. The one case in which triclosan appears earlier than expected, Lake Shagawa, is discussed in detail below. Lead-210 dating is most robust for this period of interest, owing to its limited decay over 2−3 half-lives. Dating precision based on counting uncertainty is less than ±4 years (±1 S.D.) for sediments deposited c. 1960. However, several cores (Shagawa, Winona, Duluth Harbor) that exhibit low $^{210}Pb$ activities in their upper sections—a consequence of high mass accumulation rates—were also analyzed for $^{137}Cs$ to independently verify the dating. In all three cases, peak radiocesium (c. 1963) corresponds well with the $^{210}Pb$ chronologies (SI Tables S9−S20).

*Lake Pepin and Lake St. Croix.* Sediment cores collected in large-scale, wastewater-impacted riverine systems provide insight into the accumulation of triclosan and its byproducts in aquatic environments. In both lakes, triclosan accumulation rates increase with time, reflecting consumer usage since the mid-1960s (Figure 1a,b). A similar trend in the 2,8-DCDD profile, the known photoproduct of triclosan, is observed. Furthermore, trends for 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD, the photoproducts of CTDs, generally parallel triclosan trends in each core. The Metropolitan WWTP (250 million gallons per day, MGD) is a major wastewater source to the Mississippi River 80 km upstream from Lake Pepin. Since its inception in 1938, the plant has disinfected its effluent with various forms of free chlorine. The effect of chlorine disinfection, coupled with increased triclosan use over the last 40 years, is directly realized in the CTD and higher chlorinated PCDD profiles.

The visible inflection in the CTD profile in the St. Croix sediment core around 1990 may be due to a change in disinfection technology. The St. Croix Valley WWTP (4.5 MGD) is 10 km upstream from the coring site. The facility treated effluent with $Cl_2$ until 1993 and both triclosan and CTD accumulation rates increase to this point. UV disinfection technology was then installed, and there is a marked drop in the CTD levels, potentially because CTDs were no longer produced in the wastewater disinfection process. The inflection, however, is not present in the 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD profile, but may be difficult to discern given the low levels present. The continued presence of CTDs and their PCDDs, may be due to other wastewater discharges, including that from the City of Hudson, WI (2.5 km upstream, $Cl_2$ disinfection; 2.2 MGD).

*East Lake Gemini and Lake Winona.* In contrast to large-scale riverine systems that integrate many wastewater sources, sediment cores collected from East Lake Gemini and Lake Winona highlight the impact of triclosan, CTDs, and their PCDDs on small-scale lakes with a single wastewater source.

From 2000 to 2008, a hydrologic balance on Lake Winona indicated that 63% of total inflow was derived from the Alexandria Lakes Area Sanitation District (ALASD) WWTP (3.75 MGD).[42] Although there is a slight discrepancy between radiometric dating and the onset of triclosan, which shows triclosan and its derivatives apparently appearing ∼5 years prior to its introduction, analyte trends provide important insight into the exposure of Lake Winona to these compounds. Triclosan concentrations reach as high as 175 ng/g in sections of the core, followed by a steady decrease to 50 ng/g in recent sediment (see SI Figure S6c). When analyzing the accumulation rate, however, triclosan loading is relatively constant since 1970 (Figure 1c). The ALASD WWTP has consistently disinfected its wastewater with $Cl_2$, leading to total CTD concentrations of over 2000 pg/g in the sediment core.

While peak accumulation rates (but not the trends) in East Lake Gemini (Figure 1d) are similar to those in Lake Pepin or

Lake Winona, concentrations (SI Figure S6d), are higher in this system, reflecting the direct discharge of wastewater from the St. John's University WWTP (0.16 MGD) into a small impoundment (0.1 km$^2$). Moreover, accumulation rates of triclosan, CTDs, and their derived PCDDs consistently decrease from 1966 to 2008. Prior to 1978, concentrations of triclosan, CTDs, and their PCDDs are all high, namely due to poor removal of triclosan and disinfection with $Cl_2$ at the treatment plant.

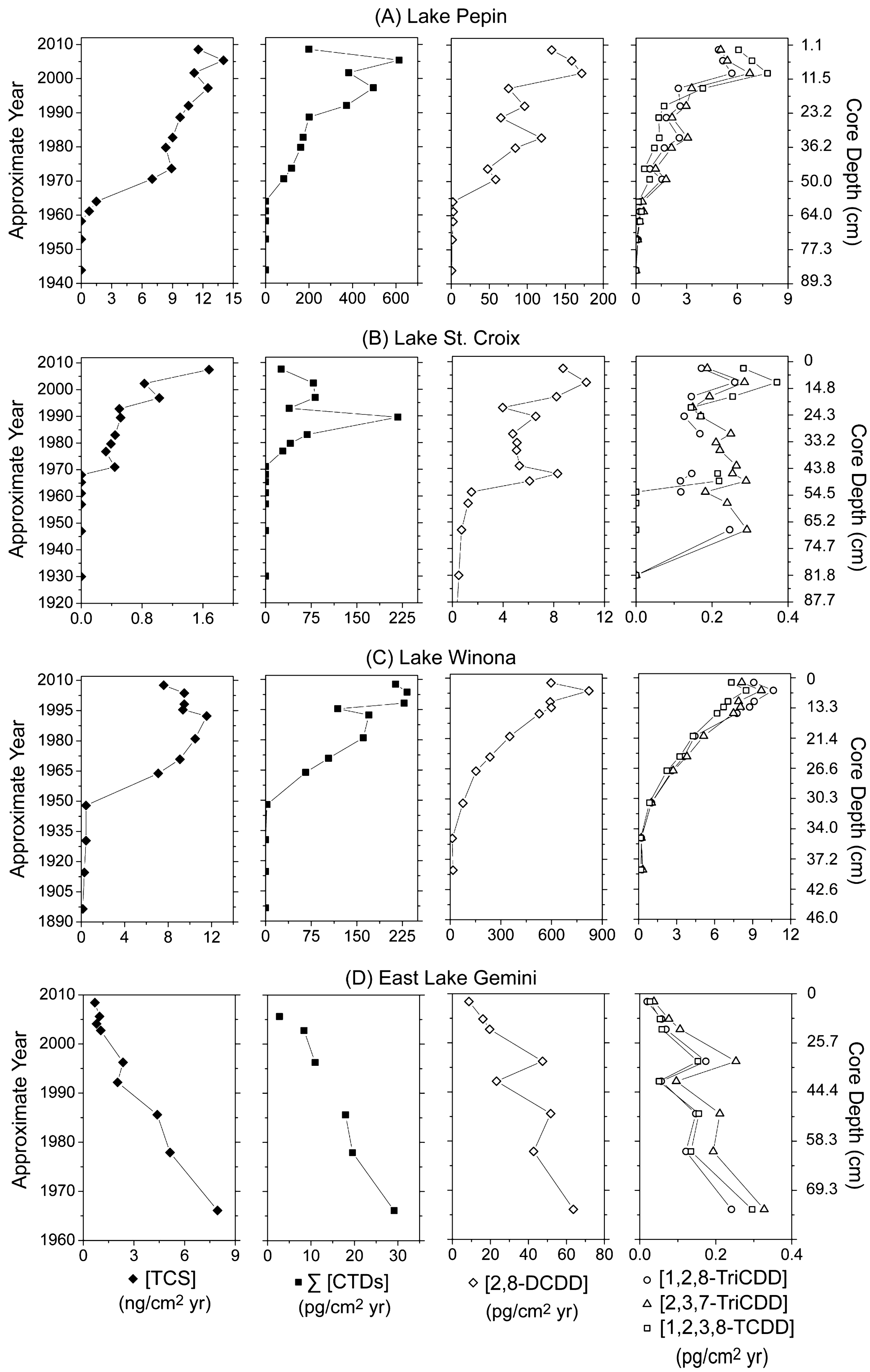



**Figure 1.** continued


dx.doi.org/10.1021/es3045289 | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

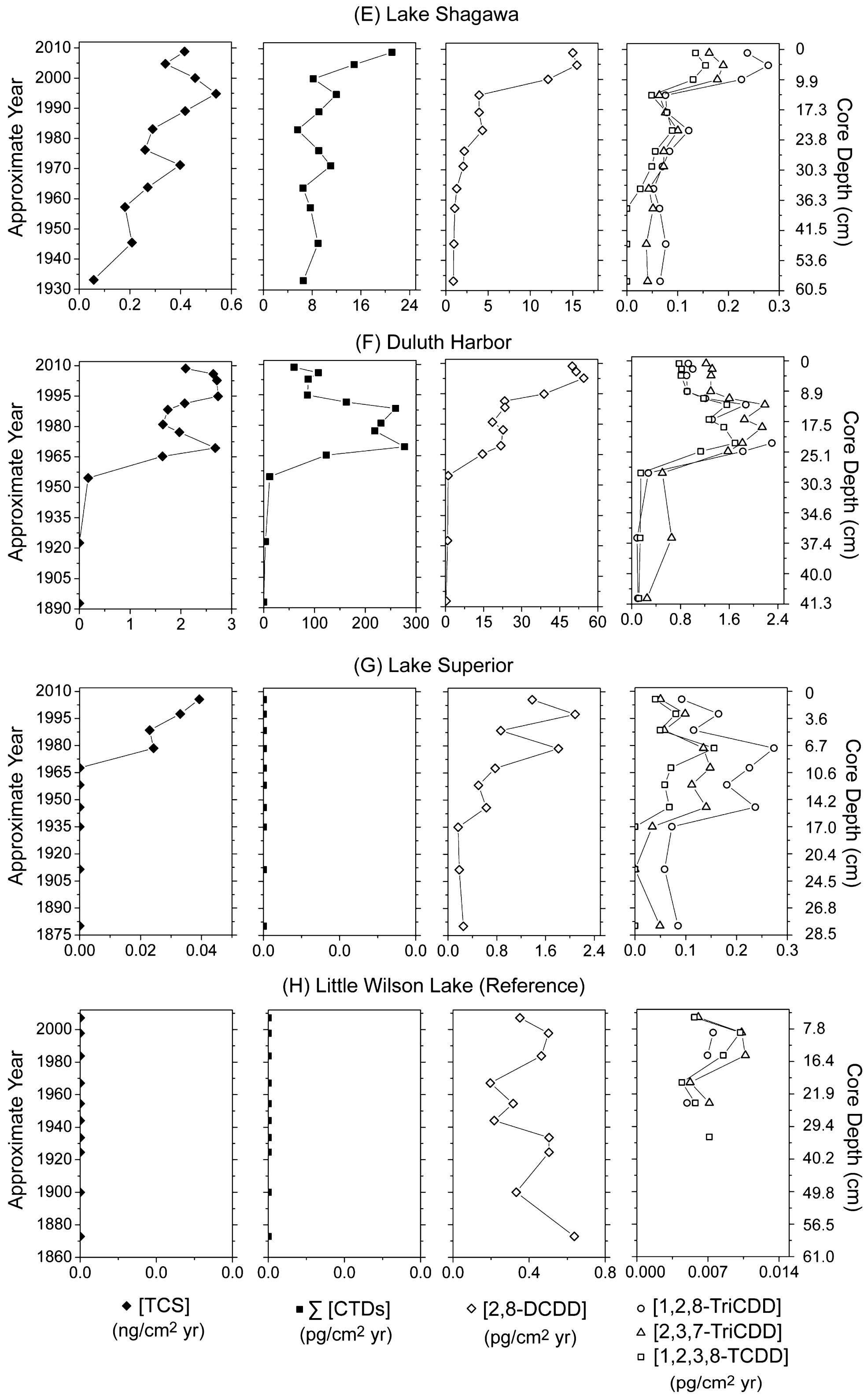



**Figure 1.** Focus-corrected accumulation rates of triclosan, the sum of chlorinated triclosan derivatives (∑CTDs), and triclosan/CTD-derived dioxins in the sediments of Minnesota lakes. Values shown as zero for accumulation rate had concentrations below the limit of quantification.

The transition to other forms of disinfection (e.g., ozonation in 1978 and UV in 1995), stabilization of wastewater flow, and improved activated sludge aeration likely contributed to a reduction in analyte sediment concentrations in this aquatic system. Details of these upgrades and additional discussion are in the SI. In recent East Lake Gemini sediment, CTDs are present, even though the effluent is treated with UV (and not chlorinated). This is consistent with the detection of CTDs in the wastewater effluent by Buth et al.,[10] and we previously hypothesized that CTD formation arises from reaction of triclosan with bleach-containing cleaning products, because the drinking water is not chlorinated.[10]


dx.doi.org/10.1021/es3045289 | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

*Lake Shagawa.* The triclosan and CTD sediment profiles in Lake Shagawa (which receives effluent from the Ely WWTP (1.5 MGD) that has disinfected with $Cl_2$ since 1954) both have slight positive trends over the majority of the core. Moreover, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD trends are similar, with increasing accumulation rates in more recent sediments. There is a discrepancy, however, between the dating and the first detection of triclosan, which might suggest that 1930 in the current dating profile corresponds to ∼1960, based on the analyte trends. The $^{137}Cs$ results, however, confirm the $^{210}Pb$ dating, making a dating error of this magnitude unlikely. The early appearance of TCS and CTDs in this core are thus enigmatic and suggest sedimentological problems (e.g., a sediment slump) or analyte drawdown during extrusion. Such problems may also be why analyte trends are not as dramatic as they are in other lake systems.

*Duluth Harbor and Lake Superior.* The Duluth Harbor core was collected approximately 2 km from the Western Lake Superior Sanitation District (WLSSD; 40 MGD) wastewater outfall in St. Louis Bay. In the mid-1970s, the effluent was disinfected year-round with $Cl_2$. In 1994, the treatment plant was granted a variance to disinfect wastewater effluent only when fecal coliform levels exceeded 100 MPN/100 mL.

Triclosan, CTD, and PCDD trends clearly demonstrate the impact of WLSSD wastewater effluent on St. Louis Bay (Figure 1f). Triclosan and 2,8-DCDD accumulation rates have increased since the mid-1960s. The CTDs and their PCDDs, however, tend to covary with changes in wastewater disinfection at WLSSD. Specifically, total CTD accumulation rates drop from approximately 250 $pg/cm^{-2}\ y^{-1}$ in 1988 to 40 $pg/cm^{-2}\ y^{-1}$ in 2002. Concentrations also drop in this period (see SI). A corresponding decrease occurs in the CTD derived tri- and tetra-CDDs around the same time period.

When examining the temporal trends of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in Duluth Harbor, it is apparent that these PCDD congeners are present at low concentrations in the sediment core, prior to the patenting of triclosan in the mid-1960s. 2,8-DCDD, for example, is present at approximately 10 pg/g in core sections dating back to the late-1800s. (We cannot rule out, however, that this is not another DCDD dioxin congener coeluting with 2,8-DCDD). Furthermore, concentrations of the tri- and tetra-CDDs average around 4 pg/g during the same time period. The same PCDD congeners, however, are at much lower concentrations at the base of the Lake Pepin and Lake St. Croix cores. 2,8-DCDD is present at <1 pg/g prior to 1930 in these cores. Moreover, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD are not detectable in the St. Croix core and are at very low levels (<0.06 pg/g) in the Lake Pepin core before 1947. Although evidence suggests that triclosan and CTDs are the primary source of these PCDDs, their presence at the base of the Duluth Harbor core may suggest either a secondary, region-specific source or that the higher sedimentation rates in Lake Pepin and Lake St. Croix led to dilution of this background signal. Nevertheless, it is clear that the introduction of triclosan led to an increase in the levels of these specific PCDDs.

In the Lake Superior core, triclosan is first detected around 1975, with accumulation rates/concentrations increasing with time (Figure 1g and SI Figure S6g). CTDs were not detected in the core, but may be present below the LOQs. The source of triclosan to this site on the open lake may be from distal wastewater sources, such as WLSSD or the City of Superior. Another possible source is the WWTP in Two Harbors, MN, where an average triclosan concentration of 572 ng/L in wastewater effluent was recently documented.[43]

Similar to Duluth Harbor, background levels of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD are present at the base of the Lake Superior core. Concentrations of 2,8-DCDD increase between 1975 and 2005, likely reflecting a contribution of this PCDD congener from the phototransformation of triclosan. The tri- and tetra-CDD congeners, however, do not follow a particular trend relative to triclosan. A fraction of these PCDDs may be derived from CTDs after 1975, but this cannot be confirmed with the data in this study.

It is important to note that 2,8-DCDD is present at ∼10 pg/g in the Lake Superior core, prior to the detection of triclosan in the system. Furthermore, the CTD derived tri- and tetra-CDD congeners range from 1 to 6 pg/g throughout the core profile. These levels (and accumulation rates) are similar to those observed in Duluth Harbor sediment before 1960, which may provide additional support for a secondary, region-specific source of these PCDDs.

*Little Wilson Lake.* For this lake, triclosan and CTDs were not quantifiable in any core segments (Figure 1h). 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD, however, are present at low levels throughout the core. 2,8-DCDD, for example, is present from 1872 to 2007 at an average concentration of 25 pg/g. The target tri- and tetra-CDD congeners are only detectable from 1933 to 2007 and at much lower concentrations (∼0.5 pg/g). The accumulation rates, however, are lower than those at any site except Lake Superior. Due to the remote nature of Little Lake Wilson, it is likely that these PCDD congeners, among others, entered the lake via atmospheric deposition. Several studies have investigated the deposition of PCDDs in the Great Lakes region.[44−46] Although the studies above did not quantify di- or tri-CDD congeners, it is possible that these PCDDs were present. Relevant potential sources include, the burning of coal and wood[47−51] and forest fires.[50,52,53] Gullet and Touati[52] found that the type of biomass affects PCDD congener patterns emitted during forest fires. Due to the distinct differences in forest biomes in MN (e.g., coniferous in the northeast, deciduous in the central and southeast), it is feasible that PCDD emissions/abundances from these environments are unique. This may explain why triclosan and CTD derived PCDDs are observed at low levels during the late 1800s in the Duluth Harbor, Lake Superior, and Little Wilson Lake cores, but are virtually nondetectable in the Lake Pepin and Lake St. Croix cores during the same time period. While it is possible that other sources contribute to the 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD deposition at the sites studied herein, it is clear that triclosan and CTDs are typically the dominant source of these congeners after 1965 in systems impacted by wastewater.

**PCDD Trends.** Evaluating the congener-specific trends of PCDDs in a sediment core can help fingerprint the dominant dioxin sources to an aquatic environment over time. SI Figure S7 illustrates the accumulation rate (corrected for sediment focusing) of PCDDs organized by chlorination level. In general, the levels of di-, tri-, and tetra-chlorinated dioxins have been increasing since 1965, while the higher chlorinated dioxins derived from incineration have been decreasing. The increase in di- and tri-CDD flux since 1965 in wastewater-impacted systems is indicative of 2,8-DCDD, 1,2,8-TriCDD, and 2,3,7-TriCDD loading from triclosan and CTDs. Similarly, the increase in TCDD flux from 1970 to 2008 is largely due to 1,2,3,8-TCDD, the primary photoproduct of 4,6-Cl-TCS. The higher chlorinated

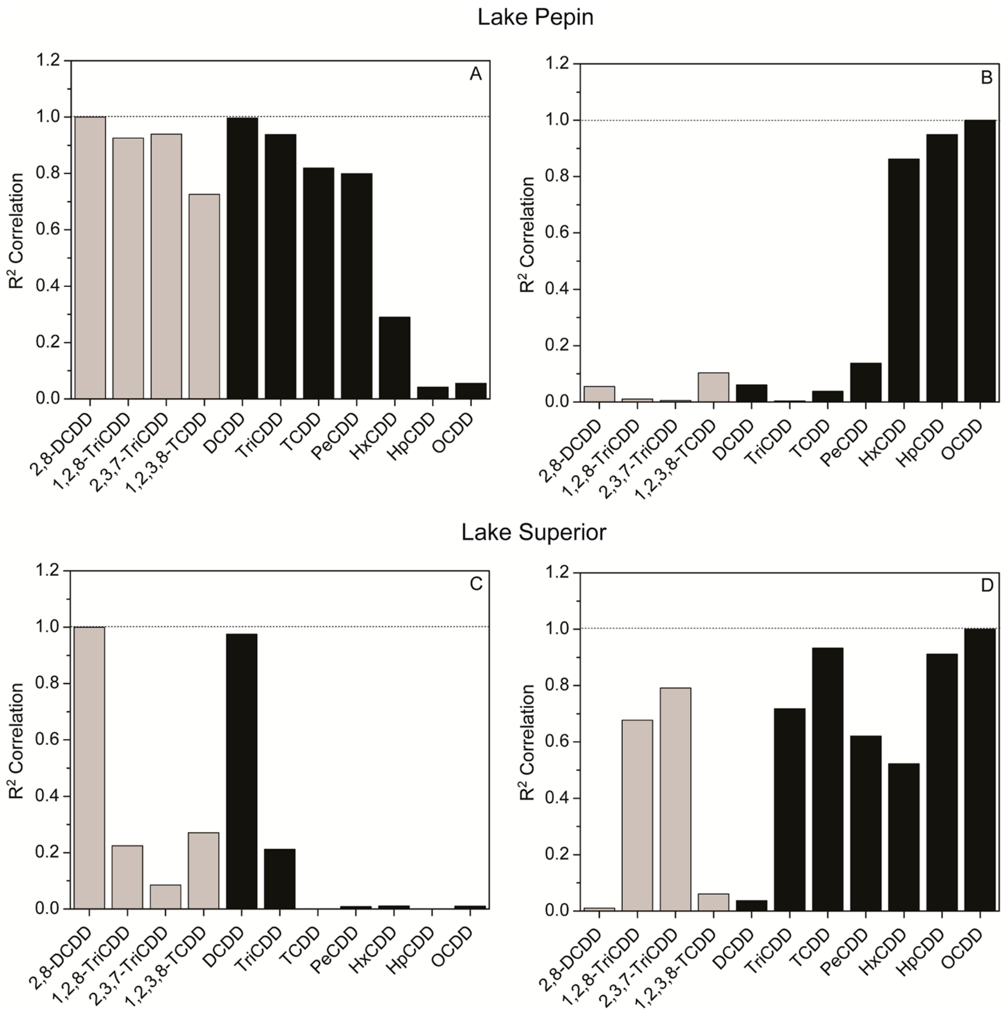



**Figure 2.** Correlation of 2,8-DCDD (A for Lake Pepin, C for Lake Superior) or OCDD (B for Lake Pepin, D for Lake Superior) accumulation profiles against triclosan- and CTD-derived PCDD profiles and PCDD profiles of specific chlorination levels. Similar plots for the other lakes are in the SI.

PCDD isomers, however, follow a different trend. The OCDD accumulation rate in Lake Pepin, for example, increases in the 1940s and 1950s, peaks around 1970, and subsequently decreases after 1980. Similar trends are seen in Lake St. Croix, Duluth Harbor, and Lake Superior.

East Lake Gemini is obviously an exception, where PCDD congeners at all chlorination levels decrease over time (likely due to concurrent improvements in incineration control and wastewater treatment plant upgrades). While the triclosan-derived dioxin levels are increasing in Lake Winona, these increases are mirrored by increasing accumulation rates of the higher chlorinated PCDDs as well. This suggests that there may be recent and local sources of PCDDs, perhaps backyard trash burning at cabins in this vacation area, but this is only one of many potential sources. While accumulation rates for all PCDDs are also increasing in Little Wilson Lake, these values are generally much smaller than for any of the directly impacted lakes.

To illustrate the differences between PCDD sources in the sediment cores, specific congener and isomer profiles were correlated against 2,8-DCDD, the known photoproduct of triclosan, and OCDD, the most abundant PCDD derived from incineration sources. Figure 2 depicts the results of these correlations for Lake Pepin and Lake Superior. All triclosan-derived species were detected in Lake Pepin, and this lake represents a system that integrates many wastewater sources. Because CTDs were not detected in Lake Superior, it presents the opportunity to evaluate the role of triclosan in the production of 2,8-DCDD in a system that is less impacted by wastewater inputs. Similar plots and discussion of the correlations for the other lakes are in the SI.

For Lake Pepin, CTD-derived PCDDs positively correlate with 2,8-DCDD, with $R^2$ values of 0.93, 0.94, and 0.73 for 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD, respectively. Overall, 2,8-DCDD also correlates well with the DCDD, TriCDD, and TCDD congener groups. Higher chlorinated isomers, however, do not correlate well with 2,8-DCDD, suggesting a different source. OCDD correlates well with other higher chlorinated PCDDs, but poorly with lower chlorinated isomers and the congeners derived from triclosan and CTDs. This suggests that triclosan and CTDs are a distinct and emerging PCDD source in Lake Pepin.

As a contrast to Lake Pepin, PCDD trends were examined in Lake Superior, a large lake with a less pronounced wastewater impact. Interestingly, 2,8-DCDD does not correlate well with 1,2,8-TriCDD or 2,3,7-TriCDD in the core. OCDD, however, does correlate relatively well with these congeners, which may support the theory of a secondary source in the region. 2,8-DCDD also does not correlate with OCDD. This is likely due to the contribution of this congener from triclosan in more recent


dx.doi.org/10.1021/es3045289 | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

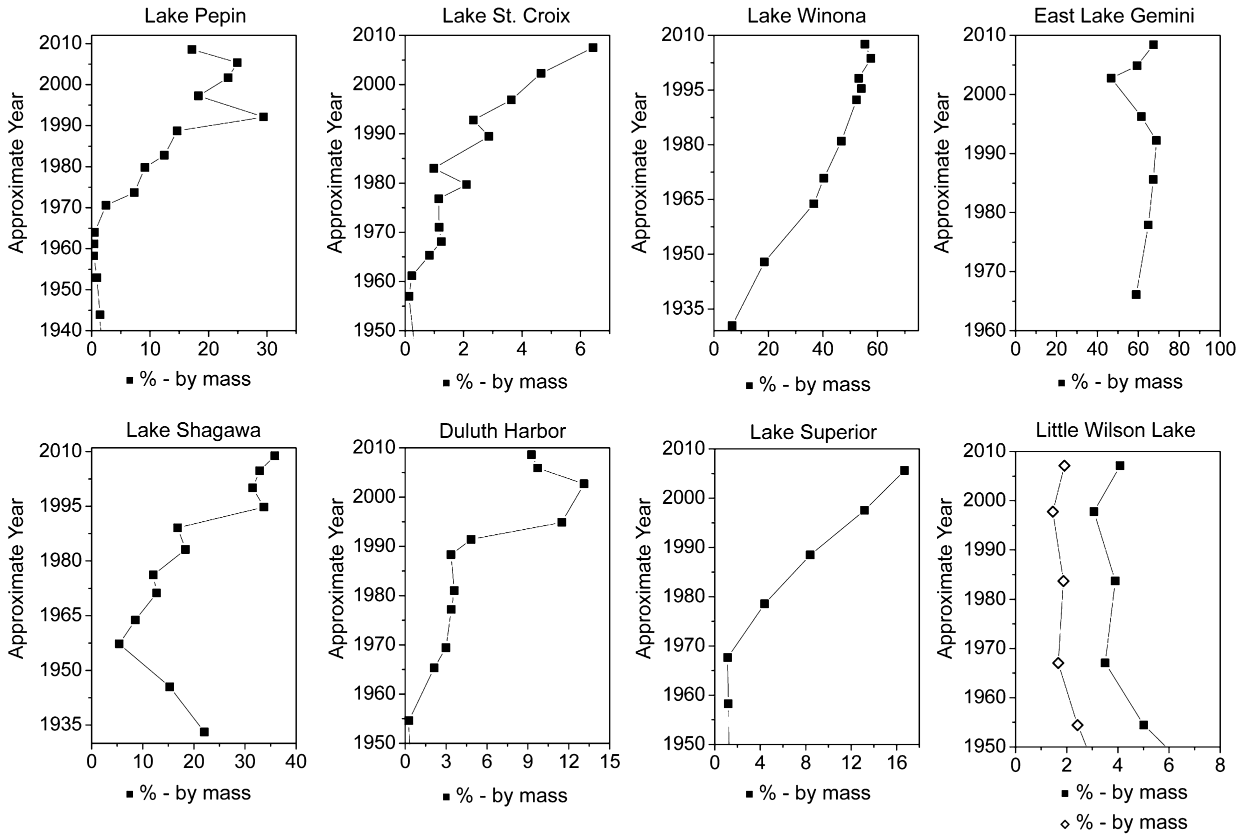



**Figure 3.** Triclosan- and CTD-derived PCDD loadings by mass as a percentage of total PCDD loading in eight Minnesota Lakes as a function of time. The open symbols for Little Wilson Lake are the result if the abnormally high recovery of 2,8-DCDD in the spike and recovery sample is taken into account.

sections of the core. The PCDD trends in Figure S7 and correlations in Figure 2 for Lake Superior clearly illustrate that there may be a series of PCDD sources to Lake Superior, of which triclosan is only a one component. Low levels of di- through octa-CCD at the base of the core may suggest that natural sources, such as forest fires, have contributed to a background level of PCDDs in this environment. Moreover, because low levels of higher chlorinated PCDD congeners are present at the base of the core, one cannot discount the potential for anaerobic reductive dechlorination as potential source of lower chlorinated PCDDs in old sediments.

**Environmental Implications.** The depositional trends of triclosan and CTDs in lake sediments provide important insight into the historical exposure of wastewater-impacted aquatic ecosystems to these compounds. This exposure is dynamically linked to the size of the receiving water body and degree of wastewater impact. For example, in small-scale wastewater-impacted lakes, such as East Lake Gemini and Lake Winona, high concentrations of triclosan and CTDs in the sediment record likely reflect the long-term exposure of aquatic organisms to elevated levels of these contaminants. Consequently, this exposure to triclosan and CTDs may be adversely impacting algal and macrophyte community structure and enhancing bioaccumulation in higher trophic levels.[54−61] Moreover, because wastewater typically contains a diverse array of PPCPs, triclosan and CTDs are only part of a larger complex mixture of bioactive and persistent compounds, leading to unknown consequences for the receiving aquatic ecosystem.

Due to the harmful effects of PCDDs in the environment, the loading of triclosan and CTD derived PCDDs to aquatic ecosystems is of clear concern. The contributions of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TriCDD to the total PCDD pool, in terms of mass, were determined for the lakes in this study (Figure 3). In the Lake Pepin core, the contribution of these PCDD congeners has been increasing since the patent of triclosan in 1964, reaching up to 30% of total PCDD mass in recent sediment, consistent with the results of Buth et al.[35] This trend is reflective of the photochemical transformation of triclosan and CTDs in the Mississippi River. A similar trend is observed in the Lake St. Croix sediment core. Due to a less pronounced wastewater impact to this system, however, these PCDD congeners only constitute up to 6.5% of total PCDD mass in recent years.

The contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD to the East Lake Gemini and Lake Winona PCDD pools is reflective of the heavy wastewater impact in each system. In East Lake Gemini, these PCDD congeners consistently account for greater than 46% of total PCDD loading to the system. Although the formation of these PCDDs in East Lake Gemini has decreased since the 1960s, atmospheric loading of higher chlorinated PCDDs to the lake has been reduced over a similar timeline. Thus, the overall contribution of triclosan and CTD derived PCDDs to this system remains substantial. In Lake Winona, the di-, tri-, and tetra-CDDs derived from triclosan and CTDs contribute up to 57% of PCDD mass loading. Triclosan and CTD derived PCDDs contribute at least 5% and up to 36% of total PCDD mass in Lake Shagawa sediment.

Based on the conclusion that there is likely a secondary source that has contributed to the loading of lower chlorinated dioxins


dx.doi.org/10.1021/es3045289 | *Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

near Duluth, MN, it is possible that a fraction of each profile in Duluth Harbor, Lake Superior, and Little Wilson Lake should be attributed to this secondary source. In the Duluth Harbor core, triclosan and CTDs have clearly been the dominant source of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD since the 1960s. Nevertheless, the contribution of these congeners to total PCDD mass in harbor sediment is relatively low. This is due to heavy contamination of the sediments with higher chlorinated congeners. There is likely a diverse array of PCDD sources to the Lake Superior coring site, some of which may have contributed to the di-, tri-, and tetra-CDD loading to the sediment. After 1975, however, the PCDD contribution by mass from 2,8-DCDD increased by a factor of 5. This is likely attributed to the photochemical transformation of triclosan in the lake and suggests that triclosan is a dominant source of 2,8-DCDD to Lake Superior today.

The presence of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in Little Wilson Lake suggest that traces of these PCDDs can be derived from atmospheric sources. The mass contributions of these PCDD congeners are depicted in Figure 3 from 1950 to 2010, a time period relevant to triclosan and CTDs in the environment. During this time interval, the di-, tri-, and tetra-CDDs consistently account for 4% of total PCDD mass. Accounting for the high relative recovery of 2,8-DCDD in Little Wilson Lake sediment (up to 238%, see SI), however, gives mass contributions of ~1.5%.

The convention is to report dioxin levels in terms of toxicity equivalents (TEQs). There is limited information regarding the toxicity equivalency factors for di- and tri-CDDs. A recent study using a chemically activated luciferase gene expression cell bioassay (CALUX), however, found that 2,8-DCDD and 2,3,7-TriCDD have relative potency factors of 0.0001 and 0.0025, respectively, compared to 2,3,7,8-TCDD.[62] The latter value is the same as that for OCDD. This suggests triclosan derived dioxins may contribute a fraction of the total dioxin toxicity in the lakes studied, but more study of these specific congeners is necessary.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


### Corresponding Author

*Phone: 612-625-8582; fax: 612-626-7750; e-mail: arnol032@umn.edu.


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Funding for this project was provided by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-Citizen Commission on Minnesota Resources and the National Science Foundation (CBET 0967163). C.T.A. was also supported by an AMEC Summer Fellowship. Thanks to Dr. Peter Villalta and Brock Matter in the University of Minnesota Masonic Cancer Center Mass Spectrometry Services for their assistance with triclosan and CTD analysis, and R. Noah Hensley, Hao Pang, Prof. Michael Ross (St. John's University/College of St. Benedict), and Jill Kerrigan for assistance with core collection and sectioning. The Office of the U of MN VP for Research provided the time on the R/V *Blue Heron*. The magnetic susceptibility measurements were performed in the LacCore (National Lacustrine Core Facility), Department of Earth Sciences, University of Minnesota-Twin Cities. Erin Mortenson and Shawn Schottler contributed to the $^{210}Pb$ and $^{137}Cs$ dating at the St. Croix Watershed Research Station.

## ■ REFERENCES


(1) Schweizer, H. P. Triclosan: a widely used biocide and its link to antibiotics. *FEMS Microbiol. Lett.* **2001**, *202*, 1−7.

(2) Perencevich, E. N.; Wong, M. T.; Harris, A. D. National and regional assessment of the antibacterial soap market: A step toward determining the impact of prevalent antibacterial soaps. *Am. J. Infect. Control* **2001**, *29*, 281−283.

(3) Sabaliunas, D.; Webb, S. F.; Hauk, A.; Jacob, M.; Eckhoff, W. S. Environmental fate of triclosan in the River Aire Basin, UK. *Water Res.* **2003**, *37*, 3145−3154.

(4) Chau, W.; Wu, J.; Cai, Z. Investigation of levels and fate of triclosan in environmental waters from the analysis of gas chromatography coupled with ion trap mass spectrometry. *Chemosphere* **2008**, *73*, S13−S17.

(5) Cantwell, M. G.; Wilson, B. A.; Zhu, J.; Wallace, G. T.; King, J. W.; Olsen, C. R.; Burgess, R. M.; Smith, J. P. Temporal trends of triclosan contamination in dated sediment cores from four urbanized estuaries: Evidence of preservation and accumulation. *Chemosphere* **2010**, *78*, 347−352.

(6) Halden, R. U.; Paull, D. H. Co-occurrence of triclocarban and triclosan in US water resources. *Environ. Sci. Technol.* **2005**, *39*, 1420−1426.

(7) Singer, H.; Müller, S.; Tixier, C.; Pillonel, L. Triclosan: Occurrence and fate of a widely used biocide in the aquatic environment: Field measurements in wastewater treatment plants, surface waters, and lake sediments. *Environ. Sci. Technol.* **2002**, *36*, 4998−5004.

(8) Heidler, J.; Halden, R. U. Mass balance assessment of triclosan removal during conventional sewage treatment. *Chemosphere* **2007**, *66*, 362−369.

(9) McAvoy, D. C.; Schatowitz, B.; Jacob, M.; Hauk, A.; Eckhoff, W. S. Measurement of triclosan in wastewater treatment systems. *Environ. Toxicol. Chem.* **2002**, *21*, 1323−1329.

(10) Buth, J. M.; Ross, M. R.; McNeill, K.; Arnold, W. A. Removal and formation of chlorinated triclosan derivatives in wastewater treatment plants using chlorine and UV disinfection. *Chemosphere* **2011**, *85*, 284−289.

(11) Bester, K. Triclosan in a sewage treatment process—balances and monitoring data. *Water Res.* **2003**, *37*, 3891−3896.

(12) Bester, K. Fate of triclosan and triclosan-methyl in sewage treatment plants and surface waters. *Arch. Environ. Contam. Toxicol.* **2005**, *49*, 9−17.

(13) Thomas, P. M.; Foster, G. D. Tracking acidic pharmaceuticals, caffeine, and triclosan through the wastewater treatment process. *Environ. Toxicol. Chem.* **2005**, *24*, 25−30.

(14) Lindström, A.; Buerge, I. J.; Poiger, T.; Bergqvist, P. A.; Müller, M. D.; Buser, H. R. Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. *Environ. Sci. Technol.* **2002**, *36*, 2322−2329.

(15) Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999−2000: A national reconnaissance. *Environ. Sci. Technol.* **2002**, *36*, 1202−1211.

(16) Boyd, G. R.; Reemtsma, H.; Grimm, D. A.; Mitra, S. Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. *Sci. Total Environ.* **2003**, *311*, 135−149.

(17) Hua, W.; Bennett, E. R.; Letcher, R. J. Triclosan in waste and surface waters from the upper Detroit River by liquid chromatography-electrospray-tandem quadrupole mass spectrometry. *Environ. Int.* **2005**, *31*, 621−630.

(18) Waltman, E. L.; Venables, B. J.; Waller, W. T. Triclosan in a North Texas wastewater treatment plant and the influent and effluent of an experimental constructed wetland. *Environ. Toxicol. Chem.* **2006**, *25*, 367−372.

(19) Ying, G. G.; Kookana, R. S. Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. *Environ. Int.* **2007**, *33*, 199−205.

(20) Buth, J. M. Transformation of pharmaceutical and personal care product pollutants by wastewater chlorine disinfection and aqueous photolysis. Ph.D. Thesis, Minneapolis, MN, 2009, .

(21) Onodera, S.; Ogawa, M.; Suzuki, S. Chemical changes of organic compounds in chlorinated water* 1:: XIII. Gas chromatographic–mass spectrometric studies of the reactions of Irgasan DP 300 [5-chloro-2-(2, 4-dichlorophenoxy_phenol] with chlorine in dilute aqueous solution. *J. Chromatogr., A* **1987**, *392*, 267−275.

(22) Rule, K. L.; Ebbett, V. R.; Vikesland, P. J. Formation of chloroform and chlorinated organics by free-chlorine-mediated oxidation of triclosan. *Environ. Sci. Technol.* **2005**, *39*, 3176−3185.

(23) Canosa, P.; Morales, S.; Rodriguez, I.; Rubi, E.; Cela, R.; Gomez, M. Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine. *Anal. Bioanal. Chem.* **2005**, *383*, 1119−1126.

(24) Fiss, E. M.; Rule, K. L.; Vikesland, P. J. Formation of chloroform and other chlorinated byproducts by chlorination of triclosan-containing antibacterial products. *Environ. Sci. Technol.* **2007**, *41*, 2387−2394.

(25) Kolpin, D. W.; Skopec, M.; Meyer, M. T.; Furlong, E. T.; Zaugg, S. D. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. *Sci. Total Environ.* **2004**, *328*, 119−130.

(26) Tixier, C.; Singer, H. P.; Canonica, S.; Müller, S. R. Phototransformation of triclosan in surface waters: A relevant elimination process for this widely used biocide laboratory studies, field measurements, and modeling. *Environ. Sci. Technol.* **2002**, *36*, 3482−3489.

(27) Loraine, G. A.; Pettigrove, M. E. Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in southern California. *Environ. Sci. Technol.* **2006**, *40*, 687−695.

(28) Venkatesan, A. K.; Pycke, B. F. G.; Barber, L. B.; Lee, K. E.; Halden, R. U. Occurrence of triclosan, triclocarban, and its lesser chlorinated congeners in Minnesota freshwater sediments collected near wastewater treatment plants. *J. Hazard. Mater.* **2012**, 29−35.

(29) Buth, J. M.; Grandbois, M.; Vikesland, P. J.; McNeill, K.; Arnold, W. A. Aquatic photochemistry of chlorinated triclosan derivatives: Potential source of polychlorodibenzo-p-dioxins. *Environ. Toxicol. Chem.* **2009**, *28*, 2555−2563.

(30) Latch, D. E.; Packer, J. L.; Arnold, W. A.; McNeill, K. Photochemical conversion of triclosan to 2, 8-dichlorodibenzo-p-dioxin in aqueous solution. *J. Photochem. Photobiol. A* **2003**, *158*, 63−66.

(31) Latch, D. E.; Packer, J. L.; Stender, B. L.; VanOverbeke, J.; Arnold, W. A.; McNeill, K. Aqueous photochemistry of triclosan: Formation of 2, 4-dichlorophenol, 2, 8-dichlorodibenzo-*p*-dioxin, and oligomerization products. *Environ. Toxicol. Chem.* **2005**, *24*, 517−525.

(32) Mezcua, M.; Gómez, M. J.; Ferrer, I.; Aguera, A.; Hernando, M. D.; Fernández-Alba, A. R. Evidence of 2, 7/2, 8-dibenzodichloro-*p*-dioxin as a photodegradation product of triclosan in water and wastewater samples. *Anal. Chim. Acta* **2004**, *524*, 241−247.

(33) Aranami, K.; Readman, J. W. Photolytic degradation of triclosan in freshwater and seawater. *Chemosphere* **2007**, *66*, 1052−1056.

(34) Van den Berg, M.; Birnbaum, L.; Bosveld, A.; Brunström, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* **1998**, *106*, 775.

(35) Buth, J. M.; Steen, P. O.; Sueper, C.; Blumentritt, D.; Vikesland, P. J.; Arnold, W. A.; McNeill, K. Dioxin photoproducts of triclosan and its chlorinated derivatives in sediment cores. *Environ. Sci. Technol.* **2010**, *44*, 4545−4551.

(36) Miller, T. R.; Heidler, J.; Chillrud, S. N.; DeLaquil, A.; Ritchie, J. C.; Mihalic, J. N.; Bopp, R.; Halden, R. U. Fate of triclosan and evidence for reductive dechlorination of triclocarban in estuarine sediments. *Environ. Sci. Technol.* **2008**, *42*, 4570−4576.

(37) Dean, W. E. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition; comparison with other methods. *J. Sediment. Res.* **1974**, *44*, 242−248.

(38) Heiri, O.; Lotter, A. F.; Lemcke, G. Loss on ignition as a method for estimating organic and carbonate content in sediments: Reproducibility and comparability of results. *J. Paleolimnol.* **2001**, *25*, 101−110.

(39) Appleby, P. Chronostratigraphic techniques in recent sediments. In *Tracking Environmental Change Using Lake Sediments: Basin Analysis, Coring, And Chronological Techniques*, Eds.; Last, W. M., Smol, J. P.; Kluwer Academic Publishers: Dordrecht, 2002; pp 171−203.

(40) Blumentritt D. J., Engstrom D. R. and Balogh S. J. A novel repeat-coring approach to reconstruct recent sediment, phosphorus, and mercury loading from the upper Mississippi River to Lake Pepin, USA. *J. Paleolimnol.* **2012** (in review).

(41) U.S. EPA. *Method 1613 Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS*; U.S. Environmental Protection Agency: Washington, DC, 1994; http://www.epa.gov/waterscience/methods/method/dioxins/1613.pdf (accessed November 6, 2012).

(42) Minnesota Pollution Control Agency. Draft Lake Winona site-specific nutrient criteria development. http://www.pca.state.mn.us/index.php/view-document.html?gid=15853 (accessed November 6, 2012).

(43) Minnesota Pollution Control Agency. Statewide Endocrine Disrupting Compound Monitoring Study − 2007 to 2008. St. Paul, MN, 2010. http://www.pca.state.mn.us/index.php/view-document.html?gid=10280 (accessed November 6, 2012).

(44) Hites, R. A. Environmental behavior of chlorinated dioxins and furans. *Acc. Chem. Res.* **1990**, *23*, 194−201.

(45) Baker, J. I.; Hites, R. A. Siskiwit Lake revisited: Time trends of polychlorinated dibenzo-p-dioxin and dibenzofuran deposition at Isle Royale, Michigan. *Environ. Sci. Technol.* **2000**, *34*, 2887−2891.

(46) Pearson, R. F.; Swackhamer, D. L.; Eisenreich, S. J.; Long, D. T. Atmospheric inputs of polychlorinated dibenzo-p-dioxins and dibenzofurans to the Great Lakes: Compositional comparison of PCDD and PCDF in sediments. *J. Great Lakes Res.* **1998**, *24*, 65−82.

(47) Nestrick, T.; Lamparski, L. Isomer-specific determination of chlorinated dioxins for assessment of formation and potential environmental emission from wood combustion. *Anal. Chem.* **1982**, *54*, 2292−2299.

(48) Sheffield, A. Sources and releases of PCDD's and PCDF's to the Canadian environment. *Chemosphere* **1985**, *14*, 811−814.

(49) Alcock, R. E.; Jones, K. C. Dioxins in the environment: A review of trend data. *Environ. Sci. Technol.* **1996**, *30*, 3133−3143.

(50) Gribble, G. W. The natural production of chlorinated compounds. *Environ. Sci. Technol.* **1994**, *28*, 310−319.

(51) Thomas, V. M.; Spiro, T. G. Peer reviewed: The U.S. dioxin inventory: Are there missing sources? *Environ. Sci. Technol.* **1996**, *30*, 82−85.

(52) Gullett, B. K.; Touati, A. PCDD/F emissions from forest fire simulations. *Atmos. Environ.* **2003**, *37*, 803−813.

(53) Grandesso, E.; Gullett, B.; Touati, A.; Tabor, D. Effect of moisture, charge size, and chlorine concentration on PCDD/F emissions from simulated open burning of forest biomass. *Environ. Sci. Technol.* **2011**, *45*, 3887−3894.

(54) Coogan, M. A.; Edziyie, R. E.; La Point, T. W.; Venables, B. J. Algal bioaccumulation of triclocarban, triclosan, and methyl-triclosan in a North Texas wastewater treatment plant receiving stream. *Chemosphere* **2007**, *67*, 1911−1918.

(55) Wilson, B. A.; Smith, V. H.; Denoyelles, F., Jr; Larive, C. K. Effects of three pharmaceutical and personal care products on natural freshwater algal assemblages. *Environ. Sci. Technol.* **2003**, *37*, 1713−1719.

(56) Coogan, M. A.; Point, T. W. L. Snail bioaccumulation of triclocarban, triclosan, and methyltriclosan in a North Texas, USA,

stream affected by wastewater treatment plant runoff. *Environ. Toxicol. Chem.* **2008**, *27*, 1788−1793.

(57) Orvos, D. R.; Versteeg, D. J.; Inauen, J.; Capdevielle, M.; Rothenstein, A.; Cunningham, V. Aquatic toxicity of triclosan. *Environ. Toxicol. Chem.* **2002**, *21*, 1338−1349.

(58) Adolfsson-Erici, M.; Pettersson, M.; Parkkonen, J.; Sturve, J. Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden. *Chemosphere* **2002**, *46*, 1485−1489.

(59) Valters, K.; Li, H.; Alaee, M.; D'Sa, I.; Marsh, G.; Bergman, Å.; Letcher, R. J. Polybrominated diphenyl ethers and hydroxylated and methoxylated brominated and chlorinated analogues in the plasma of fish from the Detroit River. *Environ. Sci. Technol.* **2005**, *39*, 5612−5619.

(60) Fair, P. A.; Lee, H. B.; Adams, J.; Darling, C.; Pacepavicius, G.; Alaee, M.; Bossart, G. D.; Henry, N.; Muir, D. Occurrence of triclosan in plasma of wild Atlantic bottlenose dolphins (*Tursiops truncatus*) and in their environment. *Environ. Pollut.* **2009**, *157*, 2248−2254.

(61) Stevens, K. J.; Kim, S. Y.; Adhikari, S.; Vadapalli, V.; Venables, B. J. Effects of triclosan on seed germination and seedling development of three wetland plants: *Sesbania herbacea, Eclipta prostrata,* and *Bidens frondosa*. *Environ. Toxicol. Chem.* **2009**, *28*, 2598−2609.

(62) Samara, F.; Gullett, B. K.; Harrison, R. O.; Chu, A.; Clark, G. C. Determination of relative assay response factors for toxic chlorinated and brominated dioxins/furans using an enzyme immunoassay (EIA) and chemically-activated luciferase gene expression cell bioassay (CALUX). *Environ. Int.* **2009**, *35*, 588−593.

**Quantification of Triclosan, Chlorinated Triclosan Derivatives, and their Dioxin Photoproducts in Lacustrine Sediment Cores**

A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

**Cale Thomas Anger**

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

Advisor:
William A. Arnold

September 2012

**ACKNOWLEDGMENTS**

I would first like to offer my utmost gratitude to my advisor, Bill Arnold. Bill has been an excellent mentor during my tenure in the Department of Civil Engineering. It has been an honor to work in his lab. His dedication, support, and enthusiasm for research have been an inspiration.

I also wish to thank the members of the environmental research group for their helpful comments and assistance during the last two years. Special thanks are due to David Tan and Pat McNamara for help with troubleshooting the LC/MS and providing valuable insight into method development. Additional thanks are due to Noah Hensley and Hao Pang for many productive discussions on triclosan analysis and their help with collecting sediment cores.

Thank you to my committee members, Dan Engstrom and Paul Capel, for their critical review of this thesis. Special thanks are due to Dan for his dedication to the project, help with fieldwork, and knowledge on sediment coring and dating.

This research would not have been possible without the cooperation of numerous scientific organizations around Minnesota. First, I would like to thank the St. Croix Watershed Research Station (SCWRS) for their assistance with radiometric dating and freeze drying. Special thanks to Dylan Blumentritt and Jill Coleman-Wasik for their efforts in the radiometric dating process. The Limnological Research Center (LRC) also deserves recognition for allowing us to use their facilities, providing field supplies, and assisting with the magnetic susceptibility measurements. Additionally, I would like to thank the Large Lakes Observatory (LLO) and the crew of the RV Blue Heron for their hospitality during the collection of the Duluth Harbor and Lake Superior cores.

Thank you to Peter Villalta and Brock Matter at the Masonic Cancer Research Center Mass Spectrometry lab for their help with maintaining and troubleshooting the LC-MS-$Q^3$. Both Pete and Brock were great resources when working through sample analysis issues.

I would like to acknowledge the Minnesota Natural Resources Trust Fund, the Department of Civil Engineering, and AMEC for funding this project and my graduate education. This project would not have been possible without their support.

Finally, I would like to thank friends and family that have supported me through my educational journey. Thank you to the Astashinskys, Mikhelsons, and the Westerbergs for always being there for me. Last, but certainly not least, I would like to thank my wife Yelena for her love, patience, and support throughout life.

# ABSTRACT

Triclosan (TCS) is an antimicrobial agent commonly detected in wastewater effluent. During water and wastewater disinfection with free chlorine, TCS can be transformed to a series of chlorinated triclosan derivatives (CTDs). When discharged into surface waters, TCS and CTDs may be photochemically transformed via a cyclization reaction to a series of polychlorinated dibenzo-*p*-dioxins (PCDDs). Because PCDDs are a class of compounds known to be toxic and carcinogenic in the environment, tracking their formation from TCS and CTDs in aquatic ecosystems is necessary.

To evaluate the historical exposure of surface waters to TCS, CTDs, and their derived PCDDs, sediment cores were collected from an array of wastewater-impacted Minnesota lakes. Following radiometric dating, TCS and CTDs were extracted from core sections and quantified by liquid chromatography-tandem mass spectrometry (LC-MS-$Q^3$). PCDDs were extracted from the same core sections and quantified by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS).

The concentrations and temporal trends of TCS, CTDs, and their PCDDs in aquatic sediments were found to be a function of historical wastewater treatment operations and lake system scale. Cores collected from large-scale riverine systems with many wastewater sources recorded increasing concentrations of TCS, CTDs, and their derived PCDDs since the patenting of TCS in 1964. In small-scale lakes with a single wastewater source, the depositional trends of these analytes were directly attributed to increased TCS use, local improvements in treatment, and changes in wastewater disinfection since the 1960s. Overall, concentrations of TCS, CTDs, and their PCDDs were higher in small-scale systems, reflecting a greater degree of wastewater impact.

Although specific PCDD congeners are known photoproducts of TCS and CTDs, the same PCDDs were also found at very low concentrations in northern Minnesota lakes with little or no wastewater impact. Background levels of these PCDDs were attributed to a secondary, region-specific source in the 19$^{th}$ and 20$^{th}$ centuries.

To evaluate the potential risk that TCS and CTDs pose to aquatic environments, the contribution of their derived PCDDs to the total PCDD pool, in terms of mass and toxicity, was determined for each sediment core. In heavily impacted systems, the PCDD contribution from TCS and CTDs accounted for up to 70% of total PCDD mass and 32% of total PCDD toxicity in recent sediment. Thus, the discharge of TCS and CTDs may pose a substantial threat to wastewater-impacted lakes in Minnesota.

## TABLE OF CONTENTS

**Acknowledgments** ........ **i**

**Abstract** ........ **iii**

**Table of Contents** ........ **v**

**List of Tables** ........ **vii**

**List of Figures** ........ **x**

**Chapter 1: Introduction** ........ **1**

1.1 Pharmaceuticals and Personal Care Products in the Aquatic Environment ........ **1**

1.2 Outline of Thesis ........ **2**

**Chapter 2: Background and Literature Review** ........ **5**

2.1 Triclosan as a Personal Care Product ........ **5**

2.2 Detection in Wastewater and the Environment ........ **6**

2.3 Fate and Transformation in Natural and Engineered Waters ........ **11**

2.3.1 Wastewater Chlorination ........ **11**

2.3.2 Aqueous Photolysis ........ **15**

**Chapter 3: Quantification of Triclosan, Chlorinated Triclosan Derivatives, and their Dioxin Photoproducts in Lacustrine Sediment Cores** ........ **21**

3.1 Introduction and Objectives ........ **21**

3.2 Experimental ........ **23**

3.2.1 Chemicals and Laboratory Procedures ........ **23**

3.2.2 Sediment Core Collection ........ **24**

3.2.3 Radiometric Dating ........ **27**

3.2.4 Triclosan (TCS) and Chlorinated Triclosan Derivative (CTD) Analysis ........ **28**

3.2.5 Polychlorinated dibenzo-*p*-dioxin (PCDD) and furan (PCDF) Analysis ........ **36**

3.3 Results and Discussion ........ **38**

3.3.1 Analytical Method Performance ........ **38**

3.3.2 TCS, CTDs, and their PCDDs in MN Lakes ........ **44**

3.3.3 TCS and CTDs – An Emerging PCDD Source ........ **63**
3.4 Environmental Implications ........ **72**
**Chapter 4: Conclusions** ........ **79**
**References** ........ **82**
**Appendices**
Appendix A ........ **93**
Appendix B ........ **95**
Appendix C ........ **96**
Appendix D ........ **99**
Appendix E ........ **107**
Appendix F ........ **117**

## List of Tables


Table 3-1: Differential global positioning system (dGPS) coordinates for sediment core locations ....24

Table 3-2: Optimized parameters for $^{13}C_{12}$-TCS, TCS, and CTD extraction from sediment on the ASE 350 ....29

Table 3-3: Mean organic content of sediment cores ....30

Table 3-4: Selected reaction monitoring (SRM) transitions for $^{13}C_{12}$-TCS, TCS, and CTD quantification and confirmation ....34

Table 3-5: Absolute recovery of $^{13}C_{12}$-TCS in sediment cores....41

Table 3-6: Relative recovery of TCS and CTDs for extraction procedures (Methods 1 and 2) ....42

Table 3-7: Absolute recovery range of $^{13}C_{12}$- PCDD/F isomers....42

Table 3-8: Relative recovery range of PCDD/F isomers ....43

Table 3-9: Ratio of 2,8-DCDD to TCS in sediment core intervals....63

Table 3-10: Ratio of 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD to CTDs in sediment core intervals ....64

Table 3-11: Toxic equivalency factors (TEFs) for PCDD congeners and isomers, relative to 2,3,7,8-TCDD ....73


**Appendix D**


Table AD-1: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Pepin sediment core ....99

Table AD-2: Relative PCDD/F recovery in Lake Pepin sediment ....99

Table AD-3: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake St. Croix sediment core ....100

Table AD-4: Relative PCDD/F recovery in Lake St. Croix sediment....100

Table AD-5: Absolute $^{13}C_{12}$-PCDD/F recovery in the East Lake Gemini sediment core ....101

Table AD-6: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Winona sediment core ..102

Table AD-7: Relative PCDD/F recovery in Lake Winona sediment....102

Table AD-8: Absolute $^{13}C_{12}$-PCDD/F recovery in the Duluth Harbor sediment core ....103

Table AD-9: Relative PCDD/F recovery in Duluth Harbor sediment....103

Table AD-10: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Superior sediment core .104

Table AD-11: Relative PCDD/F recovery in Lake Superior sediment..........................104

Table AD-12: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Shagawa sediment core ..........................105

Table AD-13: Relative PCDD/F recovery in Lake Shagawa sediment..........................105

Table AD-14: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Little Wilson sediment core ..........................106

Table AD-15: Relative PCDD/F recovery in Lake Little Wilson sediment..........................106

**Appendix E**

Table AE-1: $^{210}$Pb dating for the Lake St. Croix sediment core. ..........................107

Table AE-2: $^{210}$Pb dating for the East Lake Gemini sediment core. ..........................107

Table AE-3: $^{210}$Pb dating for the Lake Winona sediment core. ..........................108

Table AE-4: $^{210}$Pb dating for the Duluth Harbor sediment core. ..........................108

Table AE-5: $^{210}$Pb dating for the Lake Superior sediment core. ..........................109

Table AE-6: $^{210}$Pb dating for the Lake Shagawa sediment core. ..........................109

Table AE-7: $^{210}$Pb dating for the Lake Little Wilson sediment core. ..........................110

Table AE-8: $^{137}$Cs dating for the East Lake Gemini sediment core. ..........................110

Table AE-9: $^{137}$Cs dating for the Lake Winona sediment core. ..........................110

Table AE-10: $^{137}$Cs dating for the Duluth Harbor sediment core. ..........................111

Table AE-11: $^{137}$Cs dating for the Lake Shagawa sediment core. ..........................111

Table AE-12: $^{137}$Cs dating for the Lake Little Wilson sediment core. ..........................111

Table AE-13: Sediment focusing factors for the Lake Pepin sediment core..........................115

Table AE-14: Sediment focusing factors for the Lake St. Croix sediment core..........................115

Table AE-15: Sediment focusing factors for the East Lake Gemini, Lake Winona, Duluth Harbor, Lake Superior, Lake Shagawa, and Lake Little Wilson cores..........................115

**Appendix F**

Table AF-1: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Pepin PCDD pool. ..........................117

Table AF-2: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake St. Croix PCDD pool. ..........................117

Table AF-3: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the East Lake Gemini PCDD pool....................................................118

Table AF-4: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Winona PCDD pool...........................................................118

Table AF-5: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Duluth Harbor PCDD pool. .........................................................118

Table AF-6: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Superior PCDD pool...........................................................119

Table AF-7: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Shagawa PCDD pool. ..........................................................119

Table AF-8: Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Little Wilson PCDD pool. ..................................................119

## List of Figures


Figure 2-1: Chemical structure of TCS ............ 5

Figure 2-2: Chlorination of TCS to form CTDs ............ 14

Figure 2-3: Fundamental pathways for direct and indirect photochemical degradation ............ 16

Figure 2-4: Formation of PCDDs from the direct photolysis of TCS and CTDs ............ 18

Figure 2-5: General structure of PCDDs ............ 19

Figure 3-1: Sediment coring sites in MN ............ 25

Figure 3-2: Cleanup procedure for ASE extracts ............ 32

Figure 3-3: LC-MS-$Q^3$ chromatograms of $^{13}C_{12}$-TCS, TCS, and CTD SRM transitions in a representative standard ............ 39

Figure 3-4: LC-MS-$Q^3$ chromatograms of $^{13}C_{12}$-TCS, TCS, and CTD SRM transitions in a Lake Pepin sediment extract ............ 40

Figure 3-5: Concentration profiles and focus-corrected accumulation rates of TCS, CTDs, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the Lake Pepin core ............ 45

Figure 3-6: Concentration profiles and focus-corrected accumulation rates of TCS, CTDs, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the Lake St. Croix core ............ 46

Figure 3-7: Concentration profiles and focus-corrected accumulation rates of TCS, CTDs, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the East Lake Gemini core ............ 49

Figure 3-8: Concentration profiles and focus-corrected accumulation rates of TCS, CTDs, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the Lake Winona core ............ 50

Figure 3-9: Concentration profiles and focus-corrected accumulation rates of TCS, CTDs, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the Duluth Harbor core ............ 53

Figure 3-10: Concentration profiles and focus-corrected accumulation rates of TCS, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the Lake Superior core ............ 54

Figure 3-11: Concentration profiles and focus-corrected accumulation rates of TCS, CTDs, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the Lake Shagawa core ............ 58

Figure 3-12: Concentration profiles and focus-corrected accumulation rates of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in the Lake Little Wilson core ....61

Figure 3-13: Focus-corrected PCDD accumulation rates at the Lake Pepin core site ....66

Figure 3-14: Correlation of PCDD congener and isomer accumulation profiles with 2,8-DCDD and OCDD in the Lake Pepin core. ....67

Figure 3-15: Focus-corrected PCDD accumulation rates at the Lake Superior core site ....69

Figure 3-16: Correlation of PCDD congener and isomer accumulation profiles with 2,8-DCDD and OCDD in the Lake Superior core ....70

Figure 3-17: Percent contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD by mass and toxic equivalents (TEQ) to the total PCDD pool for Lake Pepin, Lake St. Croix, East Lake Gemini, and Lake Winona ....75

Figure 3-18: Percent contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD by mass and toxic equivalents (TEQ) to the total PCDD pool for Duluth Harbor, Lake Superior, Lake Shagawa, and Lake Little Wilson ....77

**Appendix C**

Figure AC-1: Example TCS calibration curve ....96

**Appendix E**

Figure AE-1: Total $^{210}$Pb activity in the Lake St. Croix (A), East Lake Gemini (B), Lake Winona (C), and Duluth Harbor (D) cores ....112

Figure AE-2: Total $^{210}$Pb activity in the Lake Superior (A), Lake Shagawa (B), and Lake Little Wilson (C) cores ....113

Figure AE-3: Total $^{137}$Cs activity in the East Lake Gemini (A), Lake Winona (B), Duluth Harbor (C), and Lake Shagawa (D) cores. ....114

# Chapter 1: Introduction

## 1.1 Pharmaceuticals and Personal Care Products in the Aquatic Environment

Pharmaceuticals and personal care products (PPCPs) represent a diverse group of micro-pollutants that are of increasing environmental concern. Ranging from prescription drugs and hormones, to antimicrobials and fragrences, PPCPs are designed to evoke a specific biochemical response during human use [1-3]. Unfortunately, many of these compounds are incompletely metabolized and/or are directly disposed of in regular household or commercial settings [1,4,5]. When released into the environment, the physiochemical properties of PPCPs and their metabolites may contribute to an array of ecological problems, including acute and chronic toxicity [6], endocrine disruption [7], and reproductive impairment in organisms [8,9].

The primary route of entry for PPCPs into an aquatic environment is through the discharge of municipal and industrial wastewater. Traditional wastewater treatment plants (WWTPs) are designed to remove suspended solids, pathogens, and nutrients, but not low concentrations of PPCPs. Consequently, many of these micro-pollutants are present in wastewater effluent at ng/L to low μg/L levels [8,10,11]. From 1999-2000, the U.S. Geological Survey (USGS) found that 80% of 139 U.S. waterways impacted by urbanization or agriculture contained organic wastewater contaminants, including steroids, reproductive hormones, antibiotics, and prescription drugs [8]. Due to the biological activity of these compounds at low concentrations, coupled with the possible synergistic effects of chemical mixtures on aquatic toxicity, the presence of PPCPs in surface waters is of great concern [12].

The risk that individual PPCPs pose to an aquatic ecosystem is highly dependent on their fate and transport in wastewater treatment and aquatic environments. In traditional WWTPs, PPCPs may sorb to particles during primary and secondary settling, or be biologically transformed in the activated sludge process [13]. Abiotic processes, such as hydrolysis, may also play a role in PPCP transformation in wastewater treatment [13]. Reactions with disinfectants, including free chlorine ($Cl_2$, NaOCl), ozone ($O_3$), and ultraviolet light (UV), often reduce the flux of PPCPs into surface waters [14-17]. These reactions, however, may also produce harmful disinfection byproducts (DBPs) that are more toxic than the parent pollutant [18,19].

Once PPCPs and DBPs are discharged into the environment, their behavior will be dictated by their physical and chemical properties, including water solubility, lipophilicity, hydrophobicity, vapor pressure, and overall reactivity. Persistent pollutants may sorb to sediment or bioaccumulate in aquatic organisms. More reactive compounds will degrade rapidly by a host of transformation processes, including microbial degradation, photolysis, and redox reactions. In many aquatic systems, even the most reactive PPCPs can be “pseudo-persistent”, primarly due to a constant source from wastewater effluent [1]. Consequently, a combination of persistence and biological activity leads to potential risks for environmental receptors.

**1.2 Outline of Thesis**

The primary goal of this research is to better understand the fate of triclosan (TCS), a well known PPCP, and its byproducts in aquatic systems. TCS is a common antimicrobial agent found in personal care products that are routinely washed down the drain. Previous research has shown that TCS is transformed during water and wastewater disinfection with free-chlorine [20-23]. Specific disinfection byproducts, known as chlorinated triclosan derivatives (CTDs), are discharged with TCS into surface waters [24, 25]. TCS and its CTDs may subsequently be photochemically transformed to specific polychlorinated dibenzo-*p*-dioxins (PCDDs), a class of compounds that are known to be toxic and carcinogenic in the environment [26].

To assess the impact of TCS, CTDs, and their derived PCDDs on aquatic ecosystems, sediment cores were collected from a series of wastewater-impacted lakes in Minnesota (MN). Analyte concentrations and temporal trends were discerned in each core to provide insight into the historical exposure of each lake to these compounds. Furthermore, the influence of wastewater treatment practices (e.g., improvements in treatment or type of disinfection) and lake system scale were probed to evaluate how they influence analyte trends. Finally, the PCDD contribution from TCS and CTDs to the total PCDD pool, in terms of mass and toxicity, was determined for each core. Through this analysis, the potential risk that TCS, CTDs, and their derived PCDDs pose to an array of MN lakes could be examined.

This thesis includes:

**Chapter 1: Introduction.**

**Chapter 2: Background and Literature Review.** This chapter provides background on triclosan (TCS) as a personal care product and its occurrence in the environment. Furthermore, information is provided on the transformation of TCS during wastewater disinfection and in surface waters.

**Chapter 3: Quantification of Triclosan, Chlorinated Triclosan Derivatives, and their Dioxin Photoproducts in Lacustrine Sediment Cores.** This chapter presents results on the occurrence of TCS, chlorinated triclosan derivatives (CTDs), and their derived polychlorinated dibenzo-*p*-dioxins (PCDDs) in a series of wastewater-impacted Minnesota lakes.

**Chapter 4: Conclusions**

# Chapter 2: Background and Literature Review

## 2.1 Triclosan as a Personal Care Product

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol; TCS) is a broad-spectrum antimicrobial agent that is present in a wide array of medical and personal care products (Figure 2-1). After being patented in 1964, initial use of TCS was confined to hospital and health care settings [27,28]. Since 1980, however, the compound has been integrated into common household items, including liquid hand soaps (0.1 – 0.3% w/w), bar soaps, dental care products, textiles, and plastics [29-31].

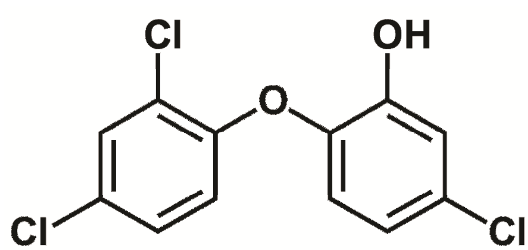


**Figure 2-1:** Chemical structure of TCS.

With a continually increasing demand for products with antibacterial properties, production of TCS has increased dramatically over the last 30 years. In 2001, it was estimated that 76% of liquid hand soaps and 29% of bar soaps contained TCS (45% of all soaps available to consumers) [28]. In the United States and Europe, annual use is estimated at 300 and 350 metric tons/year, respectively [32,33]. Furthermore, recent estimates suggest that TCS usage rates may increase by 5% each year in the future, leading to greater environmental exposure from this compound [11].

## 2.2 Detection in Wastewater and the Environment

*Removal in Wastewater Treatment.* Approximately 96% of TCS used in personal care products is washed down the drain, leading to concentrations on the order of 1-10 μg/L in wastewater influents [11,24,25,33-37]. Removal rates of TCS can vary, depending on the secondary unit operations employed in a wastewater plant. Facilities with activated sludge, a secondary treatment process applied in 75% of U.S. WWTPs, tend to remove TCS at high rates (90-98%) [11,24,29,32,34,35]. Field-scale wastewater mass balances have confirmed that 50-79% of this removal is due to aerobic biodegradation in the sludge matrix, while the remainder is due to sorption to biosolids [11,33]. No evidence of anaerobic biodegradation has been reported in the timescale of wastewater treatment [38,39].

TCS removal rates in other, less common secondary treatment processes are poorly characterized. McAvoy et al. [24] found that facilities with trickling filters, a secondary treatment process employed by 5% of U.S. WWTPs, tend to remove TCS at variable rates (58-86%). The lower and more variable removal rates are attributed to short hydraulic retention times in the trickling filters, providing less time for aerobic biodegradation during secondary treatment.

*Detection in Wastewater Effluent and Surface Waters.* Although most secondary treatment facilities can remove TCS at high rates, a significant amount persists through treatment and into surface waters. Effluent concentrations ranging from 10-600 ng/L, to as high as 2.7 μg/L, have been reported at WWTPs in the U.S., Europe, and Australia [7,24,25,33,34,36,37,40-42]. In the U.S., recent studies have estimated annual TCS loading to surface waters. Based on an estimated per capita usage rate of 3-5 mg/day, loading rates on the order of 10-20 metric tons/year have been determined [32,43].

Concentrations of TCS in impacted surface waters vary greatly, depending on the scale of the water body and the extent of contamination from treatment facilities. Typical surface water concentrations range from 1-200 ng/L in riverine and lacustrine systems impacted by WWTPs [8,29,33,35,37,40,44,45]. In the landmark study by Koplin et al. [8], TCS was detected in 58% of 85 impacted U.S. waterways at median and maximum concentrations of 140 ng/L and 2.3 μg/L, respectively. In arid regions, where wastewater effluent may dominate stream flows, TCS contamination may be more severe. The Metropolitan Water District of Southern California (MWDSC), for example, imports water from the Sacramento-San Joaquin River (SSJR). During the 2001 dry season (August-September), 70% of the SSJR flow was comprised of wastewater, leading to TCS concentrations as high as 734 ng/L in raw MWDSC drinking water [46].

*Detection in Sediments.* Due to its low solubility (10 mg/L at 20°C), low vapor pressure ($4\times10^{-6}$ mmHg at 20°C) and high hydrophobicity (log $K_{ow}$ = 4.8, neutral pH), TCS has the potential to persist in sediments or bioaccumulate in aquatic organisms. Several studies have confirmed long-term preservation of TCS in lake and estuarine sedimentary environments. Buth et al. [47], for example, investigated two sediment cores from a depositional zone along the Mississippi River. Dated sediment cores provided evidence of TCS accumulation, reflecting consumer usage since the 1960s.

In a similar study, Cantwell et al. [31] investigated four urbanized estuaries along the U.S. Atlantic coast. Spatial and temporal trends of TCS in these cores reflect increased consumer usage and improvements in wastewater treatment processes (e.g. activated sludge treatment) over the last 40 years. Singer et al. [33] reported similar depositional trends when conducting a TCS mass balance in Lake Greifensee, Switzerland.

The temporal trends of TCS in dated sediment cores suggest that this antimicrobial is recalcitrant in anaerobic environments. Halden and Paull [32] estimated the environmental half-life of TCS in anaerobic sediments to be 540 days, based on a quantitative structure-activity relationship (QSAR) analysis. To date, no experimental evidence has been presented to confirm this estimate. A study by Miller et al. [48] found that TCS levels directly parallel heavy metal concentrations in estuarine sediment near a WWTP in Jamaica Bay, New York. Treated wastewater effluent is known to be the principal source of heavy metals to this aquatic environment. Due to the conservative nature of heavy metals, along with the analogous depositional trend of TCS, Miller et al. assert that TCS is not being degraded to an appreciable extent in these sediments.

A recent study conducted by the USGS found that TCS is ubiquitous in the freshwater bed sediments of wastewater-impacted surface waters in Minnesota [49]. TCS concentrations ranging from 0.4 to 85 ng/g were found in the top 10 cm of sediment near WWTPs. TCS concentrations in bed sediments collected from lake systems were up to three times higher than observed in rivers and streams. Furthermore, TCS was detected both upstream and downstream of WWTPs, confirming the widespread occurrence and persistence of TCS in these environments.

*Detection and Toxicity in Aquatic Organisms.* As a lipophilic compound, TCS has been detected in an array of aquatic organisms, including algae and aquatic plants [50,51], snails [52], fish [53-55], and even dolphins [56]. Coogan et al. [50] specifically looked at algal bioaccumulation factors (BAFs) in a wastewater-impacted stream in Texas. The study found that TCS concentrations ranged from 50-400 ng/g fresh weight in algae, yielding BAFs on the order of 1000 in this environment.

As primary producers, algae are essential components of aquatic food webs. Bioaccumulation in these organisms increases the potential for trophic transfer of TCS, potentially leading to high concentrations in aquatic consumers (e.g., fish) and humans. Adolfsson-Erici et al. [54], for example, found TCS concentrations as high as 4.4 μg/g in wild fish bile in Sweden. The same study also collected random samples of human milk and recorded TCS concentrations up to 300 ng/g lipid weight.

In conjunction with the potential for bioaccumulation in aquatic systems, TCS can have a range of toxic effects on specific organisms. A study by Orvos et al. [53] found that typical TCS surface water concentrations have little effect on specific invertebrates and fish. For example, the chronic no-effect concentration (NOEC) of TCS on rainbow trout over a 61 day period is 34 μg/L. Similarly, the NOEC for *Daphnia magna* over a 21 day period is 40 μg/L. Several studies, however, have confirmed that TCS is chronically toxic to algae and macrophytes at environmentally relevant concentrations. The 96 hr chronic NOEC for a species of green algae (*Scenedesmus subspicatus)* has been estimated at 690 ng/L [53]. Furthermore, TCS concentrations ranging from 15 ng/L to 1.5 μg/L have been shown to induce major shifts in algal community structure [51] and effect macrophyte growth [57]. These community shifts have the potential to modify the trophic structure and function of aquatic ecosystems that receive WWTP effluent.

*Detection in Biosolids and Soils.* The incorporation of activated sludge treatment into conventional WWTPs has greatly reduced the flux of TCS into aquatic environments. Biosolids derived from this treatment process, however, typically contain high concentrations of TCS. Even after aerobic biodegradation during wastewater treatment, TCS concentrations have been documented on the order of 1-50 μg/g dry weight in digested sludge [11,24,34,42,58-62]. In the U.S., approximately 50% of biosolids derived from wastewater treatment are land-applied [63]. Consequently, elevated concentrations of TCS can leach into soils and impact surface waters that receive agricultural runoff.

The persistence of TCS in biosolid-amended soils is directly a function of biosolid application, soil properties, biodegradation rates, and runoff in the surrounding watershed. Amended soil concentrations on the order of 1-100 ng/g, to as high as 833 ng/g have been documented [9,62,64]. Several studies have suggested that aerobic biodegradation is the most important mechanism for TCS dissipation in soils. Half-lives from 18 to 108 days have been reported in laboratory and field-scale studies [38,61,62,65,66]. Higher rates of aerobic biodegradation have been attributed to the mode of biosolids application. Namely, application of biosolids in liquid form tends to make TCS more bioavailable in soils. Dewatered biosolids, however, tend to have limited contact with soil, minimizing TCS diffusion into the surrounding environment [67].

Although application of liquid biosolids promotes biodegradation, this also increases the mobility of TCS, promoting runoff to surrounding surface waters. A study by Lapen et al. [68] documented TCS concentrations as high as 3.7 μg/L in drain tile effluent, shortly after the application of liquid biosolids. A similar study reported drain tile concentrations of 200 ng/L [69]. As a result, land application of biosolids can contribute to TCS contamination in impacted surface waters, at concentrations known to effect aquatic primary producers.

## 2.3 Fate and Transformation in Natural and Engineered Waters

The chemical fate of TCS during wastewater treatment and in the environment has been well documented. In addition to removal via activated sludge treatment, TCS has been shown to be chemically transformed during chlorine disinfection. TCS and its chlorinated DBPs can subsequently be discharged into surface waters, where they are susceptible to photochemical transformation.

### 2.3.1 Wastewater Chlorination

Chlorination is the most commonly practiced mode of wastewater disinfection. Historically, the use of chlorine as a disinfectant has been favored, primarily for its low cost, effectiveness at inactivating most pathogens, and ability to control odors [70]. Today, approximately 72% of WWTPs in the U.S. continue to use forms of chlorine in wastewater treatment [71].

*Chemistry of Chlorination.* In modern wastewater treatment, chlorine gas ($Cl_{2(g)}$) and hypochlorite salts (e.g. NaOCl) are commonly used for disinfection [72]. $Cl_{2(g)}$

hydrolyzes rapidly when added to water to chloride ($Cl^-$) and hypochlorous acid (HOCl) (Eq. 1).

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^- \tag{1}$$

HOCl in (Eq. 1) will simultaneously dissociate in aqueous solution to form an equilibrium solution of HOCl and hypochlorite ($OCl^-$) (Eq. 2).

$$HOCl \rightleftarrows H^+ + OCl^- \qquad pK_a\ (25\ °C) = 7.54 \tag{2}$$

Together, $Cl_2$, HOCl, and $OCl^-$ are known as free chlorine. At environmentally relevant pH values, HOCl and $OCl^-$ represent the main free chlorine species in solution available for reaction [14].

In non-nitrified wastewater, ammonia ($NH_3$) concentrations are generally on the order of 10 – 40 mg/L. At these $NH_3$ levels, free chlorine can react to form a series of chloramines (Eqs. 3-5):

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \tag{3}$$

$$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O \tag{4}$$

$$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O \tag{5}$$

Mono- ($NH_2Cl$), di- ($NHCl_2$), and tri- ($NCl_3$) chloramines tend to be less reactive and more substrate specific, when compared to free chlorine [14].

*Disinfection Byproducts.* Although chlorination has been instrumental in protecting public health and aquatic ecosystems, there are disadvantages to its use. Over the last several decades, a suite of harmful DBPs have been characterized in chlorinated wastewater and drinking water. Trihalomethanes (THMs) and haloacetic acids (HAAs), for example, are DBPs formed when free chlorine non-selectively reacts with dissolved organic matter (DOM). Several THMs and HAAs have been implicated as carcinogens to humans and wildlife, leading to their regulation by the U.S. Environmental Protection Agency (EPA) [18].

More recently, formation of DBPs from micropollutants, including PPCPs and pesticides, have been of increasing concern. Due to the diverse structural moieties of many micropollutants, DBPs can be formed through an array of chemical mechanisms. For PPCPs like TCS, a common reaction mechanism is electrophilic substitution of chlorine on its phenolic moiety [14]. This reaction has been attributed to the formation of chlorinated triclosan derivatives (CTDs) in chlorinated aqueous solutions [21].

*Chlorinated Triclosan Derivatives (CTDs).* Several studies have investigated the primary factors that influence CTD formation during water and wastewater chlorination [20-23]. When reacting with free chlorine, the phenolic moiety on TCS activates its *ortho* and *para* positions. Electrophilic addition of chlorine at these positions forms three CTD congeners: 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol (4-Cl-TCS), 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol (6-Cl-TCS), and 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol (4,6-Cl-TCS) (Figure 2-2). Depending on the amount of excess free chlorine present in aqueous solution, ether or ring cleavage can occur on the TCS and CTD molecules, forming toxic chlorophenols and chloroform [22,23].

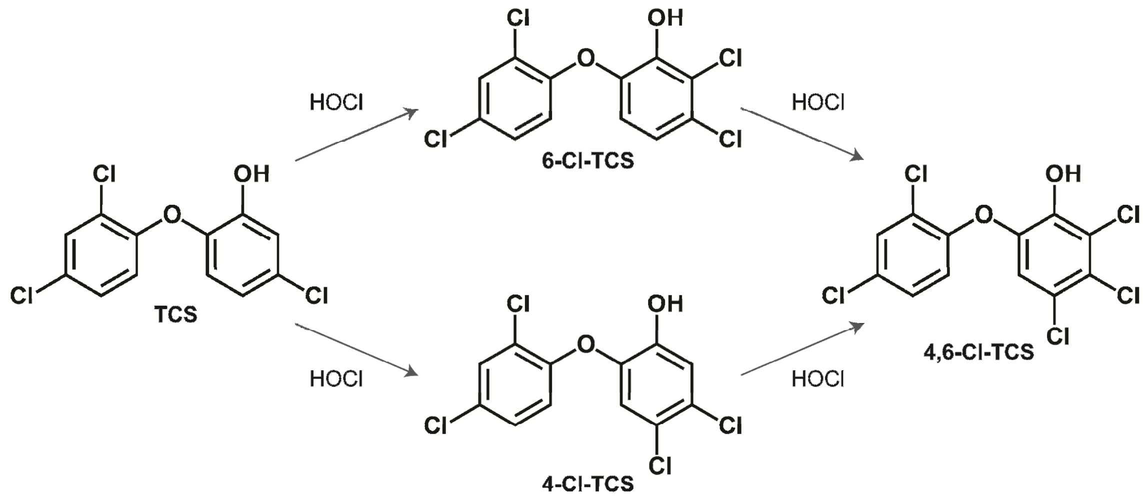



**Figure 2-2**: Chlorination of triclosan (TCS) to form three chlorinated triclosan derivatives (CTDs): 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol (4-Cl-TCS), 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol (6-Cl-TCS), and 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol (4,6-Cl-TCS) (adapted from [43]).

The electrophilic substitution of TCS during free chlorination is highly dependent on pH. Rule et al. [21] found maximum pseudo-first order rate constants for TCS substitution at neutral pH, with markedly lower rates at low and high pH. This trend in reactivity is attributed to the speciation of free chlorine and TCS in natural waters. Namely, HOCl tends to be the more reactive free chlorine species in solution. Furthermore, the phenolate ($O^-$) form of TCS is better at activating sites on the aromatic ring for electrophilic substitution than its phenol (OH) conjugate [21]. Thus, with $pK_a$ values of 7.54 and 7.6 for free chlorine ($HOCl/OCl^-$) and TCS ($OH/O^-$), the formation of CTDs is maximized at pH values relevant to water and wastewater treatment. Similar reactivity trends are observed in chloraminated waters. CTD formation rates, however, are 2-4 orders of magnitude slower when compared to free chlorine [73].

Recent studies have characterized the removal and generation of CTDs in wastewater treatment [24,25]. Buth et al. [25] systematically investigated the presence of TCS and CTDs in a large WWTP that disinfects with free chlorine. Low levels of CTDs were detected in wastewater influent, presumably due to reaction of TCS with residual chlorine in tap water. Due to their hydrophobic nature, the CTDs were removed at high rates during activated sludge treatment and subsequently reformed during disinfection. Up to 14% of the TCS present in the disinfection stage was degraded, yielding total CTD concentrations as high as 35 ng/L in wastewater effluent.

Few papers have been published on the environmental occurrence and toxicity of CTDs. As chlorinated phenoxy phenols, CTDs are likely to have deleterious effects on aquatic environments, including chronic toxicity and endocrine disruption. The extent of these effects, however, have yet to be quantified.

### 2.3.2 Aqueous Photolysis

*Fundamentals of Aqueous Photolysis.* The photochemical transformation of organic chemicals can occur via two processes: direct and indirect photolysis. Direct photolysis occurs when a compound, or substrate, absorbs light within the UV-visible range (290-600 nm) and is electronically excited to a higher energy state [74]. The excited substrate may then be transformed to a different chemical (Figure 2-3). During indirect photolysis, however, the substrate of interest does not absorb light. In this case, a secondary solute, known as a sensitizer, becomes excited. The sensitizer may (1) directly react with the substrate, or (2) produce a series of reactive transients that degrade the compound of interest. Dissolved organic matter (DOM), and to a lesser extent, nitrate

($NO_3^-$) and iron ($Fe^{III}$), are common sensitizers in natural waters. Once excited, a number of transients can be derived from these species, including hydroxyl radicals ($^{\bullet}OH$), singlet oxygen ($^1O_2$), oxy and peroxy radicals ($^{\bullet}RO$, $^{\bullet}ROO$), superoxide radical anions ($O_2^{\bullet -}$) and peroxides ($H_2O_2$) [72].

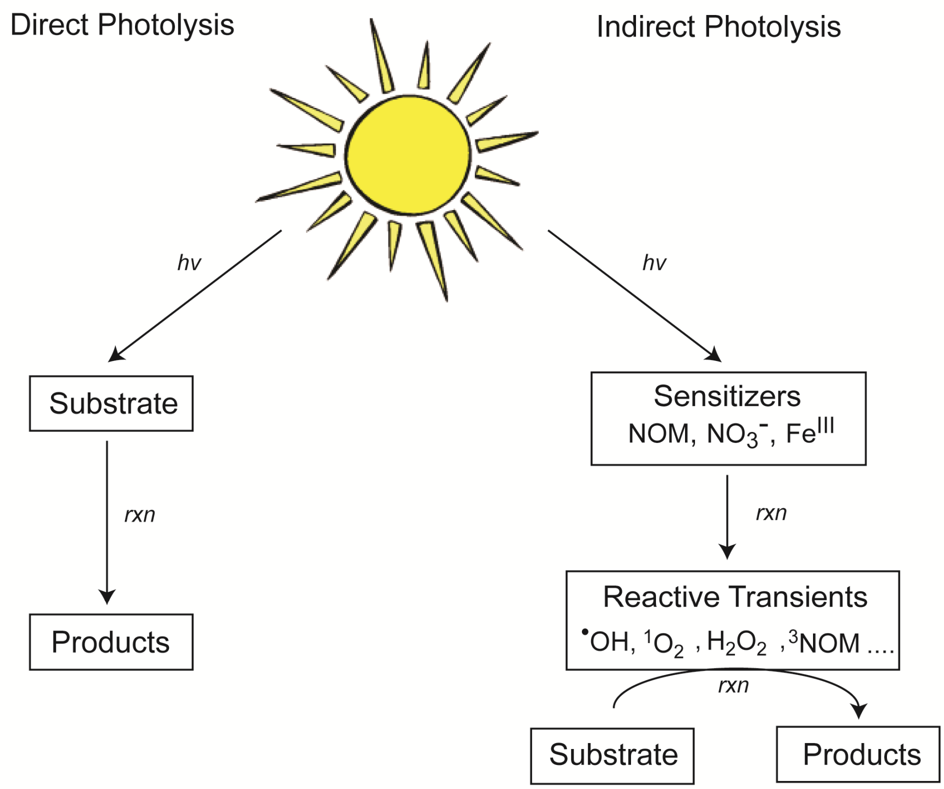



**Figure 2-3:** Fundamental pathways for direct and indirect photochemical degradation.

*Aqueous Photolysis of TCS and CTDs.* Direct photochemical degradation has been shown to be a major removal mechanism of TCS and CTDs in aqueous environments [26,33,37,75-78]. Buth et al. [26], for example, investigated the photochemical fate of these compounds in river and pure, buffered waters. Results from the study demonstrated that the pH-dependent speciation of TCS and CTDs greatly affects their photochemistry. Phenolate forms were found to degrade 44 to 584 times faster than their phenol conjugates, primarily due to a greater spectral overlap with sunlight irradiance. With p$K_a$ values ranging from 5.9-7.6, a substantial fraction of TCS and CTDs will be in the phenolate form in surface waters (pH 6-9), leading to a high potential for photodegradation. Moreover, experiments conducted in river water (pH 8.2) indicated that indirect photochemical reactions with reactive transients are negligible when compared to direct photolysis.

Several studies have confirmed that photolysis is an important loss mechanism for TCS at the field scale [33,37,45,79]. Tixier et al. [45] found that direct photolysis accounted for 80% of total TCS removal from Lake Greifensee during summer and early fall. Similarly, Morrall et al. [79] documented a TCS half-life of 11 hrs in a wastewater-impacted river, leading to a 78% reduction over an 8 km reach. Photolysis half-lives for TCS on the order of 1-10 days were estimated for a number of global water bodies during summer months [45]. Degradation rates, in general, are greatly dependent on a series of environmental factors, including latitude, season, time of day, and water chemistry (e.g. pH, turbidity).

*Formation of Polychlorinated dibenzo-p-dioxins (PCDDs).* Concern has grown about potential deleterious photoproducts derived from TCS and CTDs in the environment. As polychlorinated phenoxyphenols, these compounds are susceptible to photochemical cyclization, leading to the production of polychlorinated dibenzo-*p*-dioxins (PCDDs) [80-83]. A number of studies have confirmed that the direct photolysis of TCS in pure and natural water yields a specific PCDD congener: 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD) [26,75-78]. Similarly, 4-Cl-TCS, 6-Cl-TCS, and 4,6-Cl-TCS have been show to produce 2,3,7-trichlorodibenzo-*p*-dioxin (2,3,7-TriCDD), 1,2,8-trichlordibenzo-*p*-dioxin (1,2,8-TriCDD), and 1,2,3,8-tetrachlorodibenzo-*p*-dioxin (1,2,3,8-TCDD), respectively [26] (Figure 2-4). Photochemical yields of these PCDDs from TCS and CTDs vary with experimental conditions, but generally range from 0.5-3% [26,75].

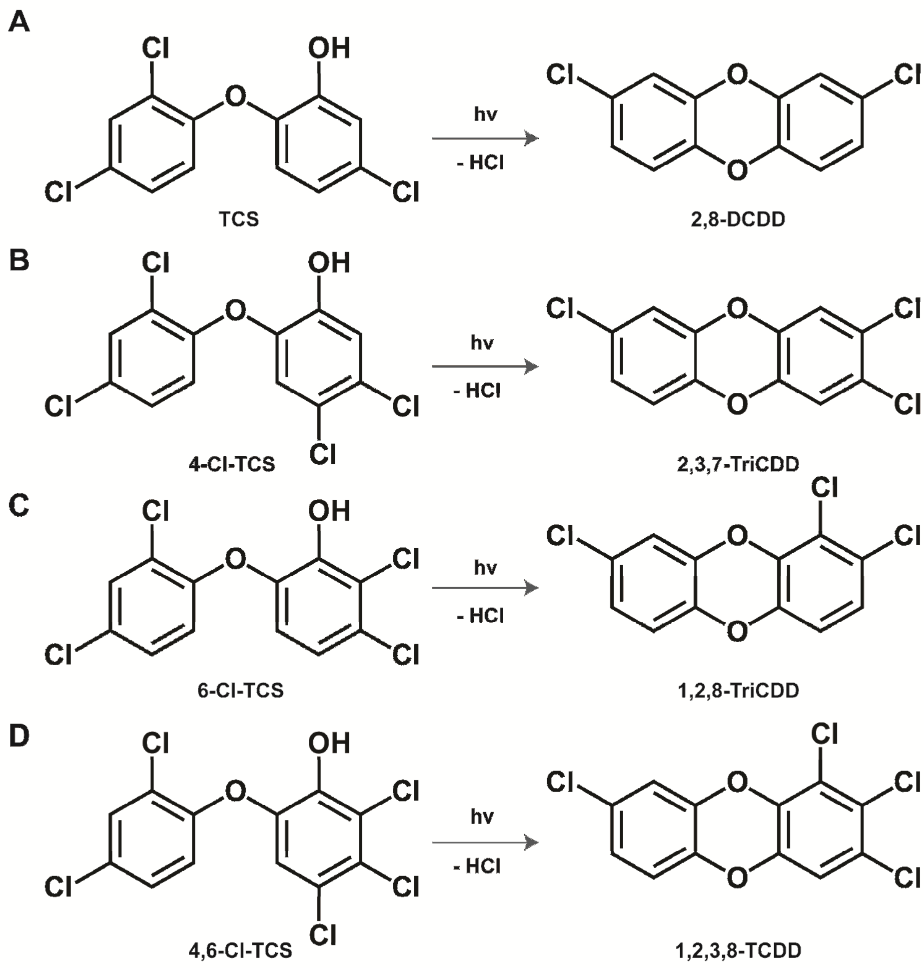



**Figure 2-4:** Formation of PCDDs from the direct photolysis of TCS and CTDs. (A) TCS → 2,8-DCDD, (B) 4-Cl-TCS → 2,3,7-TriCDD, (C) 6-Cl-TCS → 1,2,8-TriCDD, (D) 4,6-Cl-TCS → 1,2,3,8-TCDD.

PCDDs are among a class of 210 chlorinated tricyclic aromatic compounds that are known to be persistent in the environment. Due to their hydrophobicity and resistance to metabolism, PCDDs tend to bioaccumulate in animals and humans [84-87]. Several congeners have been found to be toxic, carcinogenic, mutagenic, and cause adverse effects on animal reproductive systems [86]. These effects are magnified with increased chlorine substitution of PCDDs in the lateral positions, where 2,3,7,8-TCDD is the most toxic congener (Figure 2-5). Although toxicity data for TCS and CTD derived PCDDs is lacking, two of the four congeners (2,3,7-TriCDD, 1,2,3,8-TCDD) have three lateral positions filled. Thus, TCS derived dioxins may pose a risk to aquatic environments.

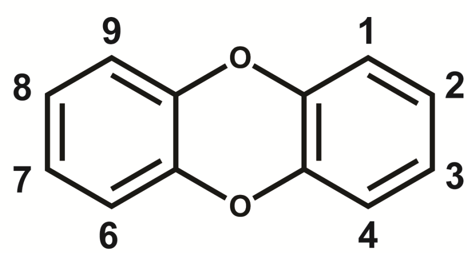



**Figure 2-5:** General structure of PCDDs. Toxicity of congeners increase with chlorines substituted in the lateral positions (2, 3, 7, or 8).

Historically, the dominant source of PCDDs has been attributed to two major processes: combustion and chemical production. Municipal and industrial incineration, forest fires, and vehicle exhaust comprise the majority of the combustion source. PCDDs produced in chemical production are generally derived from the manufacturing of chlorinated organic compounds (e.g. pentachlorophenol (PCP) or herbicides). The production of paper products from chlorine bleached wood pulp and metal smelting have also been recognized as important PCDD sources [88].

Since the 1970s, PCDD emissions from incineration and chemical production sources have been reduced, primarily due to regulation by the U.S. EPA [89,90]. Recent studies, however, have illustrated that TCS and CTD derived PCDDs are accounting for an increasing fraction of total dioxin loading to the environment. A pivotal study by Buth et al. [47] recently found that up to 31% of the total PCDD loading in Lake Pepin sediment is attributed to TCS and CTDs. This substantial load of PCDDs from a single antimicrobial is a direct input into the aquatic environment. Thus, further investigation is warranted on the impacts of TCS, CTDs, and their derived PCDDs on wastewater-impacted aquatic systems.

## Chapter 3: Quantification of Triclosan, Chlorinated Triclosan Derivatives, and their Dioxin Photoproducts in Lacustrine Sediment Cores.

### 3.1 Introduction and Objectives

Triclosan (TCS) is a common antimicrobial found in a wide array of personal care products, including liquid handsoaps, bar soaps, and plastics [29-31]. Up to 96% of TCS in these personal care products is washed down the drain during normal use, leading to concentrations on the order of 1-10 μg/L in wastewater treatment plant (WWTP) influent [11,24,25,33-37]. Although WWTPs with conventional activated sludge treatment typically remove > 90% of TCS through sorption to biosolids or biodegradation, a significant amount persists through treatment and into surface waters [8,11]. As a lipophilic compound, TCS has been shown to bioaccumulate in organisms in natural waters [50,52,54]. Moreover, environmentally relevant TCS concentrations have the potential to induce major changes in the community structure of primary producers, and thus, influence higher trophic levels in an aquatic ecosystem [51,53,57].

During the disinfection of water and wastewater with free-chlorine, TCS can be chemically transformed to a series of chlorinated triclosan derivatives (CTDs) [20-23]. Electrophilic addition of chlorine on the *ortho* and *para* positions of the TCS phenolic moiety has been shown to yield three CTD congeners: 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol (4-Cl-TCS), 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol (6-Cl-TCS), and 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol (4,6-Cl-TCS). Upon formation in wastewater, TCS and CTDs are discharged into surface waters, where they are susceptible to photochemical transformation.

Direct photolysis is the primary mechanism by which TCS and CTDs are photochemically transformed in surface waters [26,75,76]. Several studies have observed that TCS and CTDs undergo a cyclization reaction, yielding a suite of polychlorinated dibenzo-*p*-dioxins (PCDDs) in natural waters. Specifically, TCS has been documented to form a specific PCDD congener: 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD) [26,75-78]. Furthermore, 4-Cl-TCS, 6-Cl-TCS, and 4,6-Cl-TCS yield 2,3,7-trichlorodibenzo-*p*-dioxin (2,3,7-TriCDD), 1,2,8-trichlordibenzo-*p*-dioxin (1,2,8-TriCDD), and 1,2,3,8-tetrachlorodibenzo-*p*-dioxin (1,2,3,8-TCDD), respectively [26]. Because PCDDs are a class of compounds known to be toxic and carcinogenic in the environment, their production from TCS and CTDs is of clear concern [86].

The aim of this study was to investigate the depositional trends of TCS, CTDs, and their derived PCDDs in sediment cores from an array of wastewater-impacted Minnesota (MN) lakes. Due to their hydrophobicity, these compounds tend to sorb to suspended sediment and deposit in the sedimentary record. Thus, sediment cores provide a useful proxy for evaluating the exposure of an aquatic ecosystem to TCS, CTDs, and their PCDDs over time. Cores were collected in large and small scale aquatic systems with varying degrees of wastewater impaction. Furthermore, changes in historical treatment practices at relevant WWTPs were probed to evaluate how they influenced the trends of TCS, CTDs, and their PCDDs in the sediment record. Finally, the contribution of TCS and CTD derived PCDDs to total PCDD loading and toxicity was evaluated for each lake system.

## 3.2 Experimental

### 3.2.1 Chemicals and Laboratory Procedures

*Chemicals and Materials.* TCS (>97%) was purchased from Sigma-Aldrich. $^{13}C_{12}$-triclosan ($^{13}C_{12}$-TCS; >99% chemical and isotopic purity) was obtained in methanol from Wellington Laboratories. The three chlorinated triclosan derivatives (CTDs), 4-Cl-TCS, 6-Cl-TCS, and 4,6-Cl-TCS were synthesized and purified by Matthew Grandbois, Ph.D. (see [43]). All polychlorinated dibenzo-*p*-dioxin (PCDD) standards were purchased by Pace Analytical Services, with the exception of select congeners. Solutions of 2,8-DCDD and 2,3,7-TriCDD (50 μg/mL) in isooctane were purchased from AccuStandard. A mixture of 1,2,3,7/1,2,3,8-TCDD (50 μg/mL) in *n*-nonane was obtained from Cambridge Isotopes, along with $^{13}C_{12}$-2,3-DCDD (99% chemical and isotopic purity; 50 μg/mL) and $^{13}C_{12}$-2,3,7-TriCDD (99% chemical and isotopic purity; 50 μg/mL). Sulfuric acid ($H_2SO_4$) and sodium hydroxide (NaOH) were purchased from BDH. Ultrapure water (18.2 MΩ-cm) was obtained from a Millipore Simplicity UV purification system. All solvents used for extractions and cleaning were of HPLC grade, with the exception of methyl-*tert*-butyl-ether (MTBE). MTBE was purchased from Sigma-Aldrich at >99% purity. Ottawa sand (OS) was acquired from Fisher Scientific. Ultra-high purity and industrial-grade nitrogen were purchased through Matheson.

*Laboratory Cleaning Procedures.* To prevent analyte cross-contamination and carryover in the laboratory, a specific set of cleaning procedures were required for glassware, tools, and instrumentation. Appendix A in this thesis provides a detailed description of these cleaning procedures for TCS and CTD analysis.

### 3.2.2 Sediment Core Collection

*Coring Locations.* To characterize the impact of TCS, CTDs, and their derived PCDDs on regional lake systems, sediment cores were collected from eight sampling sites around Minnesota (MN) (Figure 3-1). Differential global positioning system (dGPS) coordinates are provided for each site in Table 3-1.

From July to August 2010, cores were collected from two fluvial lakes: Lake Pepin and Lake St. Croix. Lake Pepin is 34 km-long wastewater-impacted depositional zone along the Mississippi River. With a watershed of over 122,000 km$^2$, Lake Pepin drains approximately two-thirds of the state of MN and integrates many wastewater sources. The Metropolitan WWTP in St. Paul, MN is a major wastewater source in this watershed, serving approximately 1.8 million people and discharging up to 251 million gallons per day (MGD) directly into the Mississippi River. Lake St. Croix is an impacted depositional zone along the St. Croix River that drains approximately 20,000 km$^2$. The major wastewater source in this system is from the St. Croix Valley WWTP in Stillwater, MN, a facility serving 30,000 people and discharging up to 4.5 MGD.

**Table 3-1:** Differential global positioning system (dGPS) coordinates for sediment core locations.

| Sediment Core | GPS Coordinates | |
|---|---|---|
| Lake St. Croix | 44° 56.858' N | 92° 45.325' W |
| Lake Pepin | 44° 29.987' N | 92° 17.653' W |
| East Lake Gemini | 45° 35.445' N | 94° 23.493' W |
| Lake Winona | 45° 52.425' N | 95° 24.350' W |
| Duluth Harbor | 46° 43.996' N | 92° 3.920' W |
| Lake Superior | 46° 49.059' N | 91° 51.820' W |
| Lake Shagawa | 47° 54.685' N | 91° 53.382' W |
| Lake Little Wilson | 47° 39.421' N | 91° 4.227' W |

To assess the impact of wastewater on smaller-scale aquatic systems, two lakes were cored in central MN during September 2010. One core was collected from East Lake Gemini, a 0.1 $km^2$ artificial impoundment that receives wastewater from St. Johns University (SJU) near Collegeville, MN. The SJU WWTP serves a population of 1200 during the summer and 2600 during the academic year. Wastewater discharge correspondingly varies throughout the year, with a maximum discharge of 0.23 MGD. Lake Winona, a natural lake of similar size (0.85 $km^2$), was cored near Alexandria, MN. The Alexandria Lakes Area Sanitation District (ALASD), which serves 23,000 people, discharges up to 3.8 MGD directly into Lake Winona.


**Figure 3-1:** Sediment coring sites in MN.

In October 2010, sediment cores were collected in Duluth Harbor and Lake Superior. The Duluth Harbor core was obtained in St. Louis Bay, near the outfall of the Western Lake Superior Sanitation District (WLSSD) wastewater facility. WLSSD is a large treatment plant that treats up to 40 MGD, serving approximately 130,000 people in the Duluth, MN area. Approximately half of the wastewater treated by WLSSD is derived from industrial sources. The City of Superior, with a population of 27,000, also discharges approximately 4-5 MGD of wastewater into this aquatic system. The Lake Superior core was collected 22 km northeast of St. Louis Bay on the RV Blue Heron, a research vessel affiliated with the Large Lakes Observatory.

Finally, the last two cores were collected in June 2011 on two lakes near the Boundary Waters Canoe Area (BWCA) in MN. One core was acquired at Lake Shagawa, a 9.4 $km^2$ water body that is the receiving water for the Ely, MN WWTP. The Ely WWTP discharges 1.5 MGD from a population of 3500. The last core was collected from Little Lake Wilson, a reference lake with no wastewater input and little anthropogenic contact.

*Core Collection Methods.* All sediment cores, with the exception of Lake Superior, were collected using a piston corer with a polycarbonate barrel operated from the water surface. The Lake Superior core was collected on the RV Blue Heron using an Ocean Instruments Multicorer. Upon collection, cores were vertically extruded and sectioned at designated intervals. Down-core smearing was removed from the outer circumference of each interval to prevent analyte drawdown in the core. Sections were transferred to baked glass jars, homogenized, and sub-sampled for radiometric dating. Jars were then covered with foil, cooled to 4°C, and frozen within 24 hours of collection.

One core (Lake Pepin) was transported to the Limnological Research Center (LRC) at the University of Minnesota for magnetic susceptibility analysis (see Section 3.2.3 – Radiometric Dating). The core was then sub-sampled using the aforementioned procedures.

Prior to radiometric dating or analyte extraction, loss-on-ignition (LOI) was preformed on each sediment core. Standard LOI techniques were applied to determine sediment dry density, water content, and weight percentage of organics and carbonate [91,92]. Briefly, core intervals were homogenized and sub-sampled into crucibles. Samples were sequentially dried for 12 hours at 105°C, 4 hours at 550°C, and 2 hours at 1000°C to determine sample water content, organic percent, and carbonate percent, respectively.

### 3.2.3 Radiometric Dating

*Lead-210 and Cesium-137 Dating.* Sediment cores were dated using lead-210 ($^{210}Pb$) and cesium-137 ($^{137}Cs$) methods, as described in recent literature [93,94]. Briefly, $^{210}Pb$ activity is measured through its granddaughter product, polonium-210 ($^{210}Po$), in 15-20 sections of each core. $^{210}Po$ is quantified using isotope-dilution methodology, with polonium-209 ($^{209}Po$) as an internal recovery surrogate. $^{210}Po/^{209}Po$ are distilled from dry sediment and analyzed via alpha spectrometry [94]. Total $^{210}Pb$ in the core profile is used to determine radiometric dates and sedimentation rates through the constant rate of supply (CRS) model [93].

To supplement $^{210}Pb$ dating, $^{137}Cs$ activity was measured in 6-10 sections in each core using gamma spectrometry. $^{137}Cs$ is a particularly useful radioactive isotope, as it is derived from above-ground nuclear testing. A spike of $^{137}Cs$ in the sedimentary record is known to directly correlate with the peak of testing, between 1963 and 1964. Thus, provided that a sediment profile is relatively undisturbed, $^{137}Cs$ provides a useful marker for core dating [94].

*Magnetic Susceptibility.* Many sediment cores have been collected and radiometrically dated in Lake Pepin. Moreover, several of these cores have been analyzed for magnetic susceptibility, where stratigraphic variations in ferromagnetic mineral concentrations are measured. The current Lake Pepin core was dated by conducting whole-core magnetic susceptibility measurements using a Geotek LTD multisensory core logger in the LRC. The susceptibility profile was matched to those from recently dated cores in the same depositional area of the lake, providing a dating profile for the current core.

### 3.2.4 Triclosan (TCS) and Chlorinated Triclosan Derivative (CTD) Analysis

Wet samples, corresponding to 10 g dry weight from each core interval, were freeze dried for 3-5 days at the LRC or the St. Croix Watershed Research Station (SCWRS). Dried samples were subsequently transferred to 150 mL beakers. Each sample was spiked with a dilute solution of $^{13}C_{12}$-TCS (500 ng in 1 mL of acetonitrile (ACN)) as an isotope-dilution surrogate for TCS and CTD recovery. For each core, a method blank (freeze dried Ottawa sand) was spiked with $^{13}C_{12}$-TCS and processed to ensure there was no analyte contamination. Spiked samples were covered with foil and allowed to equilibrate for 12 hours prior to extraction.

*Accelerated Solvent Extraction.* Following equilibration, samples were extracted on a Dionex Model 350 accelerated solvent extractor (ASE 350) (Sunnyvale, CA, USA). Briefly, samples were transferred to 22 or 66 mL stainless steel ASE cells. To provide cleaner extracts, two glass fiber filters were placed at the base of each ASE cell. Sediment was loaded into the cell and mixed with baked Ottawa sand. Any remaining void volume was filled with baked Ottawa sand. Finally, a single glass fiber filter was placed at the top and the cell was sealed for extraction.

Table 3-2 provides optimized parameters for $^{13}C_{12}$-TCS, TCS, and CTD extraction on the ASE 350. HPLC grade dichloromethane (100% DCM) was determined to be the most appropriate extraction solvent.

**Table 3-2:** Optimized parameters for $^{13}C_{12}$-TCS, TCS, and CTD extraction from sediment on the ASE 350.

| ASE 350 Parameter | Optimized Value |
|---|---|
| Temperature | 100 °C |
| Extraction Pressure | 1500 psi |
| Cell Heat Time | 5 mins |
| Cell Static Time | 5 mins |
| Rinse Volume | 100% |
| Purge Time | 100 s |
| Extraction Cycles | 2 |

During a typical extraction cycle, sample cells are loaded into an oven, filled with solvent, and subsequently pressurized and heated. After a designated static time, solvent is then purged from the cell with ultra-high purity nitrogen ($N_2$) into a 250 mL collection vessel. Two extraction cycles were performed to (1) maximize $^{13}C_{12}$-TCS, TCS, and

CTD recovery in complex sediment matrices, and (2) minimize the presence of common interferences (e.g. NOM) in the final ASE extract.

Due to a wide range of organic content in the sediment cores collected (Table 3-3), two separate clean-up methods were developed for ASE extracts (Figure 3-2). Methods 1 and 2 were designed for cores with high (17-40%) and low (6-16%) organic content, respectively. These methods were modified from Buth [43] to accommodate the range of sediment matrices in this study.

**Table 3-3:** Mean organic content of sediment cores. Organic content data are derived from LOI results.

| Sediment Core | Mean Organic Content (%) |
|---|---|
| Lake Superior | 6 |
| Duluth Harbor | 10 |
| Lake Pepin | 12 |
| Lake St. Croix | 16 |
| Lake Winona | 17 |
| Lake Shagawa | 26 |
| East Lake Gemini | 29 |
| Lake Little Wilson | 40 |

**Method 1 – High Organic Content.** For sediments with high organic content, extracts were cleaned up on solid-phase extraction (SPE) cartridges and silica columns.

*Solid-Phase Extraction.* SPE cleanup was performed using Waters Oasis HLB 6 cc/200 mg cartridges. Prior to cleanup, ASE extracts were sub-sampled (1/5 aliquot by mass; ~ 15 mL by volume; ~ 2 g dry sediment weight), transferred to 17 mL glass centrifuge tubes, and blown down to dryness with industrial-grade $N_2$. Samples were then resuspended in 500 μL of methanol (MeOH) and dissolved in 30 mL of pH 4 water ($H_2O$) adjusted with $H_2SO_4$/NaOH. A pH of 4 was selected to keep ≥ 99% of TCS and

CTDs in their neutral, phenol form, maximizing retention on lipophilic moieties in the SPE media.

Before sample loading, SPE cartridges were preconditioned with sequential 5 mL aliquots of MTBE, MeOH, and pH 4 $H_2O$ on a Restek 12-port vacuum manifold. Transfer lines between samples and cartridges were also washed with 10 mL aliquots of MTBE, MeOH, and pH 4 $H_2O$ to remove potential analyte contamination prior to use. Samples were then loaded onto cartridges at 2 mL/min. After loading, cartridges were washed with three sequential 5 mL aliquots of 50:50 MeOH:$H_2O$ (v/v) to remove polar DOM from the SPE media. Cartridges were then dried for 20-25 minutes by vacuum and eluted sequentially with 5 mL of MeOH and 5 mL of 90:10 MTBE:MeOH (v/v) into 15 mL centrifuge tubes. Final SPE extracts were blown down to ~ 500 µL with industrial-grade $N_2$ and prepped for silica column cleanup.

*Silica Column Cleanup.* Silica columns were prepared in 6 mL disposable syringes for further sample cleanup. Each column was packed with a plug of glass wool, a thin layer of baked Ottawa sand, 2 g of baked silica gel (60 – 200 µm particle size, 60 Å pore size), and an upper layer of baked sand. Prior to sample loading, each column was flushed with 10 mL of ethyl acetate to precondition the silica gel and remove any potential analyte contamination. SPE extracts were then quantitatively loaded onto the column and eluted by gravity with 12 mL of ethyl acetate. Final extracts were blown down to dryness with industrial-grade $N_2$ and resuspended in 200 µL of 50:50 ACN:$H_2O$ (v/v). 150 µL of the final extract was transferred via gas-tight syringe to amber autosampler vials with 200 µL inserts. Vials were then wrapped with Teflon tape and stored at 4 °C until analysis.

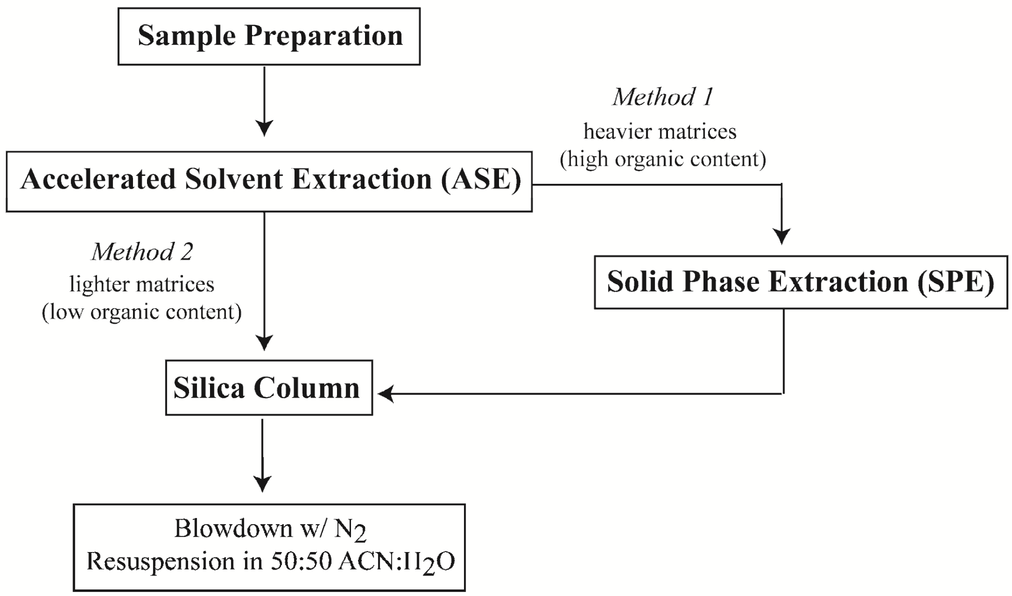



**Figure 3-2:** Cleanup procedure for ASE extracts. Methods 1 and 2 were designed for sediments with high and low organic contents, respectively.

**Method 2 – Low Organic Content.** ASE extracts from sediments with low organic content were cleaned up exclusively with silica gel columns. Namely, subsamples of ASE extracts were transferred to 17 mL glass centrifuge tubes, blown down to dryness with industrial-grade $N_2$, and suspended in ~500 μL of 55:45 MeOH:MTBE (v/v) (the final eluent compostion from the SPE step in Method 1). These extracts were the cleaned up on silica columns, blown down to dryness, and resuspended as in Method 1.

To assess the efficacy of Methods 1 and 2 for extracting TCS and CTDs in the given sediment matrices, a series of spike and recovery experiments were executed. Extractions were performed in triplicate on baked Ottawa sand and sediment from the base of the Lake Superior, Lake Pepin, and Lake Shagawa cores. Samples (10 g dry weight) were spiked with 500 ng $^{13}C_{12}$-TCS, 100 ng TCS, and 12 ng of each CTD in a 1 mL dilute solution of ACN. Method blanks, spiked with 500 ng $^{13}C_{12}$-TCS, were extracted concurrently for each matrix. The Ottawa sand, Lake Superior (low organic content), and Lake Pepin (medium organic content) were extracted with Method 2, while Lake Shagawa (high organic content) was extracted with Method 1. Spike and recovery results from each matrix are provided in Table 3-6 in Section 3.3.1.

*LC-MS-$Q^3$ Analysis.* Sediment core extracts in this study were analyzed on an Agilent 1100 capillary HPLC equipped with a Finnigan TSQ Quantum Discovery MAX MS-$Q^3$ tandem mass spectrometer. Analyte separation was achieved with 8 μL sample injections on a Phenomenex Synergi MAX-RP reverse-phase column (150 × 0.5 mm, 4 μm particle size, 80 Å pore size) maintained at 30 °C during sample runs. A flow rate of 10 μL/min was established with a binary gradient of (A) 15 mM ammonium acetate buffer, and (B) 100% HPLC grade ACN. The gradient began at 50% B, ramped to 100% B over 20 mins, and then ramped down to 50% B from 20 to 23 minutes. 50% B was maintained from 23 to 35 minutes to allow for column re-equilibration. Column effluent was diverted to waste during first and last 10 minutes of each sample run to minimize contamination of the MS-$Q^3$ ion source.

$^{13}C_{12}$-TCS, TCS, and CTDs were quantified using selected reaction monitoring (SRM) in negative electrospray ionization ($ESI^-$) mode on the MS-$Q^3$. Specific precursor and product mass-to-charge (*m/z*) ratios were selected for optimal sensitivity (Table 3-4).

**Table 3-4:** Selected reaction monitoring (SRM) transitions for $^{13}C_{12}$-TCS, TCS, and CTD quantification and confirmation.

| Analyte | Precursor Ion (*m/z*) | | Product Ion (*m/z*) | Role of *m/z* |
|---|---|---|---|---|
| TCS | 287 | → | 35 | quantification |
| | 289 | → | 37 | confirmation |
| 4-Cl-TCS | 321 | → | 35 | quantification |
| | 323 | → | 37 | confirmation |
| 6-Cl-TCS | 321 | → | 35 | quantification |
| | 323 | → | 37 | confirmation |
| 4,6-Cl-TCS | 355 | → | 35 | quantification |
| | 357 | → | 37 | confirmation |
| $^{13}C_{12}$-TCS | 299 | → | 35 | quantification |

In the MS-$Q^3$, precursor ions are selected by the first quadrupole. These precursor ions are then further fragmented, producing product ions that are detected by the third quadrupole. Buth [43] found that chloride ion ($^{35}Cl^-$; *m/z* 35) was the dominant product ion for TCS and CTDs. Thus, SRM transitions with $^{35}Cl^-$ as the product ion were selected for analyte quantification. Furthermore, SRM transitions corresponding to $^{37}Cl^-$, the second most common isotope of $Cl^-$, were monitored for analyte confirmation. Prior to running on the MS-$Q^3$, a high concentration of $^{13}C_{12}$-TCS (20 mg/L) was directly infused into the ion source to tune the instrument for the analytes of interest. Furthermore, to maximize analyte response on the MS-$Q^3$, a clean ion transfer tube was preconditioned with existing sediment extracts. The rational for this procedure is discussed in Appendix B.

*Analyte Quantification and Quality Control.* Calibration standards for LC-MS-$Q^3$ analysis were prepared in 50:50 ACN:$H_2O$ (v/v) over a range of TCS and CTD concentrations. A constant concentration of $^{13}C_{12}$-TCS was maintained in each standard.

Seven to eight point calibration curves were prepared by plotting the ratio of analyte to $^{13}C_{12}$-TCS peak area (y-axis) as a function of analyte concentration (x-axis). From these calibration curves, a response factor was obtained for each analyte. This response factor was then (1) multiplied by the analyte to $^{13}C_{12}$-TCS peak area ratio in the sediment matrix and, (2) the amount of $^{13}C_{12}$-TCS (in g) in the spiked sample. By using isotope-dilution methodology, this provides the amount of analyte (in g) in the sediment sample. Moreover, to assess the efficacy of individual extractions, the absolute $^{13}C_{12}$-TCS recovery was determined for each sample. Detailed information on the calculation of analyte concentrations and $^{13}C_{12}$-TCS absolute recovery is provided in Appendix C.

Several quality assurance/quality control (QA/QC) measures were followed when processing samples and running extracts on the LC-MS-$Q^3$. As indicated in the extraction procedure, method blanks, along with spike and recovery experiments, were prepared to test method performance. Furthermore, instrument blanks of 50:50 ACN:$H_2O$ (v/v) were run every 8 samples during LC-MS-$Q^3$ analysis to monitor for analyte carryover between LC injections. To calculate sediment concentrations in each core, a series of criteria were established to determine the limit of quantification (LOQ) of each analyte. These criteria include: (1) the analyte signal-to-noise ratio must be > 10 within the sediment matrix, (2) the analyte concentration must be 10 times higher than that in the method and instrument blanks, and (3) analyte quantification can only occur above the lowest calibration point in its respective calibration curve.

### 3.2.5 Polychlorinated dibenzo-p-dioxin (PCDD) and furan (PCDF) Analysis

Between 7 and 12 g (dry weight) of each core interval was analyzed for PCDD/F congeners at Pace Analytical in Minneapolis, MN. East Lake Gemini was an exception, where between 1 and 2 g (dry weight) was processed. For all cores, samples were spiked with nineteen $^{13}C_{12}$-labeled di- through octa-CDD/F isomers as isotope-dilution surrogates and analyzed using an expanded version of U.S. EPA Method 1613B [95]. Although the presence of PCDF isomers is not specifically investigated in this study, they were quantified in the sediment cores as part of Method 1613B standard procedures.

Once spiked with labeled recovery surrogates, each sample was extracted with toluene for at least 18 hours using a Soxhlet/Dean Stark apparatus. Extracts were subsequently spiked with $^{37}Cl_4$-2,3,7,8-TCDD to measure the efficiency of sample cleanup. Soxhlet/Dean Stark extracts were concentrated using a Snyder column, back-extracted with concentrated $H_2SO_4$ and NaOH, and eluted through multi-layer silica columns (2 g neutral silica, 4 g acidic silica, and 2 g basic silica) with hexane. Eluates were then added to 4 g activated aluminum oxide ($Al_2O_3$) columns and eluted with 60:40 DCM:hexane (v/v). After solvent exchange into hexane, $Al_2O_3$ column eluates were cleaned up via carbon chromatography, where samples were passed through 0.5 g of 18% activated carbon mixed with Celite. These columns were preconditioned with 5 mL of toluene, 2 mL of 75:20:5 DCM:MeOH:toluene (v/v/v), 2 mL of 50:50 DCM:cyclohexane (v/v), and 5 mL of hexane. Sample extracts were added to the column and flushed in the forward direction with 2 mL of 50:50 DCM:cyclohexane (v/v) and 2 mL of 75:20:5 DCM:MeOH:toluene (v/v/v) to remove potential interfering compounds. Finally, analytes were washed off the column in the reverse direction with 10 mL of toluene.

The toluene was then concentrated, spiked with $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as recovery standards, and concentrated to a final volume of 40 μL.

*HRGC-HRMS Analysis.* PCDD/F analysis was performed using high-resolution gas chromatography-high-resolution mass spectrometry (HRGC-HRMS). Aliquots of final extracts (1 μL) were injected into an HP 5890 gas chromatograph with a split/splitless injector and a 60 meter DB-5MS capillary column (0.25 mm ID × 0.25 μm film). The gas chromatograph was coupled to a Waters Autospec Ultima high-resolution mass spectrometer operated in selected ion monitoring (SIM) mode (positive electron impact, > 10,000 resolution, 32 eV, 280 °C). Acquisition windows were set to include all tetra- through octa-CDD/F isomers. Windows for di- and tri-CDD/F isomers were centered around the di- and tri-CDD congeners in this study. Therefore, total DCDD and TriCDD values presented should be considered an estimate, as the first and last DCDD and TriCDD eluters may have been outside the established acquisition windows for these isomers.

*Analyte Quantification and Quality Control.* Standards for HRGC-HRMS analysis were prepared using a U.S. EPA Method 1613B calibration set (tetra- through octa-CDD/F isomers). A secondary calibration set for di- and tri-CDD/Fs was prepared at similar levels to tetra-CDD/F in the Method 1613B. From these calibration sets, five-point calibration curves were constructed for each PCDD/F congener, with constant levels of $^{13}C_{12}$-PCDD/F internal standards.

Analogous to the TCS and CTD analysis method, a series of QA/QC procedures were followed during PCDD/F analysis. Method blanks were prepared to demonstrate freedom of analyte contamination during sample extraction and cleanup. Furthermore, spike and recovery experiments in clean sand and sediment were performed to validate the PCDD/F extraction method for each sediment core. Finally, all reported PCDD/F concentrations were required to be 10 times greater than levels in method blanks.

## 3.3 Results and Discussion

### 3.3.1 Analytical Method Performance

*TCS and CTD Sediment Extraction.* The LC-MS-$Q^3$ method for TCS and CTD quantification provided satisfactory peak shape and effectively separated the analytes of interest in all chromatograms. Figures 3-3 and 3-4 illustrate example chromatograms from a representative standard and Lake Pepin sediment extract, respectively. In all cases, the CTDs eluted later than $^{13}C_{12}$-TCS and TCS due to their greater hydrophobicity. TCS and CTD calibration curves were linear, with $R^2$ values consistently ≥ 0.99 for each analyte. Two calibration curves for 4,6-Cl-TCS had $R^2$ values > 0.98.

For each sediment core, trace amounts of TCS were detected in method and instrument blanks. Reported TCS sediment concentrations were at least 10 times greater than those observed in the blanks. In all cases, CTDs were not detected in procedural blanks. All reported CTD concentrations, therefore, were required to be above the lowest point in their respective calibration curves. Finally, the raw analyte signal-to-noise ratio was always > 10 for any reported TCS or CTD concentration. Using these criteria, LOQs ranging from 0.36 to 0.9 ng/g (TCS) and 60 to 70 pg/g (CTDs) were achieved.

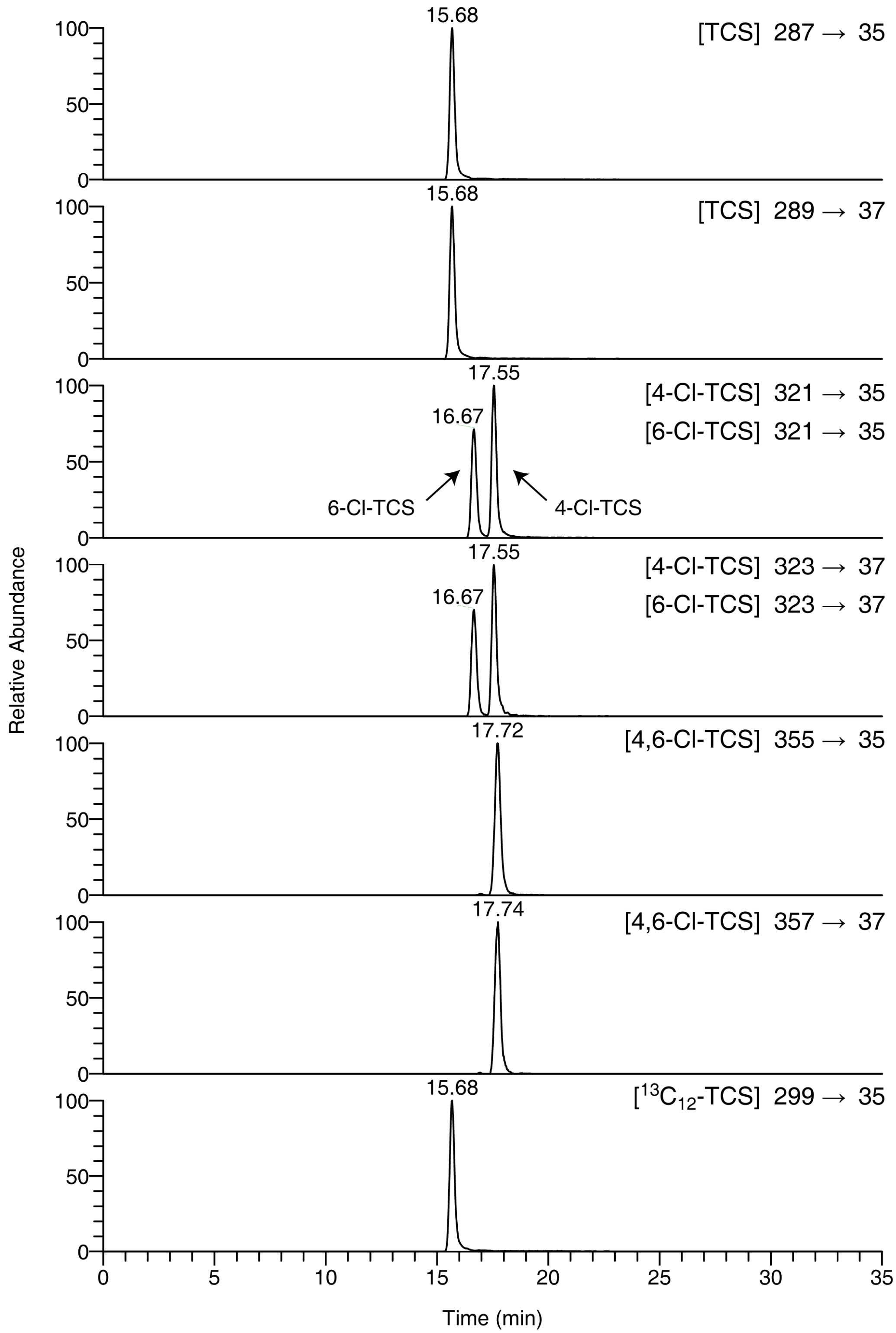



**Figure 3-3:** LC-MS-$Q^3$ chromatograms of $^{13}C_{12}$-TCS, TCS, and CTD SRM transitions in a representative standard. Analyte retention times are displayed above each peak.

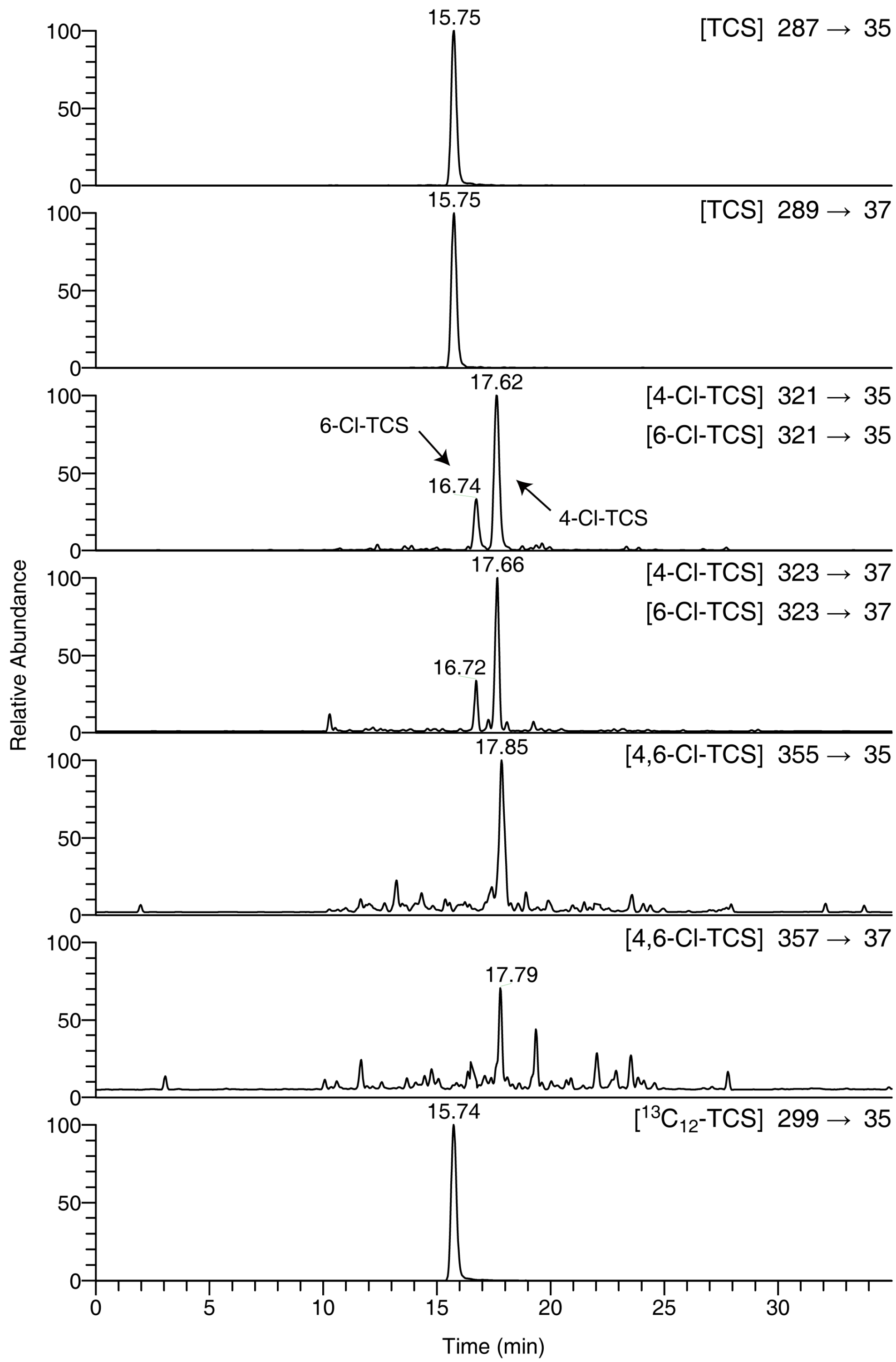



**Figure 3-4:** LC-MS-$Q^3$ chromatograms of $^{13}C_{12}$-TCS, TCS, and CTD SRM transitions in a Lake Pepin sediment extract. Analyte retention times are displayed above each peak.

Due to the wide range of sediment matrices in this study, the absolute recovery of $^{13}C_{12}$-TCS varied significantly (Table 3-5). In cores with high organic content (e.g. Lake Shagawa), the complex matrix and ion-suppression during MS-$Q^3$ analysis induced relatively low $^{13}C_{12}$-TCS recoveries. Higher recoveries were observed in cores with low organic content (e.g. Duluth Harbor), where interferences were less severe.

**Table 3-5:** Absolute recovery of $^{13}C_{12}$-TCS in sediment cores.

| Sediment Core | Absolute Recovery (%) $^{13}C_{12}$-TCS | |
|---|---|---|
| Lake Shagawa | 27 ± 9[a] | (n=12) |
| Lake Little Wilson | 33 ± 7 | (n=10) |
| East Lake Gemini | 36 ± 12 | (n=9) |
| Lake St. Croix | 37 ± 12 | (n=16) |
| Lake Winona | 41 ± 20 | (n=12) |
| Lake Superior | 61 ± 10 | (n=10) |
| Lake Pepin | 78 ± 9 | (n=16) |
| Duluth Harbor | 87 ± 17 | (n=13) |

[a] Reported values are the mean ± standard deviation

Spike and recovery results for sediment extraction procedures (Methods 1 and 2) are presented in Table 3-6. Overall, results demonstrate the utility of isotope-dilution methodology for quantifying TCS and CTDs in a range of sediment matrices. Recovery of TCS, relative to the $^{13}C_{12}$-TCS surrogate, is consistently near 100% for all matrices. Relative CTD recovery, however, generally decreases with increased matrix complexity. This may be attributed to a number of factors, including increased matrix suppression at CTD retention times or a disproportional loss of CTDs relative to $^{13}C_{12}$-TCS and TCS during sample extraction and cleanup.

**Table 3-6:** Relative recovery of TCS and CTDs for extraction Method 1 (Lake Shagawa) and 2 (Ottawa sand, Lake Superior, Lake Pepin).

| | **Absolute Recovery (%)** | **Relative Recovery (%)** | | | |
|---|---|---|---|---|---|
| **Matrix** | **$^{13}C_{12}$-TCS** | **TCS** | **4-Cl-TCS** | **6-Cl-TCS** | **4,6-Cl-TCS** |
| Ottawa sand (n=3) | 60 ± 6[a] | 109 ± 2 | 81 ± 10 | 81 ± 12 | 68 ± 18 |
| Lake Superior (n=3) | 60 ± 2 | 108 ± 3 | 52 ± 4 | 52 ± 7 | 36 ± 3 |
| Lake Pepin (n=3) | 52 ± 3 | 108 ± 7 | 56 ± 3 | 59 ± 9 | 44 ± 4 |
| Lake Shagawa (n=3) | 38 ± 5 | 106 ± 3 | 35 ± 8 | 42 ± 3 | 15 ± 4 |

[a] Reported values are the mean ± standard deviation

*PCDD/F Sediment Extraction.* The sediment extraction and HRGC-HRMS methods employed at Pace Analytical provided consistent PCDD/F recovery in the sediment cores. The absolute recovery of nineteen $^{13}C_{12}$-PCDD/F surrogates ranged from 20 – 116% in sediment extracts, all of which were within the target range specified in Method 1613B (Table 3-7). Moreover, the relative recovery of nineteen native PCDD/F isomers in sand spikes ranged from 74-129%, demonstrating the precision and accuracy of the isotope-dilution methodology.

**Table 3-7:** Absolute recovery range for $^{13}C_{12}$-PCDD/F isomers in sediment cores.

| | **Absolute Recovery (%)** |
|---|---|
| **Sediment Core** | **$^{13}C_{12}$-PCDD/F [a]** |
| Lake Shagawa | 27 - 99 |
| Lake Little Wilson | 20 - 112 |
| East Lake Gemini | 44 - 98 |
| Lake St. Croix | 30 - 107 |
| Lake Winona | 28 - 85 |
| Lake Superior | 47 - 116 |
| Lake Pepin | 34 - 101 |
| Duluth Harbor | 29 - 107 |

[a] 19 isotopically labeled di- through octa-CDD/F isomers

Spike and recovery experiments were performed in duplicate on all sediment matrices, with the exception of East Lake Gemini. East Lake Gemini spikes were fouled during extraction and are currently being reprocessed. Relative recovery of native PCDD/F isomers ranged from 72 – 126% with relative percent differences ranging from 0 – 14.2% for individual analytes between duplicate matrix spikes (Table 3-8). One recovery outlier was observed in the Little Lake Wilson core, where 2,8-DCDD exhibited a maximum relative recovery of 238%. The same PCDD congener, however, consistently exhibited relative recoveries ranging from 102-117% in sand spikes and 89-124% in other core matrices. Thus, it is likely that interference around the 2,8-DCDD retention time in Little Lake Wilson influenced its recovery during HRGC-HRMS analysis.

**Table 3-8:** Relative recovery range for PCDD/F isomers in sediment cores.

| | Relative Recovery (%) | |
|---|---|---|
| **Sediment Core** | **PCDD/F** [a] | **RPD (%)** [b] |
| Lake Shagawa (n=2) | 85 - 125 | 0.0 - 6.8 |
| Lake Little Wilson (n=2) | 73 - 116 (238) [c] | 0.0 - 14.2 |
| East Lake Gemini (n=2) | - | - |
| Lake St. Croix (n=2) | 94 - 124 | 0.4 - 12.9 |
| Lake Winona (n=2) | 72 - 124 | 0.4 - 10.2 |
| Lake Superior (n=2) | 76 - 120 | 0.3 - 17.5 |
| Lake Pepin (n=2) | 86 - 119 | 0.2 - 7.3 |
| Duluth Harbor (n=2) | 85 - 126 | 0.2 - 9.2 |

[a] 19 native di- through octa-CDD/F isomers

[b] RPD = relative percent difference between matrix spike replicates

[c] value in parenthesis represents the maximum relative recovery of 1 outlier (2,8-DCDD)

A comprehensive list of isomer-specific $^{13}C_{12}$-PCDD/F recoveries for each sediment core is provided in Appendix D. This appendix also provides isomer-specific PCDD/F recoveries for each matrix spike and recovery experiment.

For all cores, trace amounts of specific di- through octa-CDD/F isomers were detected in method blanks, most of which were well below calibration ranges. All reported PCDD/F concentrations were > 10 times the levels in these blanks.

### 3.3.2 TCS, CTDs, and their PCDDs in MN Lakes

*Lake Pepin and Lake St. Croix.* Sediment cores collected in large-scale, wastewater-impacted riverine systems provide important insight into the accumulation of TCS and its byproducts in aquatic environments. Figures 3-5 and 3-6 illustrate the temporal trend of TCS, CTDs, and their derived PCDDs for Lake Pepin and Lake St. Croix, respectively. In both cores, TCS concentrations increase with time, reflecting consumer usage since the mid-1960s. A similar trend in the 2,8-DCDD profile, the known photoproduct of TCS, is observed in these systems. Furthermore, concentrations of 2,3,7-TriCDD, 1,2,8-TriCDD, and 1,2,3,8-TCDD, the photoproducts of CTDs, generally parallel TCS trends in each core.

Wastewater treatment practices can have a profound impact on the presence of TCS, CTDs, and their derived PCDDs in aquatic sediments. The Metropolitan WWTP, for example, is a major wastewater source to the Mississippi River that is approximately 80 km upstream from Lake Pepin. Since its inception in 1938, the plant has disinfected its effluent with various forms of free chlorine (e.g. $Cl_2$ or NaOCl). The effect of chlorine disinfection, coupled with increased TCS use over the last 40 years, is directly realized in the CTD and higher chlorinated PCDD profiles in Figure 3-5.

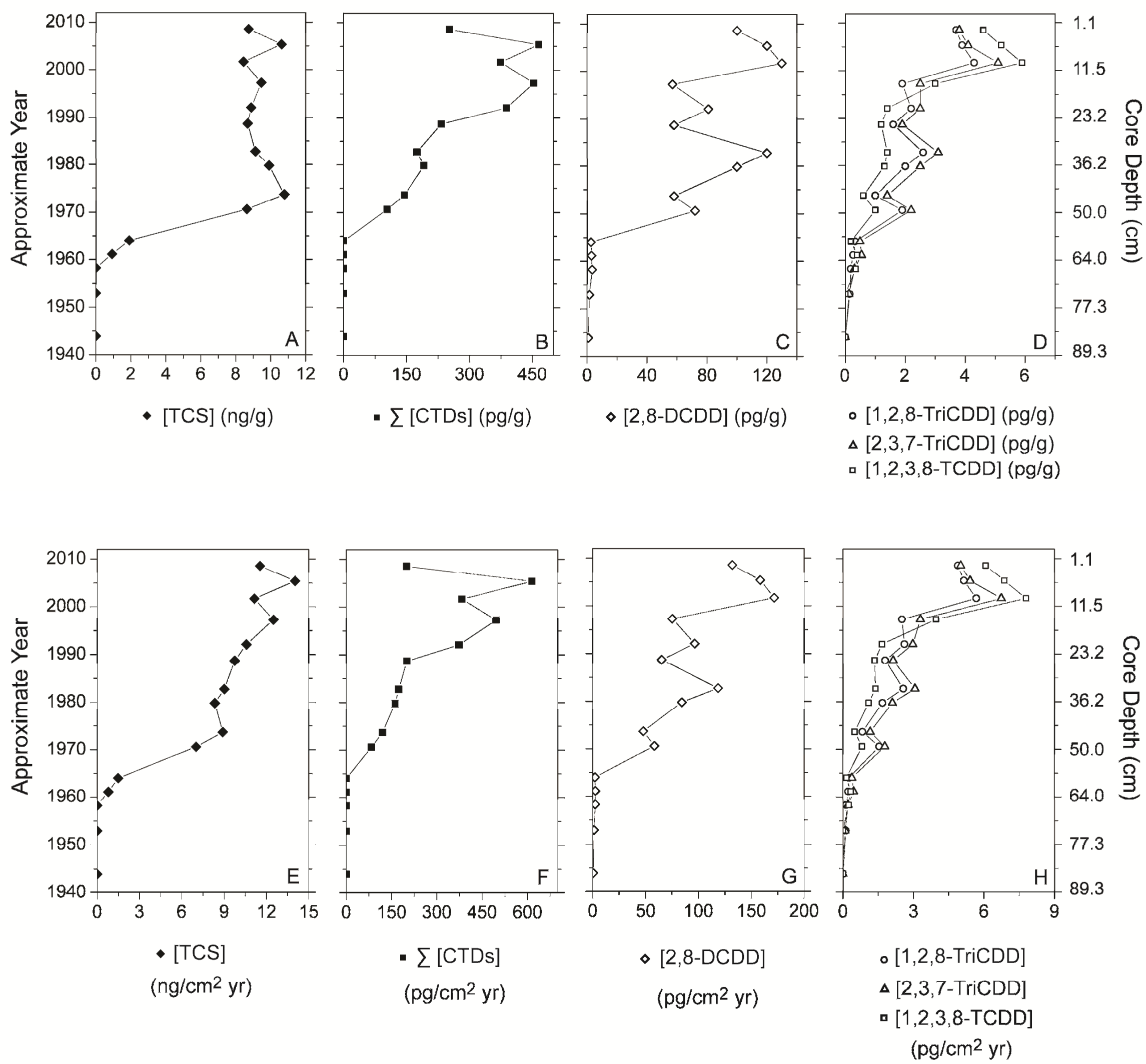



**Figure 3-5:** Concentration profiles of TCS (A); Σ CTDs (B); 2,8-DCDD (C); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (D) in the Lake Pepin core. Focus-corrected accumulation rates are presented in (E-H) for the respective analytes. Details on sediment focusing calculations can be found in Appendix E. Focusing factors specific to the Lake Pepin core are provided in Table AE-13.

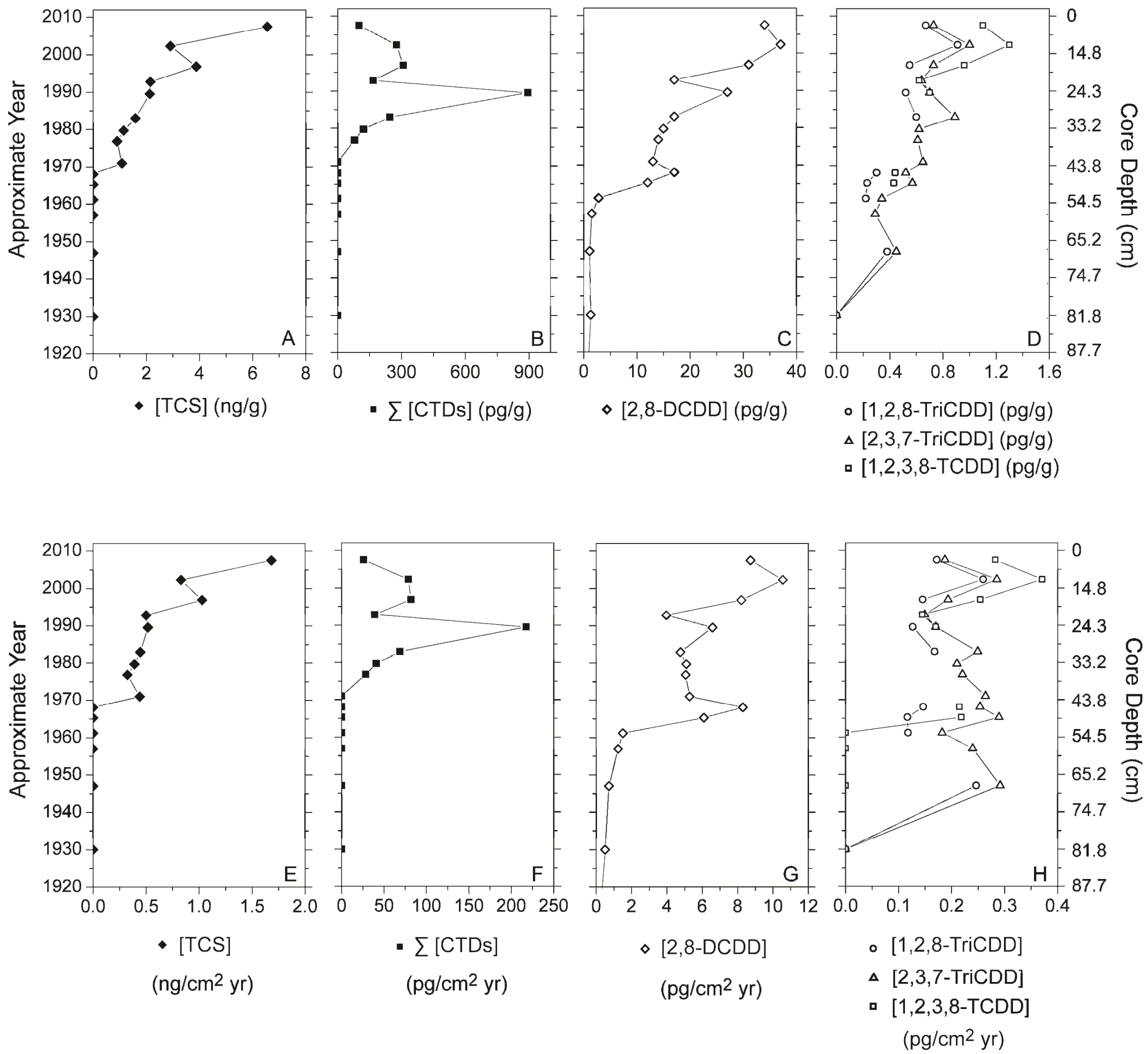



**Figure 3-6:** Concentration profiles of TCS (A); Σ CTDs (B); 2,8-DCDD (C); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (D) in the Lake St. Croix core. Focus-corrected accumulation rates are presented in (E-H) for the respective analytes. Details on sediment focusing calculations can be found in Appendix E. Focusing factors specific to the Lake St. Croix core are provided in Table AE-14.

In the St. Croix sediment core, changes in wastewater disinfection appear to be recorded in the CTD profile. The St. Croix Valley WWTP opened in 1959 approximately 10 km upstream from the selected coring site. The facility treated its effluent with $Cl_2$ until 1993, when UV disinfection technology was installed during a plant expansion.

The visible inflection in the CTD profile around 1990 may be due to this change in disinfection technology (Figure 3-6). This inflection, however, is not present in the 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD profiles, which may suggest that photochemical yields of these PCDDs from CTDs were low during this time period.

CTDs and their PCDDs are present in the St. Croix core at appreciable levels, even after UV disinfection was installed at the St. Croix Valley WWTP. This is likely due to other wastewater discharges, including that from the City of Hudson, WI WWTP, a facility 2.5 km upstream from the coring site that disinfects with $Cl_2$.

*East Lake Gemini and Lake Winona.* In contrast to large-scale riverine systems that integrate many wastewater sources, sediment cores collected from East Lake Gemini and Lake Winona highlight the impact of TCS, CTDs, and their PCDDs on small-scale lakes with a single wastewater source. Figures 3-7 and 3-8 depict analyte trends in East Lake Gemini and Lake Winona, respectively.

Improvements in wastewater treatment and changes in disinfection have greatly influenced the presence of TCS, CTDs, and their derived PCDDs in East Lake Gemini. After formation in 1966, East Lake Gemini received combined wastewater and stormwater from the SJU campus. Due to the transient nature of the campus population, coupled with extreme flows during storm events, SJU WWTP effluent was of poor quality during the 1960s and 1970s. To mitigate this problem, SJU separated stormwater and wastewater from the mid-1970s to late-1980s. Moreover, to stabilize flow through the WWTP and increase effluent quality, an 80,000 gallon equalization tank was installed upstream from secondary activated sludge treatment in 1980. The same year, the aeration system was upgraded in the activated sludge tank, dramatically improving oxygen levels. These updates allowed for more consistent hydraulic and solids retention times during treatment and, subsequently, improvements in effluent quality.

Along with changes in wastewater treatment at the SJU WWTP, the mode of effluent disinfection has been modified since 1966. $Cl_2$ was the primary disinfectant until 1978, when an ozonation system was installed. UV disinfection then replaced ozonation in 1995 and is the current mode of wastewater disinfection at the treatment plant.

When examining analyte profiles in East Lake Gemini, there are clear differences from those observed in Lake Pepin or Lake St. Croix. TCS and 2,8-DCDD concentrations, for example, are much higher in this system, reflecting the direct discharge of wastewater from the SJU WWTP into a small impoundment (0.1 $km^2$). Moreover, concentrations of TCS, CTDs, and their derived PCDDs consistently decrease from 1966 to 2008 in the sediment core. Prior to 1978, concentrations of TCS, CTDs, and their PCDDs are all high, namely due to poor removal of TCS and disinfection with $Cl_2$ at the SJU plant. The transition to other forms of disinfection (e.g. ozonation and UV), stabilization of wastewater flow, and improvement activated sludge aeration likely contributed to a reduction in analyte sediment concentrations in this aquatic system.

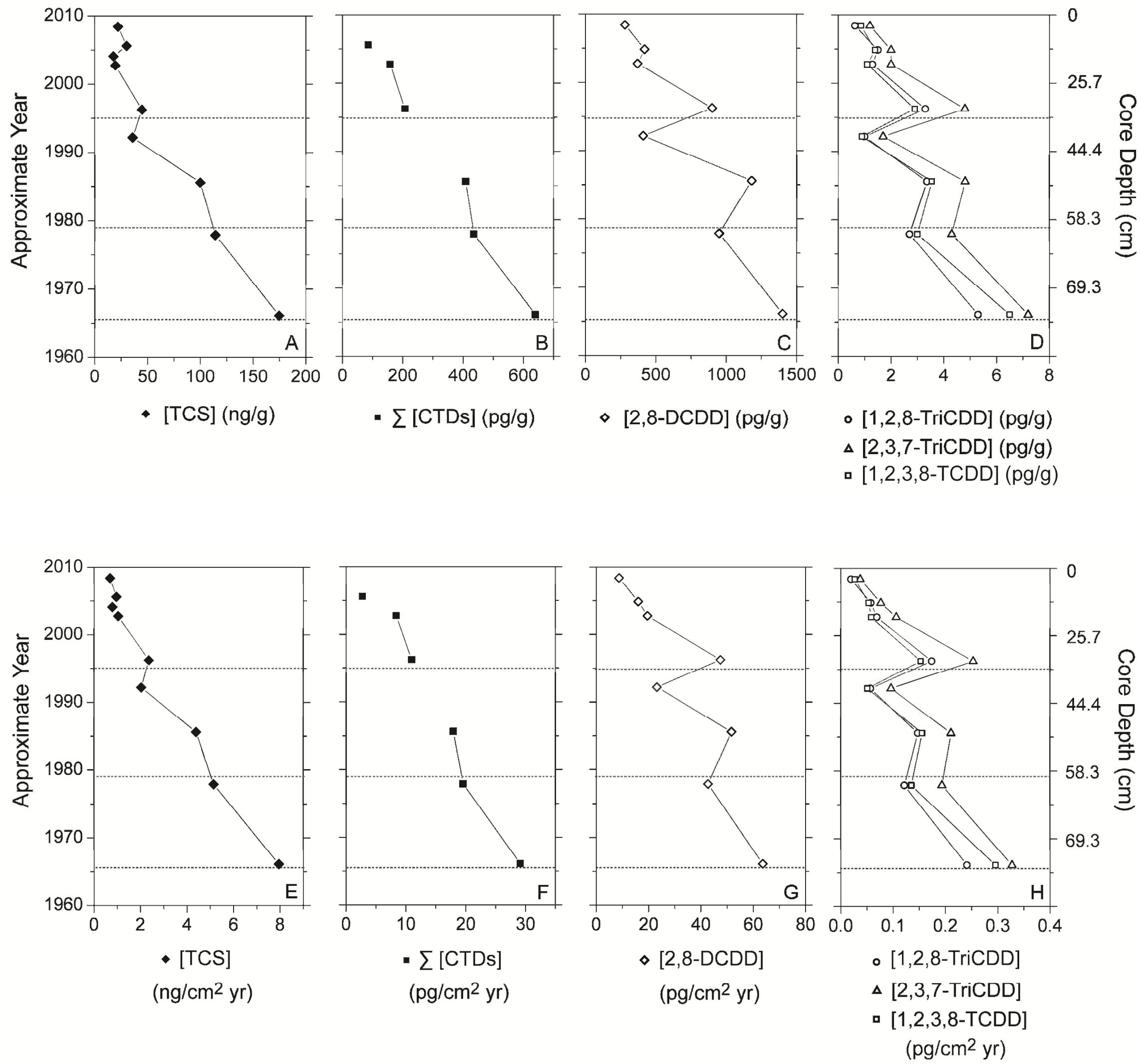



**Figure 3-7:** Concentration profiles of TCS (A); Σ CTDs (B); 2,8-DCDD (C); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (D) in the East Lake Gemini core. Focus-corrected accumulation rates are presented in (E-H) for the respective analytes. Details on sediment focusing calculations can be found in Appendix E. A focusing factor, specific to the East Lake Gemini core, is provided in Table AE-15.

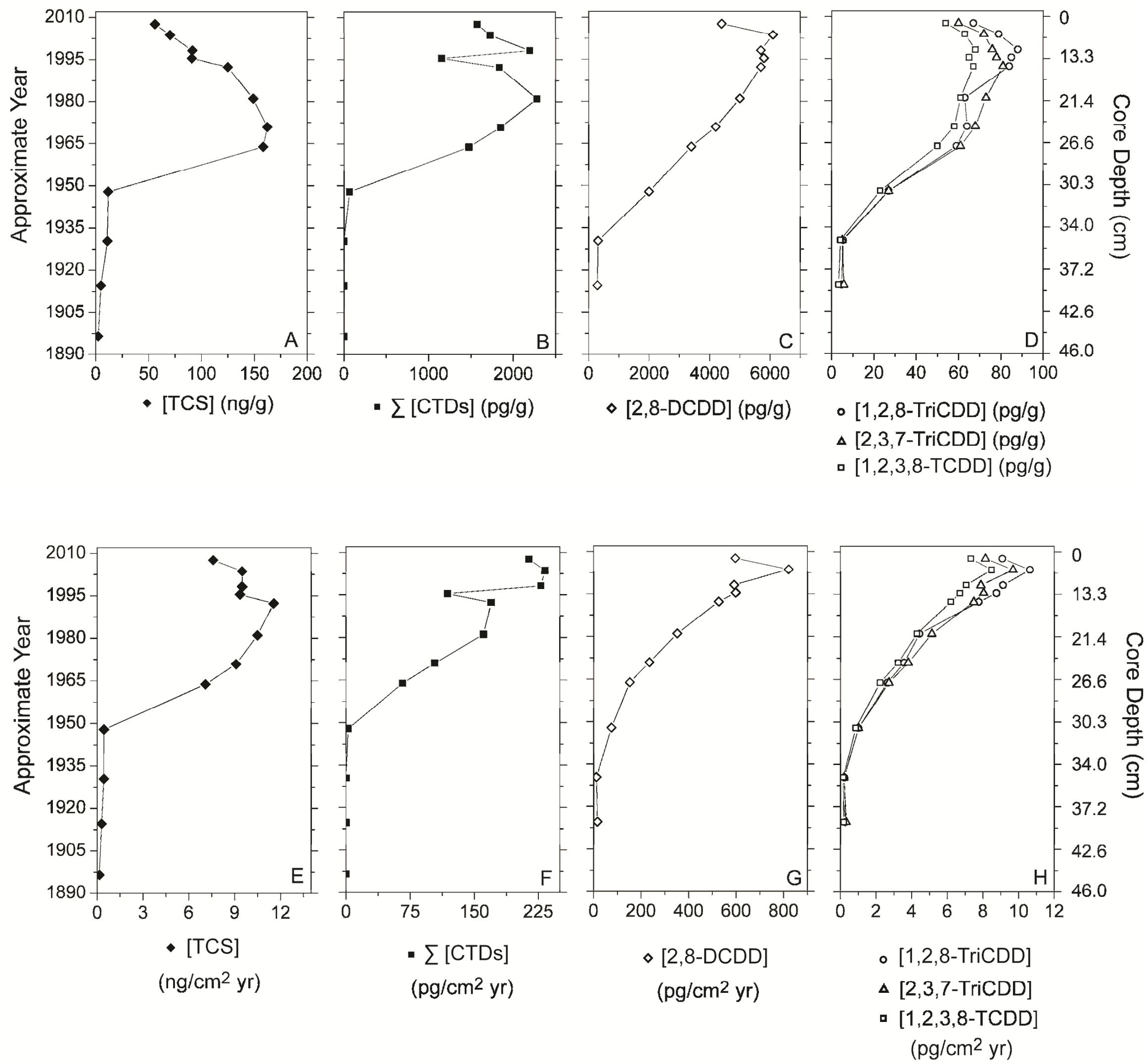



**Figure 3-8:** Concentration profiles of TCS (A); Σ CTDs (B); 2,8-DCDD (C); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (D) in the Lake Winona core. Focus-corrected accumulation rates are presented in (E-H) for the respective analytes. Details on sediment focusing calculations can be found in Appendix E. A focusing factor, specific to the Lake Winona core, is provided in Table AE-15.

In recent East Lake Gemini sediment, there is evidence that CTDs are being discharged into the lake, even without chlorinating the SJU wastewater effluent. Although SJU does not chlorinate its potable water, it is likely that CTDs are being formed by the reaction of TCS with chlorinated household products (e.g. bleach) that are washed down the drain. Like TCS, CTDs are typically removed at high rates (>90%) in plants with activated sludge treatment [24,25]. At SJU, however, this may not always be the case. Even with plant improvements, the facility is not equipped to handle such a highly transient population. During large events on the SJU campus (e.g. athletic games, concerts), wastewater flow can exceed plant capacity, leading to poor effluent quality. Conversely, during the summer months, the campus population decreases dramatically. During these time periods, wastewater flow is minimal and biomass levels in secondary activated sludge treatment decrease accordingly. Consequently, when large populations return to SJU, the WWTP is often not operating at fully capacity, which may contribute to TCS and CTD loading into East Lake Gemini.

Lake Winona is a natural water body that is heavily impacted by wastewater. In 1971, the Alexandria Lakes Area Sanitation District (ALASD) was formed, serving the City of Alexandria, MN and surrounding communities. The ALASD WWTP became operational in 1977. Since this date, elevated total phosphorus concentrations have induced hypereutrophic conditions in the lake. In 2002, the Lake Winona was listed as an impaired water body as part of Section 303(d) of the Federal Clean Water Act due excess nutrient levels [96].

From 2000 to 2008, a hydrologic balance on Lake Winona indicated that 63% of total inflow was derived from the ALASD WWTP [96]. Thus, the levels of TCS, CTDs, and their PCDDs in Lake Winona sediments are reflective of a small-scale aquatic environment heavily impacted by wastewater. Although there is a discrepancy between radiometric dating and the onset of TCS, CTDs, and their PCDDs in the sediment core (see Figure 3-8), analyte trends provide important insight into the exposure of Lake Winona to these compounds. TCS concentrations reach as high as 175 ng/g in sections of the core, followed by a steady decrease to 50 ng/g in recent sediment. When accounting for increased sedimentation rates, however, TCS loading is relatively constant since 1970 (Figure 3-8). The ALASD WWTP has consistently disinfected its wastewater with $Cl_2$, allowing CTD concentrations to rise to over 2000 pg/g in the sediment core.

Even in a hypereutrophic lake, direct photochemical transformation of TCS and CTDs to their respective PCDDs is still a concern. Lake Winona is a relatively shallow aquatic system, with a mean depth of 4.5 ft. Moreover, the current residence time and average Secchi depth for the lake are 70 days and 1.5 ft, respectively [97]. With wastewater accounting for 63% of inflow into Lake Winona, it is not surprising that TCS and CTD derived PCDDs are prevalent in sediments at this site.

*Duluth Harbor and Lake Superior.* Analyte trends are depicted in Figures 3-9 and 3-10 for the Duluth Harbor and Lake Superior cores, respectively. The Duluth Harbor core was collected approximately 2 km from the Western Lake Superior Sanitation District (WLSSD) wastewater outfall in St. Louis Bay. In the mid-1970s, the WLSSD WWTP began discharging effluent that was disinfected year-round with $Cl_2$. In June 1994, the treatment plant was granted a variance by the Minnesota Pollution Control

Agency (MPCA) to disinfect wastewater effluent only when fecal coliform levels exceeded 100 MPN/100 mL, where MPN is the most probably number of fecal coliforms in a sample. The WLSSD WWTP continues to operate under this variance today and disinfects on an as-needed basis.

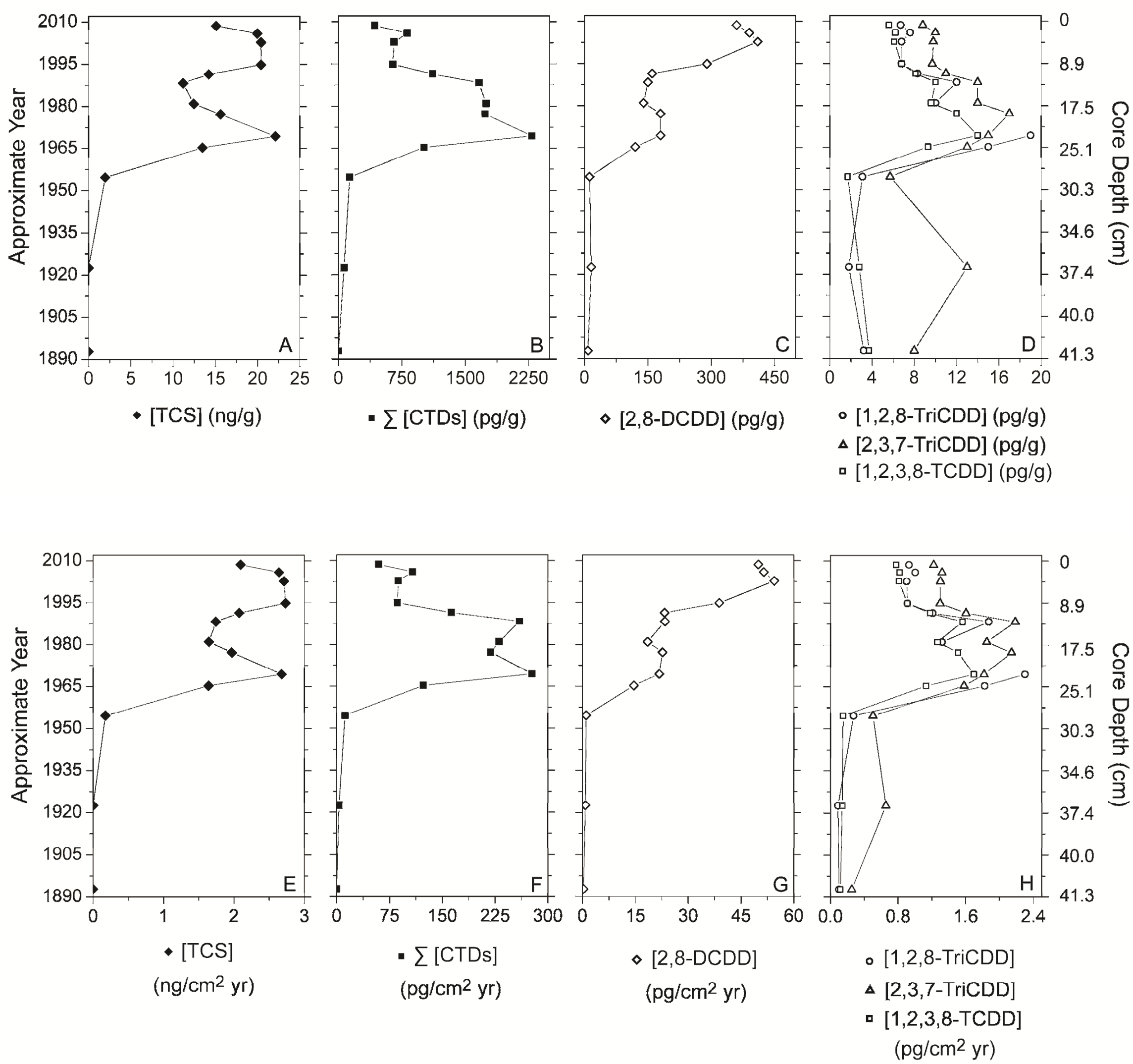



**Figure 3-9:** Concentration profiles of TCS (A); Σ CTDs (B); 2,8-DCDD (C); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (D) in the Duluth Harbor core. Focus-corrected accumulation rates are presented in (E-H) for the respective analytes. Details on sediment focusing calculations can be found in Appendix E. A focusing factor, specific to the Duluth Harbor core, is provided in Table AE-15.

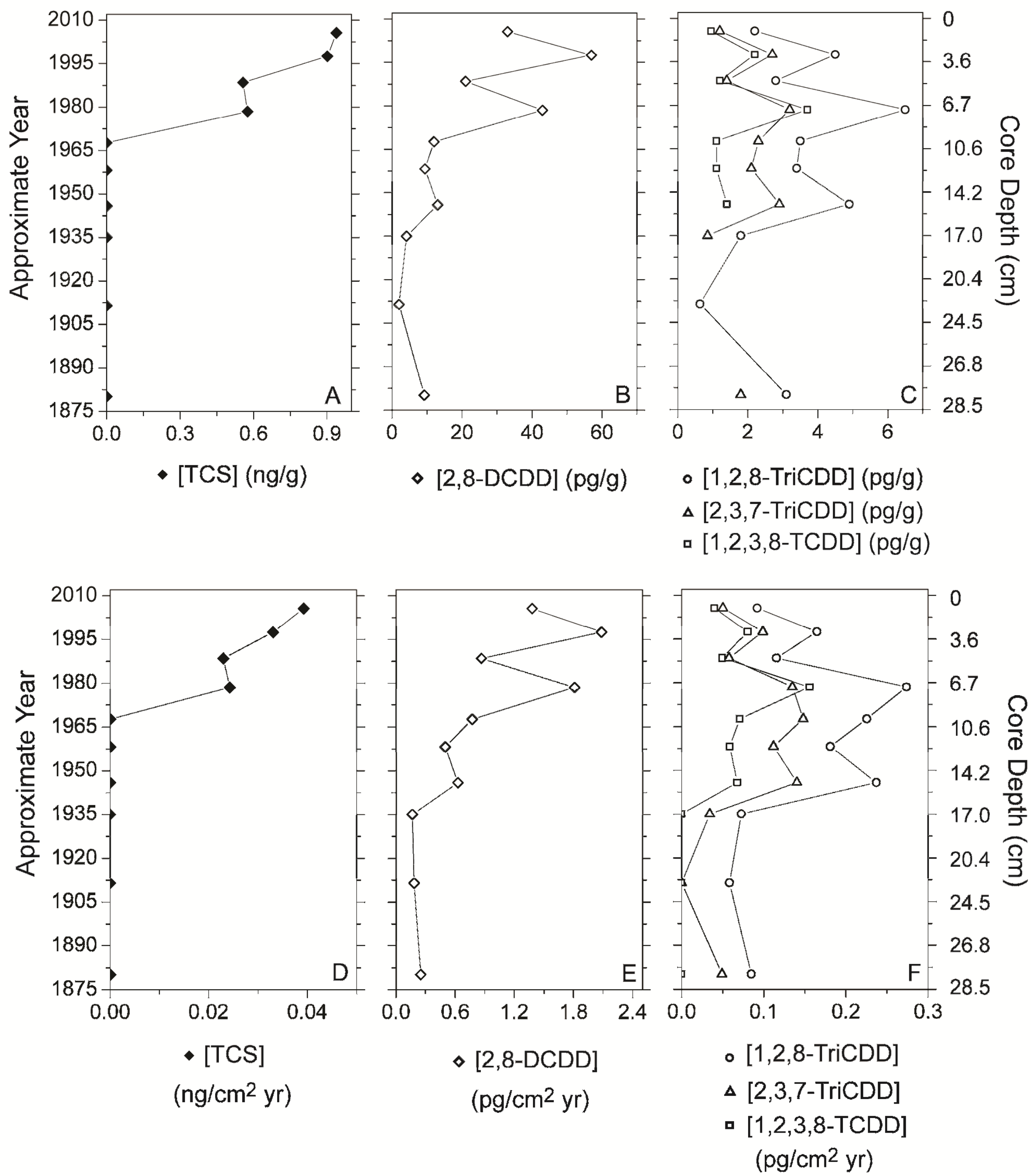



**Figure 3-10:** Concentration profiles of TCS (A); 2,8-DCDD (B); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (C) in the Lake Superior core. Focus-corrected accumulation rates are presented in (D-F) for the respective analytes. CTDs were below their respective LOQs in each core section. Details on sediment focusing calculations can be found in Appendix E. A focusing factor, specific to the Lake Superior core, is provided in Table AE-15.

TCS, CTD, and PCDD trends in Figure 3-9 clearly demonstrate the impact of WLSSD wastewater effluent on St. Louis Bay. Overall, TCS and 2,8-DCDD increase in the sediment core since the mid-1960s. The CTDs and their PCDDs, however, tend to co-vary with changes in wastewater disinfection at WLSSD. Specifically, total CTD levels drop from approximately 1700 pg/g in 1988 to 650 pg/g in 2002. A corresponding decrease is observed in the CTD derived tri- and tetra-CDDs around the same time period. Similar trends are present when accounting for varying sedimentation rates at the core site (Figure 3-9).

When examining the temporal trends of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in Duluth Harbor, it is apparent that these PCDD congeners are present at low concentrations in the sediment core, prior to the patenting of TCS in the mid-1960s. 2,8-DCDD, for example, is present at approximately 10 pg/g in core sections dating back to the late-1800s. Furthermore, concentrations of the tri-and tetra-CDDs average around 4 pg/g during the same time period. The same PCDD congeners, however, are at much lower concentrations at the base of the Lake Pepin and Lake St. Croix cores. 2,8-DCDD is present at $< 1$ pg/g prior to 1930 in these cores. Moreover, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD are not detectable in the St. Croix core and are at very low levels ($< 0.06$ pg/g) in the Lake Pepin core before 1947. Although evidence suggests that TCS and CTDs are the primary source of these PCDDs, their presence at the base of the Duluth Harbor core may suggest a secondary, region-specific source.

The sediment core collected in Lake Superior provides evidence for TCS contamination in this aquatic system, albeit at low levels. TCS is first detected in the sediment core around 1975, with concentrations increasing to 0.94 ng/g in 2005 (Figure 3-10). CTDs were not detected in the core, but may be present below the quantification limits established for this study. The source of TCS to this site on the open lake may be from distal wastewater sources, such as WLSSD or the City of Superior. Another possible source is the WWTP in Two Harbors, MN, where an average TCS concentration of 572 ng/L in wastewater effluent was recently documented [98].

Similar to Duluth Harbor, background levels of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD are present at the base of the Lake Superior core. Concentrations of 2,8-DCDD increase between 1975 and 2005, reflecting a contribution of this PCDD congener from the phototransformation of TCS in the system. The tri- and tetra-CDD congeners, however, do not follow a particular trend relative to TCS. A fraction of these PCDDs may be derived from CTDs after 1975. This, however, cannot be confirmed with the data in this study.

It is important to note that 2,8-DCDD is present at ~ 10 pg/g in the Lake Superior core, prior to the detection of TCS in the system. Furthermore, the CTD derived tri-and tetra-CDD congeners range from 1 to 6 pg/g throughout the core profile. These levels are similar to those observed in Duluth Harbor sediment before 1960, which may provide additional support for a secondary, region-specific source of these PCDDs.

*Lake Shagawa.* The City of Ely, MN has been discharging wastewater into Lake Shagawa for over a century. In the late 1880s, a primary wastewater treatment plant was established, where a single clarifier reduced the discharge of total suspended solid (TSS) and biological oxygen demand (BOD) into the lake. The city concurrently used Lake Shagawa as a drinking water source until 1932, when the water was rendered no longer suitable for potable use [99]. In 1954, the facility was upgraded to a secondary treatment plant, where a secondary clarifier, trickling filters, and disinfection with $Cl_2$ improved effluent quality [100]. This treatment facility, however, did not remove significant amounts of nutrients from wastewater effluent. By 1970, the Ely WWTP was contributing 80 percent of external total phosphorus loading to Lake Shagawa, contributing to eutrophic conditions in the water body [101].

To mitigate the nutrient loading problem to Lake Shagawa, advanced tertiary treatment, funded by the U.S. EPA, was established in 1973. In this tertiary facility, secondary wastewater effluent was treated with lime, alum, and/or polymeric flocculating agents to remove high levels of phosphorus. Following this treatment step, wastewater was passed through dual media filters (e.g., sand, anthracite) and disinfected with $Cl_2$ before being discharged into the lake.

Figure 3-11 illustrates the depositional trends of TCS, CTDs, and their PCDDs in Lake Shagawa sediment. Similar to Lake Winona, there is a discrepancy between the radiometric dating and the onset of TCS and CTD appearance in this lake system. The dating for this core, however, is currently being re-evaluated. It is anticipated that 1930 in the current dating profile corresponds to ~ 1960, based on the analyte trends.

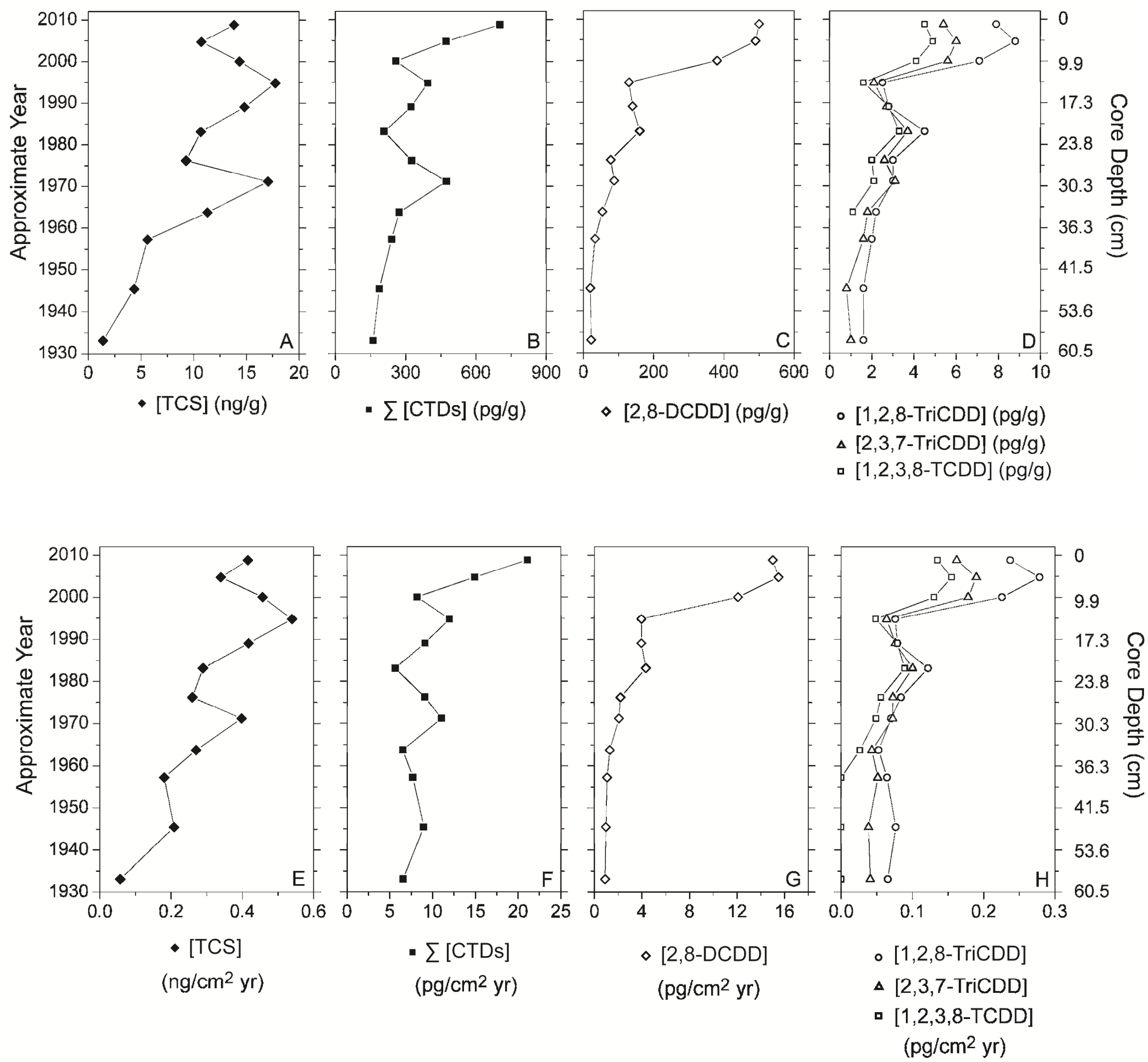



**Figure 3-11:** Concentration profiles of TCS (A); Σ CTDs (B); 2,8-DCDD (C); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (D) in the Lake Shagawa core. Focus-corrected accumulation rates are presented in (E-H) for the respective analytes. Details on sediment focusing calculations can be found in Appendix E. A focusing factor, specific to the Lake Shagawa core, is provided in Table AE-15.

The TCS profile in Lake Shagawa sediments, like that of Lake Pepin and Lake St. Croix, mirrors the increased use of TCS since the 1960s. The CTD profile directly parallels this trend, reflecting the disinfection of the Ely WWTP effluent with $Cl_2$ since 1954. Moreover, 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD trends directly follow with their TCS and CTD precursors.

*Lake Little Wilson (Reference Lake).* Figure 3-12 illustrates the analytes present in Lake Little Wilson, a remote lake with no wastewater input near the BWCA in MN. TCS and CTDs were not quantifiable in all core segments. Their derived PCDDs, however, are present at low levels throughout the core. 2,8-DCDD, for example, is present from 1872 to 2007 at an average concentration of 25 pg/g. The tri- and tetra-CDD congeners derived from CTDs are only detectable from 1933 to 2007 and at much lower concentrations (~ 0.5 pg/g). Due to the remote nature of Little Lake Wilson, it is likely that these PCDD congeners, among others, entered the lake via atmospheric deposition.

Several studies have investigated the deposition of PCDDs in the Great Lakes region [102-104]. Baker and Hites [103], for example, analyzed the temporal trends of tetra- through octa-CDD isomers in sediment cores collected from Siskiwit Lake on Isle Royale. Isle Royale is an isolated island in Lake Superior that is uninhabited and infrequently visited. Moreover, Siskiwit Lake is approximately 17 m above the elevation of Lake Superior. Thus, the only likely PCDD source to this lake is through atmospheric deposition. Through their study, Hites and Baker documented a rapid increase in total PCDD flux to their core sites from 1930 to 1970, with octa- and hepta-CDD being the most abundant isomers. This increase is attributed to the manufacturing and incineration of organochlorine-based products during and after World War II.  In 1970, emissions control devices aided in the reduction of PCDD loading to the atmosphere from incineration facilities.  The Siskiwit Lake sediment cores record this reduction, where a 50% decrease in total PCDD loading from 1970 to 1998 was observed.  A study by Pearson et al. [104] recorded similar PCDD depositional trends in a different remote lake near Lake Superior.

The presence of tetra- through octa-CDD isomers in remote lakes confirms that atmospheric deposition is an important source of higher chlorinated PCDDs to these aquatic systems.  Although the studies above did not quantify di- or tri-CDD isomers, it is possible that very low concentrations of these PCDDs are present in their sediment cores. Typically, when PCDDs are emitted from a combustion source (e.g., a municipal incinerator), they are associated with particles, mix with the ambient atmosphere, and become diluted.  During this process, lower chlorinated PCDDs have a higher potential to partition into the vapor phase.  Due to their increased hydrophobicity, higher chlorinated PCDDs, like hepta-CDD and octa-CDD, are more likely to remain sorbed onto particles.  Consequently, these particles become enriched with higher chlorinated PCDDs as they move away from the incineration source and eventually deposit in surface waters. This phenomena likely explains why most PCDD profiles derived from atmospheric sources are dominated by higher chlorinated PCDDs and only have traces of lower chlorinated congeners.

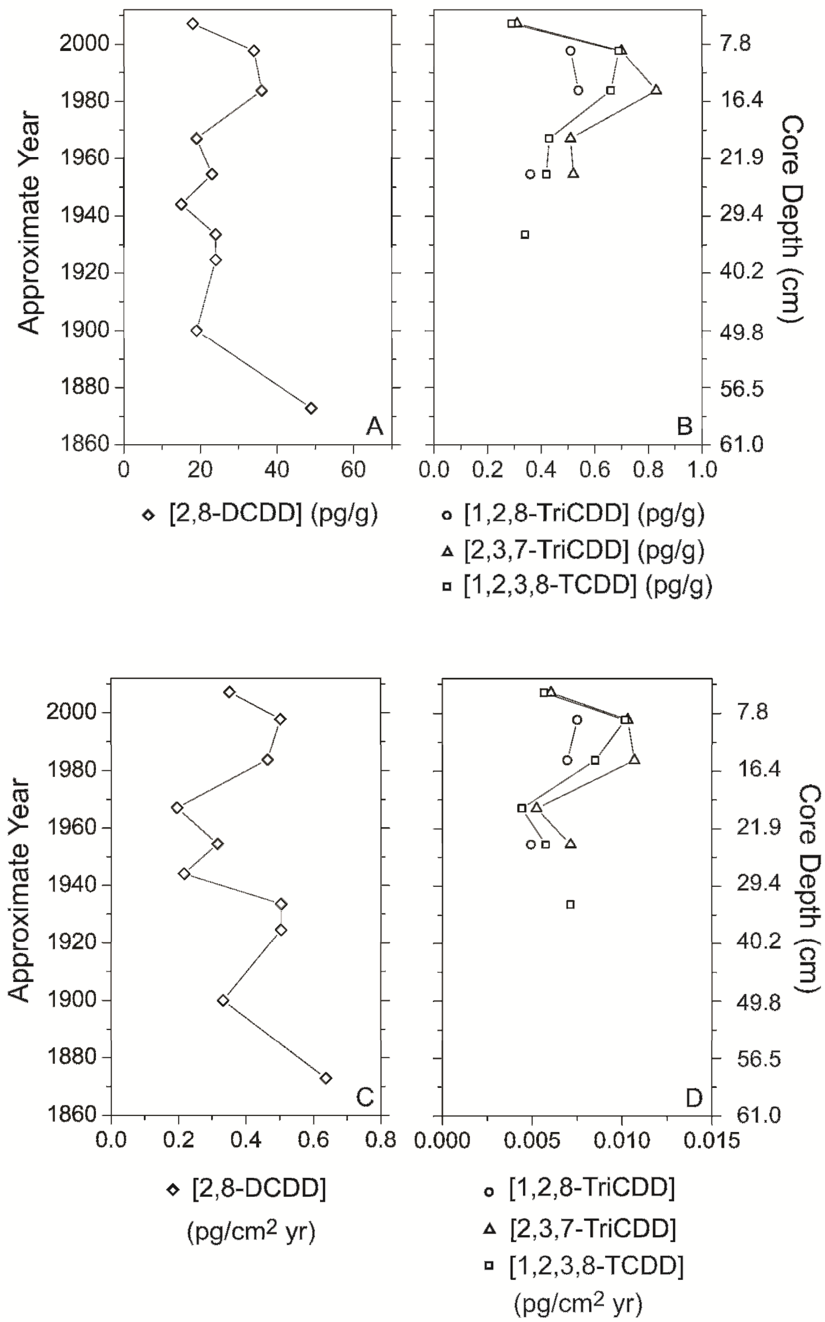



**Figure 3-12:** Concentration profiles of 2,8-DCDD (A); and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD (B) in the Lake Little Wilson core. Focus-corrected accumulation rates are presented in (C-D) for the respective analytes. TCS and CTDs are below their respective LOQs in all core segments. Details on sediment focusing calculations can be found in Appendix E. A focusing factor, specific to the Lake Little Wilson core, is provided in Table AE-15.

While it is possible that incineration contributes to the 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD deposition in aquatic environments, it is clear that TCS and CTDs are typically the dominant source of these PCDD congeners after 1965 in systems heavily impacted by wastewater. This is exemplified when comparing analyte accumulation rates at the eight coring sites (Figures 3-5 to 3-12).

The majority of atmospheric loading of PCDDs to aquatic environments in recent history has been from the combustion of chlorinated synthetic compounds. Before 1930, however, low levels of PCDDs were produced from a variety of sources. A number of studies have suggested that the burning of coal and wood were important sources in the past [105-109]. Furthermore, forest fires have been cited as natural PCDD sources [108,110-111]. Gullet and Touati [110], in particular, recently evaluated PCDD emissions from different types of forest biomass. In general, Gullet and Touati found that the type of biomass can have a significant effect on the PCDD isomer patterns emitted during forest fires. Due to the distinct differences in forest biomes in MN (e.g., coniferous in the northeast, deciduous in the central and southeast), it is feasible that PCDD emissions and isomer abundances from these environments are unique. This may explain why TCS and CTD derived PCDDs are observed at low levels during the late 1800s in the Duluth Harbor, Lake Superior, and Lake Little Wilson cores, but are virtually non-detectable in the Lake Pepin and Lake St. Croix cores during the same time period. It is also important to note that sedimentation rates in Lake Pepin and Lake St. Croix are generally higher than in the northern lakes during this time period. Thus, higher sedimentation rates may have diluted a background level of TCS and CTD derived PCDDs below detection limits in these cores.

### 1.3.3 TCS and CTDs – An Emerging PCDD Source

The temporal trends of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD provide compelling evidence that TCS and CTDs are their dominant source in wastewater-impacted aquatic systems. Further evidence is granted by examining the ratio of these PCDDs to their TCS and CTD precursors in sediment core intervals. Tables 3-9 and 3-10 present these ratios, expressed as a percentage, for the sediment cores in this study. This allows for direct comparison to PCDD yields from TCS and CTDs presented in the literature.

**Table 3-9:** Ratio of 2,8-DCDD to TCS in sediment core intervals. Values are represented as a percentage for a comparison to PCDD yields from TCS in natural waters.

| Sediment Core | [TCS derived PCDD[a] ] / [TCS] (%) | |
|---|---|---|
| Lake Pepin | 1.0 ± 0.5[b] | (n = 12) |
| Lake St. Croix | 1.2 ± 0.4 | (n = 9) |
| East Lake Gemini | 1.6 ± 0.5 | (n = 8) |
| Lake Winona | 6.4 ± 5.0 | (n = 11) |
| Duluth Harbor | 1.5 ± 0.6 | (n = 11) |
| Lake Superior | 6.0 ± 2.2 | (n = 4) |
| Lake Shagawa | 1.8 ± 1.6 | (n = 12) |

[a] [2,8-DCDD]

[b] Reported values are the mean ± standard deviation

As outlined in Chapter 2, the experimental photochemical yields of TCS and CTD derived PCDDs range from 0.5-3% in natural waters [26,75]. The ratios in Tables 3-9 and 3-10 are within or near this range, with a few exceptions. The mean ratio for Lake Winona in Table 3-10, for example, is quite high. When accounting for the relative recovery of CTDs in the sediment core extractions, however, this ratio is close to photochemical yields presented in the literature. The fact that the mean values presented in Tables 3-9 and 3-10 are close to experimental yields suggests that TCS and CTDs, when present, are the primary sources of their known photoproducts in the sediment cores.

**Table 3-10:** Ratio of 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD to CTDs in sediment core intervals. Values are represented as a percentage for a comparison to PCDD yields from CTDs in natural waters. The presented ratios should be considered overestimates, as CTD concentrations are not corrected for relative recovery.

| **Sediment Core** | **Σ([CTD derived PCDDs[a] ]) / Σ[CTDs] (%)** | |
|---|---|---|
| Lake Pepin | 2.1 ± 1.0[b] | (n = 10) |
| Lake St. Croix | 0.6 ± 0.2 | (n = 8) |
| East Lake Gemini | 2.7 ± 1.5 | (n = 6) |
| Lake Winona | 13.8 ± 3.8 | (n = 8) |
| Duluth Harbor | 4.9 ± 5.5 | (n = 12) |
| Lake Superior | - | - |
| Lake Shagawa | 1.2 ± 0.7 | (n = 12) |

[a] [1,2,8-TriCDD], [2,3,7-TriCDD], [1,2,3,8-TCDD]
[b] Reported values are the mean ± standard deviation

*PCDD Trends – Lake Pepin.* Evaluating the isomer-specific trends of PCDDs in a sediment core can help fingerprint the dominant dioxin sources to an aquatic environment over time. Figure 3-13 illustrates the focus-corrected accumulation rates of PCDD isomers to the Lake Pepin core site from 1940 to 2008. Since 1965, 2,8-DCDD has comprised at least 90% of the total DCDD loading to the system, and in many cases, was the only DCDD congener detected. Furthermore, 1,2,8-TriCDD and 2,3,7-TriCDD constituted 99% of detected TriCDD isomers. 1,2,3,8-TCDD was not detected before 1958, but constituted up to 40% of total TCDD isomers in recent sediment. Buth et al.

[47] collected two sediment cores in Lake Pepin and recorded similar contributions of these TCS and CTD derived PCDD congeners. Moreover, acquisition windows for di- and tri-CDD isomers were expanded during HRGC-HRMS analysis in Buth et al. [47] to evaluate the contribution of other DCDD and TriCDD congeners to PCDD loading. Expansion of these acquisition windows demonstrated that di- and tri-CDD congeners, other than those derived from TCS and CTDs, were not present at significant levels. Thus, the di- and tri-CDD contributions from TCS and CTDs to the total DCDD and TriCDD pool are considered representative for the current Lake Pepin core.

The temporal trends of the di- through octa-CDD isomers in Figure 3-13 illustrate distinct sources of PCDDs since 1940. The increase in di- and tri-CDD accumulation rates since 1965 is reflective of 2,8-DCDD, 1,2,8-TriCDD, and 2,3,7-TriCDD loading from TCS and CTDs. Similarly, the increase in TCDD accumulation rate from 1970 to 2008 is largely due to 1,2,3,8-TCDD, the primary photoproduct of 4,6-Cl-TCS. The higher chlorinated PCDD isomers, however, follow a different trend. OCDD accumulation in the Lake Pepin core, for example, increases in the 1940s and 1950s, peaks around 1970, and subsequently decreases after 1980. Similar to the higher chlorinated isomer profiles observed in Lake Siskiwit sediment, this trend directly mirrors the atmospheric input of PCDDs from incineration sources in the 20$^{th}$ century.

To illustrate the differences between PCDD sources in the Lake Pepin core, specific congeners and isomers profiles were correlated against 2,8-DCDD, the known photoproduct of TCS, and OCDD, the most abundant PCDD derived from incineration sources. Figure 3-14 depicts the results of these correlations.

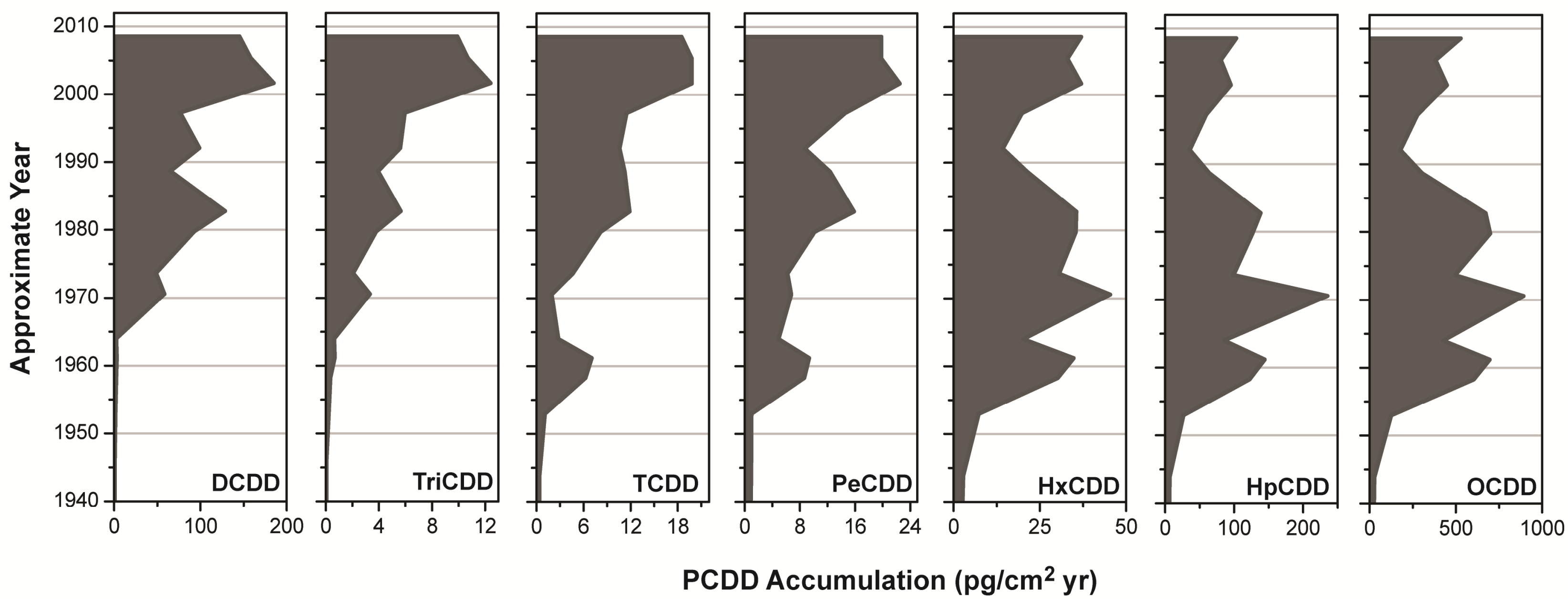



**Figure 3-13:** Focus-corrected PCDD accumulation rates at the Lake Pepin core site. DCDD, TriCDD, and TCDD profiles include the contribution of the PCDD congeners derived from TCS and CTDs. Details on sediment focusing calculations can be referenced in Appendix E.

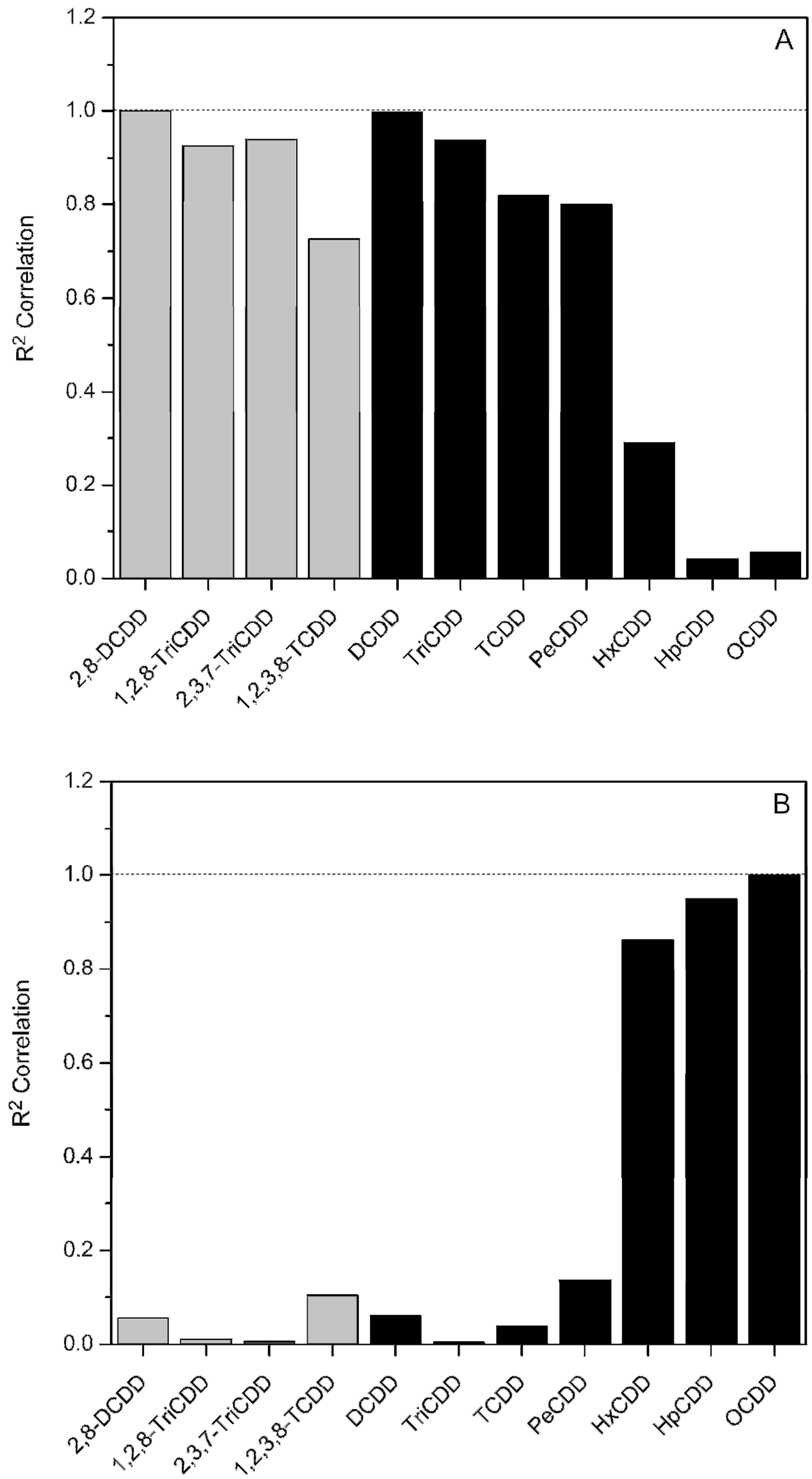



**Figure 3-14:** Correlation of PCDD congener and isomer accumulation profiles with 2,8-DCDD (A) and OCDD (B) in the Lake Pepin core. Grey bars represent the TCS and CTD derived PCDD congeners.

Results from the correlation analysis are clear for Lake Pepin. CTD derived PCDDs positively correlate with 2,8-DCDD, with $R^2$ values of 0.93, 0.94, and 0.73 for 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD, respectively. Overall, 2,8-DCDD also correlates well with the DCDD, TriCDD, and TCDD isomer groups. Higher chlorinated isomers, however, do not correlate well with 2,8-DCDD, suggesting a different source. OCDD, for example, correlates well with other higher chlorinated PCDDs, but poorly with lower chlorinated isomers and the congeners derived from TCS and CTDs. The contrasting PCDD isomer profiles in Figure 3-13, coupled with the correlations in Figure 3-14, suggest that TCS and CTDs are a distinct and emerging PCDD source in Lake Pepin.

*PCDD Trends – Lake Superior.* As a contrast to Lake Pepin, PCDD trends were examined in Lake Superior, a large lake with a less pronounced wastewater impact. Figure 3-15 illustrates the temporal loading of di- through octa-CDD isomers to the Lake Superior core site from 1880 to 2006. In this system, 2,8-DCDD contributes > 91% of total DCDD loading after 1978, a time period corresponding to the detection of TCS in the sediment profile. Before this date, however, the 2,8-DCDD contribution averages 80% and is as low as 61%. This may reflect that, prior to the presence of TCS in the lake, 2,8-DCDD was part of a broader suite of lower chlorinated PCDDs derived from a secondary source. The contribution of 1,2,8-TriCDD and 2,3,7-TriCDD to the TriCDD isomer pool is consistently > 98% throughout the core profile. This contribution may be unrepresentative, as the first and last TriCDD eluters during HRGC-HRMS analysis were not quantified. Thus, similar to 2,8-DCDD, 1,2,8-TriCDD and 2,3,7-TriCDD may be part of a larger array of lower chlorinated PCDD congeners in the core.

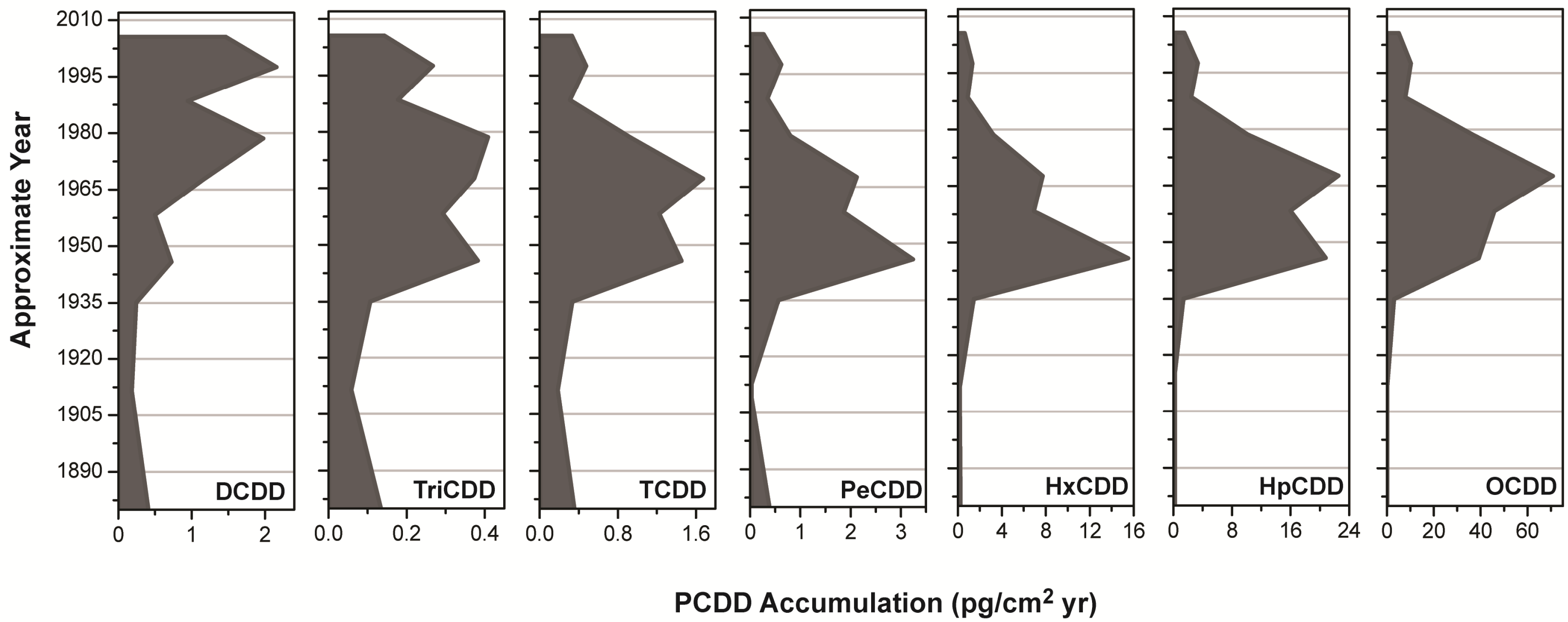



**Figure 3-15:** Focus-corrected PCDD accumulation rates at the Lake Superior core site. DCDD, TriCDD, and TCDD profiles include the contribution of the PCDD congeners derived from TCS and CTDs. Details on sediment focusing calculations can be referenced in Appendix E.

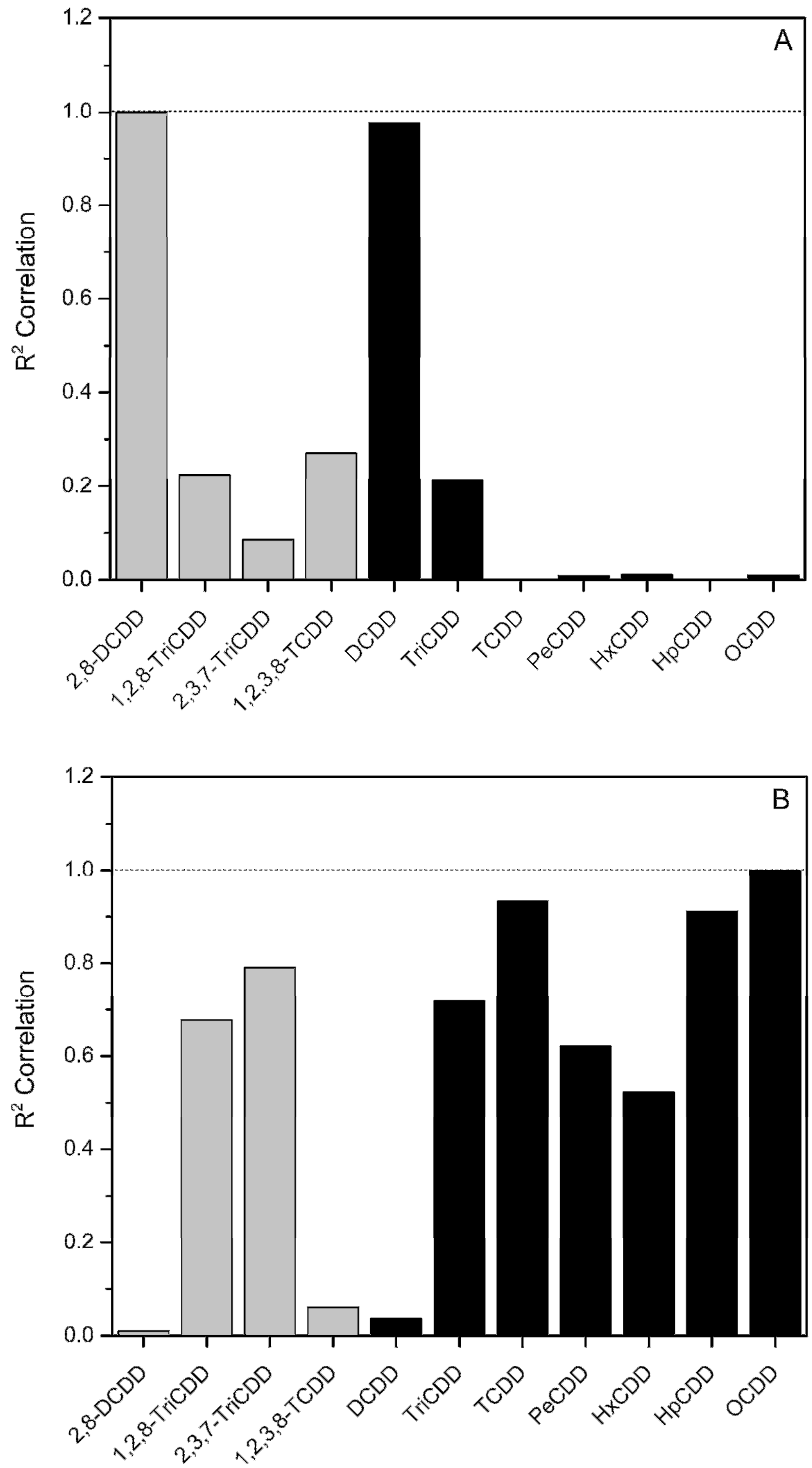



**Figure 3-16:** Correlation of PCDD congener and isomer accumulation profiles with 2,8-DCDD (A) and OCDD (B) in the Lake Superior core. Grey bars represent the TCS and CTD derived PCDD congeners.

Unlike the di- and tri-CDD analysis, all tetra-CDD congeners were quantified during HRGC-HRMS analysis for the Lake Superior core. Thus, the contribution of 1,2,3,8-TCDD to the TCDD pool should be considered representative. As indicated above, 1,2,3,8-TCDD became a prominent TCDD congener in the Lake Pepin core after 1958, contributing up to 40% of TCDD in the presence of CTDs. In the Lake Superior core, however, 1,2,3,8-TCDD contributes an average of 8% and a maximum of 17% throughout the core profile. A portion of this contribution may be derived from CTDs, below their limit of quantification in the core. However, because CTDs are not quantifiable, it is feasible that 1,2,3,8-TCDD is introduced to Lake Superior from another source.

Figure 3-16 presents the results of a correlation analysis for Lake Superior. Analogous to the Lake Pepin analysis, 2,8-DCDD and OCDD are correlated against specific PCDD congeners and isomers. Interestingly, 2,8-DCDD does not correlate well with 1,2,8-TriCDD or 2,3,7-TriCDD in the core. OCDD, however, does correlate relatively well with these congeners, which may support the theory of a secondary source in the region. 2,8-DCDD does not correlate with OCDD. This is likely due to the contribution of this congener from TCS in more recent sections of the core.

The PCDD trends and correlations in Figures 3-15 and 3-16 clearly illustrate that there may be a series of PCDD sources to Lake Superior, of which TCS is only a small component. Low levels of di-through-octaCDD at the base of the core may suggest that natural sources, such as forest fires, have contributed to a background level of PCDDs in this environment. Moreover, because low levels of higher chlorinated PCDD congeners are present at the base of the core, one cannot discount the potential for anaerobic reductive dechlorination as potential source of lower chlorinated PCDDs in old sediments. Finally, it is possible that traces of TCS and CTD derived PCDDs were introduced from nearby incineration sources, such as steel or paper mills in the Duluth, MN area throughout the $20^{th}$ century. With the data in this study, however, it is difficult to implicate a specific secondary source of these PCDDs.

### 3.4 Environmental Implications

The depositional trends of TCS and CTDs in lake sediments provide important insight into the historical exposure of wastewater-impacted aquatic ecosystems to these compounds. This exposure is dynamically linked to the size of the receiving water body and degree of wastewater impact. For example, in small-scale wastewater impacted lakes, such as East Lake Gemini and Lake Winona, high concentrations of TCS and CTDs in the sediment record likely reflect the long-term exposure of aquatic organisms to elevated levels of these contaminants. Consequently, this exposure may be adversely impacting algal and macrophyte community structure, enhancing bioaccumulation in higher trophic levels, and inducing a range of endocrine disrupting effects on aquatic biota. Moreover, because wastewater typically contains a diverse array of PPCPs, it is probable that TCS and CTDs are part of a complex mixture of bioactive and persistent compounds, leading to unknown consequences for the receiving aquatic ecosystem.

Due to the harmful effects of PCDDs in the environment, the loading of TCS and CTD derived PCDDs to aquatic ecosystems is of clear concern. Therefore, the contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TriCDD to the total PCDD pool, in terms of mass and toxicity, was determined for the lakes in this study. The contribution to total toxicity was determined by using toxic equivalency factors (TEFs), where toxicity of specific PCDD congeners and isomers are normalized to the most toxic PCDD congeners: 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD (Table 3-11). TEFs are multiplied by the concentration of a given PCDD congener or isomer to provide their toxic equivalency (TEQ) in an environmental matrix. These TEQs are then added to determine the total TEQ attributed to PCDDs in a given sample (Eq. 6):

$$\text{Total TEQ} = \Sigma\,[\text{PCDD}_i \times \text{TEF}_i] \tag{6}$$

**Table 3-11:** Toxic equivalency factors (TEFs) for PCDD congeners and isomers, relative to 2,3,7,8-TCDD.

| PCDD Congener/Isomer | Toxic Equivalency Factor (TEF) |
|---|---|
| DCDD | 0.001[a] |
| TriCDD | 0.01[a] |
| 2,3,7,8-TCDD | 1[b] |
| other TCDDs | 0.01[a] |
| 1,2,3,7,8-PeCDD | 1[b] |
| other PeCDDs | 0.1[b] |
| HxCDD | 0.1[b] |
| HpCDD | 0.01[b] |
| OCDD | 0.0003[b] |

[a] Ontario Ministry of the Environment, 1985
[b] Van den Berg et al., 2006

The TEF values presented in Table 3-11 were obtained from two sources [112,113]. Due to an abundance of toxicity data on tetra- through octa-CDDs in the literature, TEF values for these isomer groups have been well refined in recent years. The values in Table 3-11, for example, were determined by the World Health Organization (WHO) in 2005 as part of a re-evaluation of mammalian TEFs for dioxins and dioxin-like compounds. Lower chlorinated congeners (e.g., di- and tri-CDDs), however, have been poorly studied. Values for these isomers in Table 3-11 are derived from a 1985 study by the Ontario Ministry of the Environment. More recent work has proposed that di- and tri-CDDs may be less toxic, based on a series of bioassays on specific chlorinated and brominated dioxins [114]. Therefore, di- and tri-CDD TEFs presented in Table 3-11 in should be considered a worst-case scenario when calculating the TEQ for these isomers.

Figures 3-17 and 3-18 illustrate the contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD, in terms of mass and toxicity, to the PCDD pool in each sediment core. In the Lake Pepin core, the contribution of these PCDD congeners has been increasing since the patent of TCS in 1964, reaching up to 30% of total PCDD mass and 5% of total PCDD toxicity in recent sediment. This trend is reflective of the photochemical transformation of TCS and CTDs in the Mississippi River. A similar trend is observed in the Lake St. Croix sediment core. Due to a less pronounced wastewater impact to this system, however, these PCDD congeners only constitute up to 6.5% of total PCDD mass and 1.6% of PCDD toxicity in recent years.

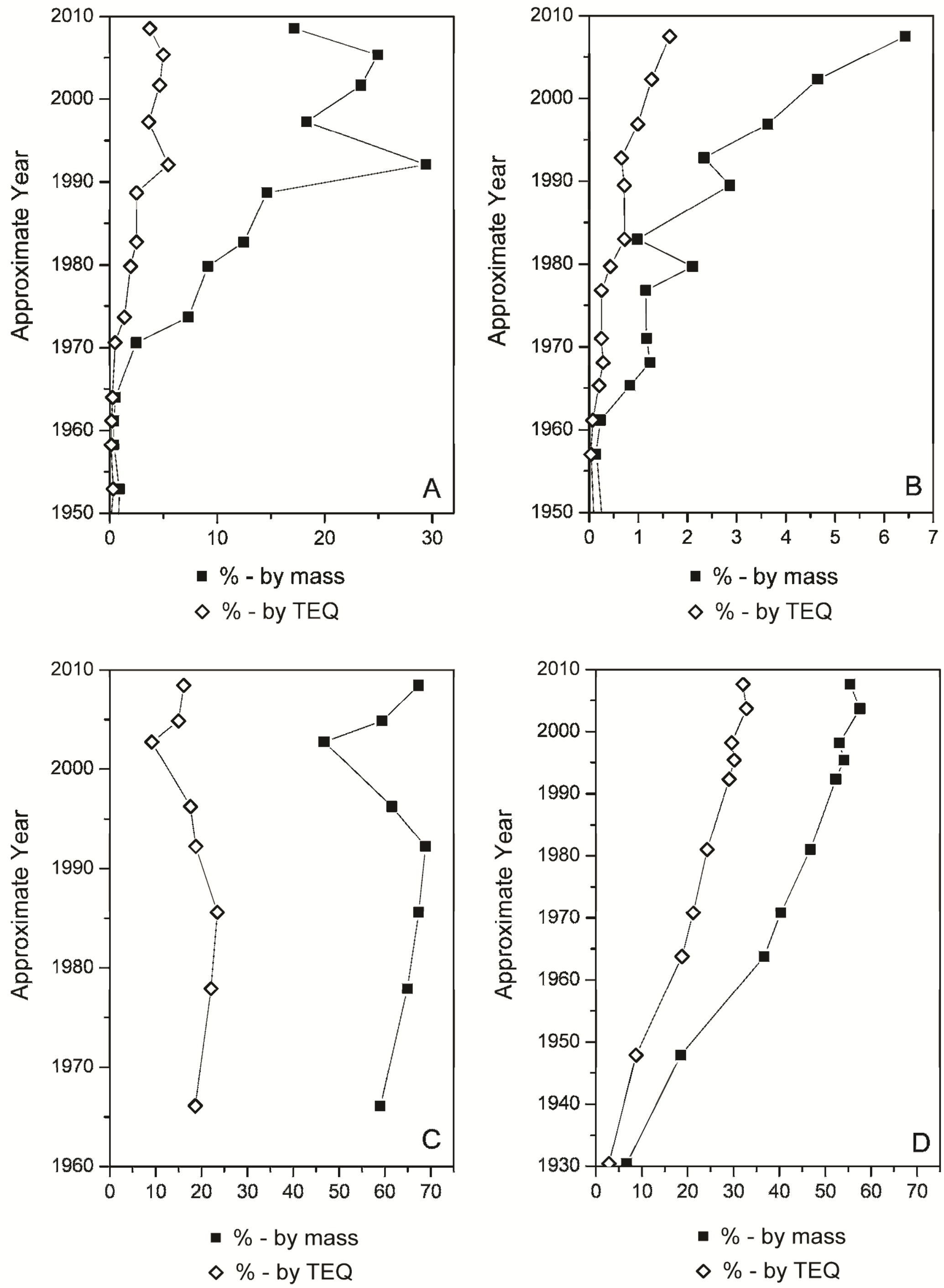



**Figure 3-17:** Percent contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD by mass and toxic equivalents (TEQ) to the total PCDD pool for Lake Pepin (A), Lake St. Croix (B), East Lake Gemini (C), and Lake Winona (D). Mass and TEQ contributions for all dated core sections are provided in Appendix F.

The contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD to the East Lake Gemini and Lake Winona PCDD pools is reflective of the heavy wastewater impact in each system. In East Lake Gemini, these PCDD congeners consistently account for greater than 46% of total PCDD loading to the system and up to 23% of PCDD toxicity. Although the formation of these PCDDs in East Lake Gemini has decreased since the 1960s, atmospheric loading of higher chlorinated PCDDs to the lake has been reduced over a similar timeline. Thus, the overall contribution of TCS and CTD derived PCDDs to this system remains significant. The photochemical transformation of TCS and CTDs has had a major impact on the PCDD loading and toxicity in Lake Winona. The di-, tri-, and tetra-CDDs derived from TCS and CTDs contribute up to 57% of PCDD mass loading and 32% of PCDD toxicity to the system.

The contribution of TCS and CTD derived PCDDs to total PCDD mass and toxicity in Duluth Harbor, Lake Superior, Lake Shagawa, and Little Lake Wilson is presented in Figure 3-18. Based on the estimation that a secondary, region-specific source has contributed to the loading of TCS and CTD derived PCDDs near Duluth, MN, it is possible that a fraction of each profile is attributed to this source. In the Duluth Harbor core, TCS and CTDs have clearly been the dominant source of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD since the 1960s. The contribution of these congeners to total PCDD mass and toxicity in harbor sediment, however, is relatively low. This is due to heavy contamination of the sediments with higher chlorinated congeners from a variety of industrial operations in near Duluth, including paper and steel mills.

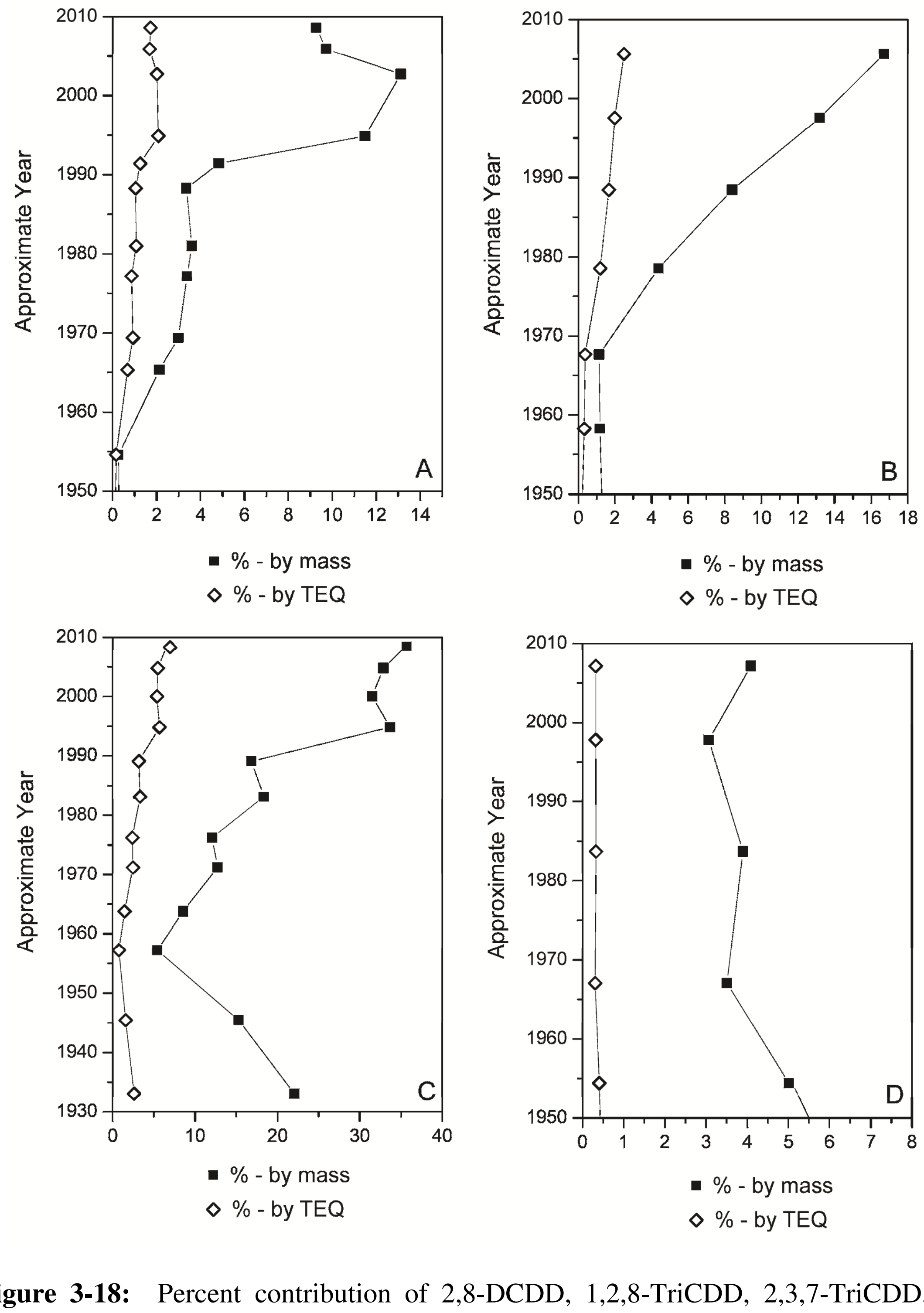



**Figure 3-18:** Percent contribution of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD by mass and toxic equivalents (TEQ) to the total PCDD pool for Duluth Harbor (A), Lake Superior (B), Lake Shagawa (C), and Lake Little Wilson (D). Mass and TEQ contributions for all dated core sections are provided in Appendix F.

As illustrated in Section 3.3.3, there is likely a diverse array of PCDD sources to the Lake Superior coring site, some of which may have contributed to the di-,tri-, and tetra-CDD loading to the sediment. After 1975, however, the PCDD contribution by mass and toxicity from 2,8-DCDD increased by a factor of 5. This is likely attributed to the photochemical transformation of TCS in the lake and suggests that TCS is a dominant source of this PCDD to Lake Superior today.

TCS and CTD derived PCDDs contribute appreciably to the total PCDD loading in Lake Shagawa. Since 1930, which likely corresponds to ~1960 in the core profile, these PCDDs have contributed at least 5% and up to 36% of total PCDD mass in Lake Shagawa sediment. Toxicity contributions reach as high as 6% in recent sediment. The visible inflection in the profiles presented in Figure 3-18 are attributed to changes in atmospheric PCDD loading throughout the 20$^{th}$ century.

The presence of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in Lake Little Wilson suggest that traces of these PCDDs can be derived from atmospheric sources. The mass and toxicity contributions of these PCDD congeners are depicted in Figure 3-18 from 1950 to 2010, a time period relevant to TCS and CTDs in the environment. During this time interval, the di-, tri-, and tetra-CDDs consistently account for 5% of total PCDD mass and ~ 0.4% of total PCDD toxicity. However, if you account for the high relative recovery of 2,8-DCDD in Lake Little Wilson sediment (up to 238% - see Section 3.3.1), then the mass and toxicity contributions are on the order of 1.5% and 0.2%, respectively.

## Chapter 4: Conclusions

Results presented in this study document the presence of TCS, CTDs, and their derived PCDDs in an array of wastewater-impacted MN lakes. Dated sediment cores provide a unique perspective on the historical exposure of regional aquatic ecosystems to these deleterious compounds. Furthermore, the sediment cores provide valuable insight into how wastewater treatment practices and lake system scale influence the depositional trends of TCS, CTDs, and their PCDDs in the sedimentary record. Finally, evaluation of the TCS and CTD derived PCDD contribution to the total PCDD pool, in terms of mass and toxicity, aids in assessing the potential risk that TCS poses to aquatic environments.

When comparing large and small-scale lake systems, there are clear differences in the concentrations and depositional trends of TCS, CTDs, and their PCDDs. Lake Pepin, for example, integrates many wastewater sources in the Mississippi River watershed, including the Metropolitan WWTP. Increasing analyte concentrations in this core are reflective of the large-scale integration of TCS and CTDs from various wastewater sources since the mid-1960s. Conversely, in small-scale systems like East Lake Gemini and Lake Winona, analyte trends are attributed to a single wastewater source. In East Lake Gemini, improvements in wastewater treatment and changes in disinfection at the SJU WWTP are directly recorded in TCS, CTD, and derived PCDD profiles. Furthermore, the high analyte concentrations found in Lake Winona are attributed to chlorinated ALASD WWTP effluent accounting for 63% of total inflow into the small, shallow water body.

Changes in wastewater disinfection can have a dramatic impact on the discharge of CTDs and formation of tri- and tetra-CDDs into aquatic environments. The Duluth

Harbor core, for example, records a 50% decrease in CTD and 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD loading from 1988 to 2002. This decrease is directly attributed to the disinfection variance granted to the WLSDD WWTP in 1994.

Several observations throughout this study suggest that TCS and CTDs are the primary sources of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD in aquatic systems heavily impacted by wastewater. The ratios of these PCDDs to their TCS and CTD precursors in the sediment cores are similar to those observed in photolysis experiments. Furthermore, the analysis of di- through octa-CDD trends in the Lake Pepin core suggest that TCS and CTDs have been a distinct and emerging source of these PCDDs since the 1960s in wastewater-impacted systems. Low levels of TCS and CTD derived PCDDs, however, are present prior to the patent of TCS in the Duluth Harbor core. Moreover, similar levels of these PCDDs are present throughout the Lake Superior core in the absence of detectable CTDs and in Lake Little Wilson, an aquatic system with no wastewater impact. This suggests that a secondary, region-specific atmospheric source may be contributing to low background levels of these PCDDs in northern MN. To delineate this secondary source, future work may analyze sediment extracts with expanded di- and tri-CDD acquisition windows during HRGC-HRMS analysis. If a broader array of DCDD and TriCDD congeners are present, this may help fingerprint a specific atmospheric source.

An integral component of this research was to determine the potential risk that TCS and its byproducts pose to aquatic ecosystems. In general, the loading of TCS and CTD derived PCDDs, in terms of mass and toxicity, has been increasing in MN lakes since the 1960s. The Lake Pepin core is a prime example of this trend, with TCS and

CTD derived PCDDs accounting for up to 30% of total PCDD mass and 5% of total PCDD toxicity in recent sediment. In small-scale lakes, like East Lake Gemini and Lake Winona, the TCS and CTD derived PCDD burden is much greater. In Lake Winona sediment, for example, these PCDDs account for up to 52% of total PCDD mass and 32% of total PCDD toxicity. This PCDD contribution, coupled with the presence of high concentrations of TCS and CTDs, likely poses a substantial risk to this aquatic ecosystem. Moreover, it is likely that similar risks are present in other small-scale aquatic systems that receive municipal and industrial wastewater around the U.S. and the world.

To better quantify the risks associated with TCS and CTD derived PCDDs, future work should focus on refining the estimated TEF values for di- and tri-CDD congeners. With improved estimates of 2,8-DCDD, 1,2,8-TriCDD, 2,3,7-TriCDD, and 1,2,3,8-TCDD toxicity to a variety of aquatic organisms, more informed risk assessments could be made on the harmful effects of TCS byproducts in surface waters. Furthermore, if TCS use continues to increase in personal care products, strict regulations may be needed for reducing levels of TCS and CTDs in wastewater effluents. Advanced oxidation processes, including ozonation [115,116] and photocatalysis [117], have been shown to rapidly degrade TCS in water with low dissolved organic carbon (DOC). Furthermore, membrane filtration may be a promising treatment option for TCS removal in wastewater effluent [118]. Consequently, integration of these processes in WWTPs may reduce TCS in wastewater effluent, minimize the formation of CTDs, and prevent the formation of their PCDDs in the environment.

## References


[1] Daughton, C.G. and Ternes, T.A. Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environ. Health Perspect.* **1999,** 907-938.

[2] Daughton, C.G. Pharmaceuticals and personal care products in the environment: overarching issues and overview. **2001,** *791,* 2-38.

[3] Brausch, J.M. and Rand, G.M. A review of personal care products in the aquatic environment: Environmental concentrations and toxicity. *Chemosphere* **2011,** *82,* 1518-1532.

[4] Heberer, T. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicol. Lett.* **2002,** *131,* 5-17.

[5] Ternes, T.A.; Joss, A.; Siegrist, H. Peer reviewed: scrutinizing pharmaceuticals and personal care products in wastewater treatment. *Environ. Sci. Technol.* **2004,** *38,* 392-399.

[6] Halling-Sørensen, B.; Nors Nielsen, S.; Lanzky, P.; Ingerslev, F.; Holten Lützhøft, H.; Jørgensen, S. Occurrence, fate and effects of pharmaceutical substances in the environment-a review. *Chemosphere* **1998,** *36,* 357-393.

[7] Boyd, G.R.; Reemtsma, H.; Grimm, D.A.; Mitra, S. Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. *Sci. Total Environ.* **2003,** *311,* 135-149.

[8] Kolpin, D.W.; Furlong, E.T.; Meyer, M.T.; Thurman, E.M.; Zaugg, S.D.; Barber, L.B.; Buxton, H.T. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: a national reconnaissance. *Environ. Sci. Technol.* **2002,** *36,* 1202-1211.

[9] Kinney, C.A.; Furlong, E.T.; Kolpin, D.W.; Burkhardt, M.R.; Zaugg, S.D.; Werner, S.L.; Bossio, J.P.; Benotti, M.J. Bioaccumulation of pharmaceuticals and other anthropogenic waste indicators in earthworms from agricultural soil amended with biosolid or swine manure. *Environ. Sci. Technol.* **2008,** *42,* 1863-1870.

[10] Suárez, S.; Carballa, M.; Omil, F.; Lema, J.M. How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? *Reviews in Environmental Science and Biotechnology* **2008,** *7,* 125-138.

[11] Heidler, J. and Halden, R.U. Mass balance assessment of triclosan removal during conventional sewage treatment. *Chemosphere* **2007,** *66,* 362-369.

[12] Schwarzenbach, R.P.; Escher, B.I.; Fenner, K.; Hofstetter, T.B.; Johnson, C.A.; Von Gunten, U.; Wehrli, B. The challenge of micropollutants in aquatic systems. *Science* **2006,** *313,* 1072-1077.

[13] Petrović, M. and Barceló, D. *Analysis, fate and removal of pharmaceuticals in the water cycle.* Elsevier Science: 2007; Vol. 50.

[14] Deborde, M. and Von Gunten, U. Reactions of chlorine with inorganic and organic compounds during water treatment--Kinetics and mechanisms: A critical review. *Water Res.* **2008,** *42,* 13-51.

[15] Huber, M.M.; GÖbel, A.; Joss, A.; Hermann, N.; LÖffler, D.; McArdell, C.S.; Ried, A.; Siegrist, H.; Ternes, T.A.; von Gunten, U. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. *Environ. Sci. Technol.* **2005,** *39,* 4290-4299.

[16] Snyder, S.A.; Wert, E.C.; Rexing, D.J.; Zegers, R.E.; Drury, D.D. Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone: Science and Engineering* **2006,** *28,* 445-460.

[17] Canonica, S.; Meunier, L.; von Gunten, U. Phototransformation of selected pharmaceuticals during UV treatment of drinking water. *Water Res.* **2008,** *42,* 121-128.

[18] Boorman, G.A. Drinking water disinfection byproducts: review and approach to toxicity evaluation. *Environ. Health Perspect.* **1999,** *107,* 207.

[19] Krasner, S.W.; Westerhoff, P.; Chen, B.; Rittmann, B.E.; Amy, G. Occurrence of disinfection byproducts in United States wastewater treatment plant effluents. *Environ. Sci. Technol.* **2009,** *43,* 8320-8325.

[20] Onodera, S.; Ogawa, M.; Suzuki, S. Chemical changes of organic compounds in chlorinated water* 1:: XIII. Gas chromatographic--mass spectrometric studies of the reactions of Irgasan DP 300 [5-chloro-2-(2, 4-dichlorophenoxy_phenol] with chlorine in dilute aqueous solution. *Journal of Chromatography A* **1987,** *392,* 267-275.

[21] Rule, K.L.; Ebbett, V.R.; Vikesland, P.J. Formation of chloroform and chlorinated organics by free-chlorine-mediated oxidation of triclosan. *Environ. Sci. Technol.* **2005,** *39,* 3176-3185.

[22] Canosa, P.; Morales, S.; Rodriguez, I.; Rubi, E.; Cela, R.; Gomez, M. Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine. *Analytical and bioanalytical chemistry* **2005,** *383,* 1119-1126.

[23] Fiss, E.M.; Krista, L.; Vikesland, P.J. Formation of chloroform and other chlorinated byproducts by chlorination of triclosan-containing antibacterial products. *Environ. Sci. Technol.* **2007,** *41,* 2387-2394.

[24] McAvoy, D.C.; Schatowitz, B.; Jacob, M.; Hauk, A.; Eckhoff, W.S. Measurement of triclosan in wastewater treatment systems. *Environmental toxicology and chemistry* **2002,** *21,* 1323-1329.

[25] Buth, J.M.; Ross, M.R.; McNeill, K.; Arnold, W.A. Removal and formation of chlorinated triclosan derivatives in wastewater treatment plants using chlorine and UV disinfection. *Chemosphere* **2011,** *85,* 284-289**.**

[26] Buth, J.M.; Grandbois, M.; Vikesland, P.J.; McNeill, K.; Arnold, W.A. Aquatic photochemistry of chlorinated triclosan derivatives: Potential source of polychlorodibenzo ‐ p ‐ dioxins. *Environmental Toxicology and Chemistry* **2009,** *28,* 2555-2563.

[27] Schweizer, H.P. Triclosan: a widely used biocide and its link to antibiotics. *FEMS Microbiol. Lett.* **2001,** *202,* 1-7.

[28] Perencevich, E.N.; Wong, M.T.; Harris, A.D. National and regional assessment of the antibacterial soap market: a step toward determining the impact of prevalent antibacterial soaps. *Am. J. Infect. Control* **2001,** *29,* 281-283.

[29] Sabaliunas, D.; Webb, S.F.; Hauk, A.; Jacob, M.; Eckhoff, W.S. Environmental fate of triclosan in the River Aire Basin, UK. *Water Res.* **2003,** *37,* 3145-3154.

[30] Chau, W.; Wu, J.; Cai, Z. Investigation of levels and fate of triclosan in environmental waters from the analysis of gas chromatography coupled with ion trap mass spectrometry. *Chemosphere* **2008,** *73,* S13-S17.

[31] Cantwell, M.G.; Wilson, B.A.; Zhu, J.; Wallace, G.T.; King, J.W.; Olsen, C.R.; Burgess, R.M.; Smith, J.P. Temporal trends of triclosan contamination in dated sediment cores from four urbanized estuaries: Evidence of preservation and accumulation. *Chemosphere* **2010,** *78,* 347-352.

[32] Halden, R.U. and Paull, D.H. Co-occurrence of triclocarban and triclosan in US water resources. *Environ. Sci. Technol.* **2005,** *39,* 1420-1426.

[33] Singer, H.; Müller, S.; Tixier, C.; Pillonel, L. Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments. *Environ. Sci. Technol.* **2002,** *36,* 4998-5004.

[34] Bester, K. Triclosan in a sewage treatment process—balances and monitoring data. *Water Res.* **2003,** *37,* 3891-3896.

[35] Bester, K. Fate of triclosan and triclosan-methyl in sewage treatment plants and surface waters. *Arch. Environ. Contam. Toxicol.* **2005,** *49,* 9-17.

[36] Thomas, P.M. and Foster, G.D. Tracking acidic pharmaceuticals, caffeine, and triclosan through the wastewater treatment process. *Environmental Toxicology and Chemistry* **2005,** *24,* 25-30.

[37] Lindström, A.; Buerge, I.J.; Poiger, T.; Bergqvist, P.A.; Müller, M.D.; Buser, H.R. Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. *Environ. Sci. Technol.* **2002,** *36,* 2322-2329.

[38] Ying, G.G.; Yu, X.Y.; Kookana, R.S. Biological degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modelling. *Environmental Pollution* **2007,** *150,* 300-305.

[39] Chen, X.; Nielsen, J.L.; Furgal, K.; Liu, Y.; Lolas, I.B.; Bester, K. Biodegradation of triclosan and formation of methyl-triclosan in activated sludge under aerobic conditions. *Chemosphere* **2011**

[40] Hua, W.; Bennett, E.R.; Letcher, R.J. Triclosan in waste and surface waters from the upper Detroit River by liquid chromatography-electrospray-tandem quadrupole mass spectrometry. *Environ. Int.* **2005,** *31,* 621-630.

[41] Waltman, E.L.; Venables, B.J.; Waller, W.T. Triclosan in a North Texas wastewater treatment plant and the influent and effluent of an experimental constructed wetland. *Environmental toxicology and chemistry* **2006,** *25,* 367-372.

[42] Ying, G.G. and Kookana, R.S. Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. *Environ. Int.* **2007,** *33,* 199-205.

[43] Buth, J.M. Ph.D. Thesis. *Transformation of pharmaceutical and personal care product pollutants by wastewater chlorine disinfection and aqueous photolysis* **2009.**

[44] Kolpin, D.W.; Skopec, M.; Meyer, M.T.; Furlong, E.T.; Zaugg, S.D. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. *Sci. Total Environ.* **2004,** *328,* 119-130.

[45] Tixier, C.; Singer, H.P.; Canonica, S.; Müller, S.R. Phototransformation of triclosan in surface waters: A relevant elimination process for this widely used biocide laboratory studies, field measurements, and modeling. *Environ. Sci. Technol.* **2002,** *36,* 3482-3489.

[46] Loraine, G.A. and Pettigrove, M.E. Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in southern California. *Environ. Sci. Technol.* **2006,** *40,* 687-695.

[47] Buth, J.M.; Steen, P.O; Sueper, C.; Blumentritt, D.; Vikesland, P.J.; Arnold W.A.; McNeill, K. Dioxin Photoproducts of Triclosan and its Chlorinated Derivatives in Sediment Cores. *Environ. Sci. Technol.* **2010,** *44,* 4545-4551.

[48] Miller, T.R.; Heidler, J.; Chillrud, S.N.; DeLaquil, A.; Ritchie, J.C.; Mihalic, J.N.; Bopp, R.; Halden, R.U. Fate of triclosan and evidence for reductive dechlorination of triclocarban in estuarine sediments. *Environ. Sci. Technol.* **2008,** *42,* 4570-4576.

[49] Venkatesan, A.K.; Pycke B.F.G.; Barber, L.B.; Lee, K. E.; Halden, R.U. Occurrence of triclosan, triclocarban, and its lesser chlorinated congeners in Minnesota freshwater sediments collected near wastewater treatment plants. *Journal of Hazardous Materials.* **2012,** 29-35.

[50] Coogan, M.A.; Edziyie, R.E.; La Point, T.W.; Venables, B.J. Algal bioaccumulation of triclocarban, triclosan, and methyl-triclosan in a North Texas wastewater treatment plant receiving stream. *Chemosphere* **2007,** *67,* 1911-1918.

[51] Wilson, B.A.; Smith, V.H.; Denoyelles Jr, F.; Larive, C.K. Effects of three pharmaceutical and personal care products on natural freshwater algal assemblages. *Environ. Sci. Technol.* **2003,** *37,* 1713-1719.

[52] Coogan, M.A. and Point, T.W.L. Snail bioaccumulation of triclocarban, triclosan, and methyltriclosan in a North Texas, USA, stream affected by wastewater treatment plant runoff. *Environmental Toxicology and Chemistry* **2008,** *27,* 1788-1793.

[53] Orvos, D.R.; Versteeg, D.J.; Inauen, J.; Capdevielle, M.; Rothenstein, A.; Cunningham, V. Aquatic toxicity of triclosan. *Environmental Toxicology and Chemistry* **2002,** *21,* 1338-1349.

[54] Adolfsson-Erici, M.; Pettersson, M.; Parkkonen, J.; Sturve, J. Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden. *Chemosphere* **2002,** *46,* 1485-1489.

[55] Valters, K.; Li, H.; Alaee, M.; D'Sa, I.; Marsh, G.; Bergman, Å.; Letcher, R.J. Polybrominated diphenyl ethers and hydroxylated and methoxylated brominated and chlorinated analogues in the plasma of fish from the Detroit River. *Environ. Sci. Technol.* **2005,** *39,* 5612-5619.

[56] Fair, P.A.; Lee, H.B.; Adams, J.; Darling, C.; Pacepavicius, G.; Alaee, M.; Bossart, G.D.; Henry, N.; Muir, D. Occurrence of triclosan in plasma of wild Atlantic bottlenose dolphins (Tursiops truncatus) and in their environment. *Environmental Pollution* **2009,** *157,* 2248-2254.

[57] Stevens, K.J.; Kim, S.Y.; Adhikari, S.; Vadapalli, V.; Venables, B.J. Effects of triclosan on seed germination and seedling development of three wetland plants: Sesbania herbacea, Eclipta prostrata, and Bidens frondosa. *Environmental Toxicology and Chemistry* **2009,** *28,* 2598-2609.

[58] Chu, S. and Metcalfe, C.D. Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry. *Journal of Chromatography A* **2007,** *1164,* 212-218.

[59] Morales, S.; Canosa, P.; Rodriguez, I.; Rubi, E.; Cela, R. Microwave assisted extraction followed by gas chromatography with tandem mass spectrometry for the determination of triclosan and two related chlorophenols in sludge and sediments. *Journal of Chromatography A* **2005,** *1082,* 128-135.

[60] Kinney, C.A.; Furlong, E.T.; Zaugg, S.D.; Burkhardt, M.R.; Werner, S.L.; Cahill, J.D.; Jorgensen, G.R. Survey of organic wastewater contaminants in biosolids destined for land application. *Environ. Sci. Technol.* **2006,** *40,* 7207-7215.

[61] Lozano, N.; Rice, C.P.; Ramirez, M.; Torrents, A. Fate of triclosan in agricultural soils after biosolid applications. *Chemosphere* **2010,** *78,* 760-766.

[62] Cha, J. and Cupples, A.M. Detection of the antimicrobials triclocarban and triclosan in agricultural soils following land application of municipal biosolids. *Water Res.* **2009,** *43,* 2522-2530.

[63] Cha, J. and Cupples, A.M. Triclocarban and triclosan biodegradation at field concentrations and the resulting leaching potentials in three agricultural soils. *Chemosphere* **2010,** *81,* 494-499.

[64] Xia, K.; Hundal, L.S.; Kumar, K.; Armbrust, K.; Cox, A.E.; Granato, T.C. Triclocarban, triclosan, polybrominated diphenyl ethers, and 4 - nonylphenol in biosolids and in soil receiving 33 - year biosolids application. *Environmental Toxicology and Chemistry* **2010,** *29,* 597-605.

[65] Armbrust, K.L.; Kwon, J.W.; Xia, K. Transformation of triclosan and triclocarban in soils and biosolids-applied soils. *J. Environ. Qual.* **2010,** *39,* 1139-1144.

[66] Wu, C.; Spongberg, A.L.; Witter, J.D. Adsorption and degradation of triclosan and triclocarban in soils and biosolids-amended soils. *J. Agric. Food Chem.* **2009,** *57,* 4900-4905.

[67] Al-Rajab, A.J.; Sabourin, L.; Scott, A.; Lapen, D.R.; Topp, E. Impact of biosolids on the persistence and dissipation pathways of triclosan and triclocarban in an agricultural soil. *Sci. Total Environ.* **2009,** *407,* 5978-5985.

[68] Lapen, D.; Topp, E.; Metcalfe, C.; Li, H.; Edwards, M.; Gottschall, N.; Bolton, P.; Curnoe, W.; Payne, M.; Beck, A. Pharmaceutical and personal care products in tile drainage following land application of municipal biosolids. *Sci. Total Environ.* **2008,** *399,* 50-65.

[69] Edwards, M.; Topp, E.; Metcalfe, C.; Li, H.; Gottschall, N.; Bolton, P.; Curnoe, W.; Payne, M.; Beck, A.; Kleywegt, S. Pharmaceutical and personal care products in tile drainage following surface spreading and injection of dewatered municipal biosolids to an agricultural field. *Sci. Total Environ.* **2009,** *407,* 4220-4230.

[70] White, G.C. *Handbook of chlorination.* Van Nostrand Reinhold Company: 1986.

[71] Leong, L.Y.C.; Kuo, J.; Tang, C.C. Disinfection of Wastewater Effluent-Comparison of Alternative Technologies. **2008.**

[72] Brezonik, P.L. and Arnold, W.A. *Water Chemistry: an introduction to the chemistry of natural and engineered aquatic systems.* Oxford Univ Pr: 2011.

[73] Greyshock, A.E. and Vikesland, P.J. Triclosan reactivity in chloraminated waters. *Environ. Sci. Technol.* **2006,** *40,* 2615-2622.

[74] Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M.; Wiley, J. *Environmental organic chemistry.* Wiley Online Library: 2003; Vol. 33.

[75] Latch, D.E.; Packer, J.L.; Arnold, W.A.; McNeill, K. Photochemical conversion of triclosan to 2, 8-dichlorodibenzo-p-dioxin in aqueous solution. *J. Photochem. Photobiol. A.* **2003,** *158,* 63-66.

[76] Latch, D.E.; Packer, J.L.; Stender, B.L.; VanOverbeke, J.; Arnold, W.A.; McNeill, K. Aqueous photochemistry of triclosan: Formation of 2, 4‐dichlorophenol, 2, 8‐dichlorodibenzo‐p‐dioxin, and oligomerization products. *Environmental Toxicology and Chemistry* **2005,** *24,* 517-525.

[77] Mezcua, M.; Gómez, M.J.; Ferrer, I.; Aguera, A.; Hernando, M.D.; Fernández-Alba, A.R. Evidence of 2, 7/2, 8-dibenzodichloro-< i> p</i>-dioxin as a photodegradation product of triclosan in water and wastewater samples. *Anal. Chim. Acta* **2004,** *524,* 241-247.

[78] Aranami, K. and Readman, J.W. Photolytic degradation of triclosan in freshwater and seawater. *Chemosphere* **2007,** *66,* 1052-1056.

[79] Morrall, D.; McAvoy, D.; Schatowitz, B.; Inauen, J.; Jacob, M.; Hauk, A.; Eckhoff, W. A field study of triclosan loss rates in river water (Cibolo Creek, TX). *Chemosphere* **2004,** *54,* 653-660.

[80] Nilsson, C.A.; Andersson, K.; Rappe, C.; Westermark, S.O. Chromatographic evidence for the formation of chlorodioxins from chloro-2-phenoxyphenols. *Journal of Chromatography A* **1974,** *96,* 137-147.

[81] Freeman, P.K. and Srinivasa, R. Photochemistry of polychlorinated phenoxyphenols: photochemistry of 3, 4, 5, 6-tetrachloro-2-(pentachlorophenoxy) phenol. *J. Agric. Food Chem.* **1983,** *31,* 775-780.

[82] Kanetoshi, A.; Ogawa, H.; Katsura, E.; Kaneshima, H.; Miura, T. Formation of polychlorinated dibenzo-p-dioxins upon combustion of commercial textile products containing 2, 4, 4'-trichloro-2'-hydroxydiphenyl ether (Irgasano DP3000. *Journal of Chromatography A* **1988a,** *442,* 289-299.

[83] Kanetoshi, A.; Ogawa, H.; Katsura, E.; Kaneshima, H.; Miura, T. Formation of polychlorinated dibenzo-p-dioxin from 2, 4, 4'-trichloro-2'-hydroxydiphenyl ether (irgasan® DP300) and its chlorinated derivatives by exposure to sunlight. *Journal of Chromatography A* **1988,** *454,* 145-155.

[84] Safe, S. Comparative toxicology and mechanism of action of polychlorinated dibenzo-p-dioxins and dibenzofurans. *Annu. Rev. Pharmacol. Toxicol.* **1986,** *26,* 371-399.

[85] Mason, G.; Farrell, K.; Keys, B.; Piskorska-Pliszczynska, J.; Safe, L.; Safe, S. Polychlorinated dibenzo-p-dioxins: quantitative in vitro and in vivo structure-activity relationships. *Toxicology* **1986,** *41,* 21-31.

[86] Van den Berg, M.; Birnbaum, L.; Bosveld, A.; Brunström, B.; Cook, P.; Feeley, M.; Giesy, J.P.; Hanberg, A.; Hasegawa, R.; Kennedy, S.W. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* **1998,** *106,* 775.

[87] Walker, M.K. and Peterson, R.E. Potencies of polychlorinated dibenzo-p-dioxin, dibenzofuran, and biphenyl congeners, relative to 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin, for producing early life stage mortality in rainbow trout (Oncorhynchus mykiss). *Aquatic Toxicology* **1991,** *21,* 219-237.

[88] Wisk, J.D. and Cooper, K.R. The stage specific toxicity of 2, 3, 7, 8 - tetrachlorodibenzo - p - dioxin in embryos of the japanese medaka (Oryzias latipes). *Environmental Toxicology and Chemistry* **1990,** *9,* 1159-1169.

[89] U.S. Environmental Protection Agency. An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000. **2006.**

[90] Hites, R.A. Dioxins: An Overview and History†. *Environ. Sci. Technol.* **2011.**

[91] Dean, W.E. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition; comparison with other methods. *Journal of Sedimentary Research* **1974,** *44,* 242-248.

[92] Heiri, O.; Lotter, A.F.; Lemcke, G. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *J. Paleolimnol.* **2001,** *25,* 101-110.

[93] Appleby, P. Chronostratigraphic techniques in recent sediments. *Tracking environmental change using lake sediments* **2002,** 171-203.

[94] Engstrom, D.R.; Almendinger, J.E.; Wolin, J.A. Historical changes in sediment and phosphorus loading to the upper Mississippi River: mass-balance reconstructions from the sediments of Lake Pepin. *J. Paleolimnol.* **2009,** *41,* 563-588.

[95] U.S. Environmental Protection Agency. Method 1613B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. **1994**.

[96] Minnesota Pollution Control Agency. Draft Lake Winona TMDL. November 2009.

[97] Minnesota Pollution Control Agency. Lake Winona site-specific nutrient criteria development. April 2011.

[98] Minnesota Pollution Control Agency. Statewide Endocrine Disrupting Compound Monitoring Study – 2007 to 2008. February 2010.

[99] Malueg, K.W. *The Shagawa Lake Project: lake restoration by nutrient removal from wastewater effluent.* US Environmental Protection Agency, Office of Research and Monitoring, National Environmental Research Center;[for sale by the Supt. of Docs., US Govt. Print. Off., Washington, DC]: 1973.

[100] Kibby, H. and Hernandez, D.J. *Environmental impacts of advanced wastewater treatment at Ely, Minnesota.* US Environemtnal Protection Agency, Office of Research and Development, Corvallis Environmental Research Laboratory, Criteria and Assessment Branch: 1976.

[101] Larsen, D.P. and Malueg, K.W. Whatever became of Shagawa Lake.? International Symposium on the Restoration of Lakes and Inland Waters, **1980.**

[102] Hites, R.A. Environmental behavior of chlorinated dioxins and furans. *Acc. Chem. Res.* **1990,** *23,* 194-201.

[103] Baker, J.I. and Hites, R.A. Siskiwit Lake revisited: Time trends of polychlorinated dibenzo-p-dioxin and dibenzofuran deposition at Isle Royale, Michigan. *Environ. Sci. Technol.* **2000,** *34,* 2887-2891.

[104] Pearson, R.F.; Swackhamer, D.L.; Eisenreich, S.J.; Long, D.T. Atmospheric inputs of polychlorinated dibenzo-p-dioxins and dibenzofurans to the Great Lakes: compositional comparison of PCDD and PCDF in sediments. *J. Great Lakes Res.* **1998,** *24,* 65-82.

[105] Nestrick, T. and Lamparski, L. Isomer-specific determination of chlorinated dioxins for assessment of formation and potential environmental emission from wood combustion. *Anal. Chem.* **1982,** *54,* 2292-2299.

[106] Sheffield, A. Sources and releases of PCDD's and PCDF's to the Canadian environment. *Chemosphere* **1985,** *14,* 811-814.

[107] Alcock, R.E. and Jones, K.C. Dioxins in the environment: a review of trend data. *Environ. Sci. Technol.* **1996,** *30,* 3133-3143.

[108] Gribble, G.W. The natural production of chlorinated compounds. *Environ. Sci. Technol.* **1994,** *28,* 310-319.

[109] Thomas, V.M. and Spiro, T.G. Peer Reviewed: The US Dioxin Inventory: Are There Missing Sources? *Environ. Sci. Technol.* **1996,** *30,* 82-85.

[110] Gullett, B.K. and Touati, A. PCDD/F emissions from forest fire simulations. *Atmos. Environ.* **2003,** *37,* 803-813.

[111] Grandesso, E.; Gullett, B.; Touati, A.; Tabor, D. Effect of moisture, charge size, and chlorine concentration on PCDD/F emissions from simulated open burning of forest biomass. *Environ. Sci. Technol.* **2011,** *45*, 3887–3894.

[112] Ontario Ministry of the Environment, Scientific Criteria Document for Standard Development, no 4-84. Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs); Ontario Ministry of the Environment: Toronto, Ontario, 1985.

[113] Van den Berg, M.; Birnbaum, L.S.; Denison, M.; De Vito, M.; Farland, W.; Feeley, M.; Fiedler, H.; Hakansson, H.; Hanberg, A.; Haws, L. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences* **2006,** *93,* 223-241.

[114] Samara, F.; Gullett, B.K.; Harrison, R.O.; Chu, A.; Clark, G.C. Determination of relative assay response factors for toxic chlorinated and brominated dioxins/furans using an enzyme immunoassay (EIA) and a chemically-activated luciferase gene expression cell bioassay (CALUX). *Environ. Int.* **2009,** *35,* 588-593.

[115] Suarez, S.; Dodd, M.C.; Omil, F.; von Gunten, U. Kinetics of triclosan oxidation by aqueous ozone and consequent loss of antibacterial activity: Relevance to municipal wastewater ozonation. *Water Res.* **2007,** *41,* 2481-2490.

[116] Chen, X.; Richard, J.; Liu, Y.; Dopp, E.; Tuerk, J.; Bester, K. Ozonation products of triclosan in advanced wastewater treatment. *Water Res.* **2012,** 2247-2256.

[117] Yu, J.C.; Kwong, T.; Luo, Q.; Cai, Z. Photocatalytic oxidation of triclosan. *Chemosphere* **2006,** *65,* 390-399.

[118] Snyder, S.A.; Adham, S.; Redding, A.M.; Cannon, F.S.; DeCarolis, J.; Oppenheimer, J.; Wert, E.C.; Yoon, Y. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* **2006,** *202,* 156-181.

[119] Lamborg, C.H.; Engstrom, D.R.; Fitzgerald W.F.; Balcom, P.H. Apportioning global and non-global components of mercury deposition through $^{210}Pb$ indexing. *Journal* **2012,** *in press.*

[120] Triplett, L.D.; Engstrom, D.R.; Edlund, M.B. A whole-basin stratigraphic record of sediment and phosphorus loading to the St. Croix River, USA. *J. Paleolimnol.* **2009,** *41,* 659-677.

## Appendix A

### General Laboratory Preparation and Practice

To prevent analyte contamination during sample preparation and extraction, a series of detailed procedures were followed in the laboratory. Freeze drying tins, plastic syringes for silica columns, and all glassware, with the exception of disposable glass pipettes, were triple washed consecutively with a dilute solution of alconox and deionized (DI) water. The glassware, including the pipettes, were then covered with foil and fired at 550 °C for 4 hours. Freeze drying tins, plastic syringes, and any glassware that could not be fired were triple rinsed with methanol and ethyl acetate. All cleaned materials were stored in a designated cabinet to prevent contamination. Silica gel, glass wool, and Ottawa sand were all fired at 550 °C for 4 hours before use in ASE cells or silica columns.

Prior to working in the laboratory, bench-tops areas and fumehoods to be used were wiped down with alconox. Surfaces were then covered with foil to help prevent contamination.

Gas-tight, glass syringes were used to prepare standards, spike samples, and transfer final extracts to autosampler vials. Three separate syringes were designated for $^{13}C_{12}$-TCS, TCS, and CTD solutions to prevent analyte cross-contamination. Moreover, one syringe was always kept clean for sample resuspension. Finally, a fifth syringe was used to transfer final extracts to autosampler vials. Regardless of use, all syringes were rinsed 5 times with acetone, acetonitrile, and methanol prior to each transfer.

**Accelerated Solvent Extraction (ASE) 350 - Cleaning Procedures**

Several cleaning procedures are required when using the ASE 350 to minimize analyte contamination. The stainless steel ASE cell end caps, in particular, must be carefully cleaned, as they tend to accumulate analytes over time. For this project, ASE end caps were triple rinsed with tap water, DI water, methanol, and ethyl acetate. Detergents, including alconox, cannot be used on the endcaps because they degrade the seals. After this washing procedure, the cells were disassembled, placed in a clean jar, and sonicated in acetone for 10 minutes. The end caps were then reassembled and subsequently rinsed three times with methanol and ethyl acetate to remove any remaining contamination.

The stainless steel bodies of the ASE cells were cleaned by triple rinsing with alconox, DI water, methanol and ethyl acetate. All specialty tools were cleaned using the same procedure.

After a sequence of ASE extractions, the solvent lines were rinsed 5 times consecutively with acetone as a preventative maintenance step. Dichloromethane (DCM), the mobile phase used for extraction in this study, is a very strong solvent that will corrode the ASE pump if left in the lines for long periods of time (e.g., for a month). To help maintain the ASE, lines should always be flushed with acetone prior to shutting the instrument down.

## Appendix B

## LC-MS-$Q^3$ – Operational Guidance for TCS and CTD Analysis

Prior to analyzing sediment extracts for TCS and CTDs on the LC-MS-$Q^3$ at the Masonic Cancer Research Center, a specific instrument preparation procedure must be followed. Specifically, a clean ion-transfer tube should be installed in the MS-$Q^3$ and preconditioned with 3-5 existing sediment extracts, before running any instrument blanks, standards, or samples. This process has been shown to provide consistent and improved analyte response in sediment matrices. For an unknown reason, the analytes of interest ($^{13}C_{12}$-TCS, TCS, and CTDs) take a period of time to equilibrate in the MS-$Q^3$ (e.g., to provide stable and consistent analytical response). Preconditioning of a clean ion-transfer tube with existing sediment extracts containing these analytes reduces this equilibration time.

## Appendix C

## Calculation of TCS and CTD Concentrations in Sediment Matrices

The following material outlines the calculations used to determine TCS and CTD concentrations in sediment matrices using isotope-dilution methodology. Concentrations are determined by multiplying (1) a response factor from the analyte calibration curve, (2) the analyte to $^{13}C_{12}$-TCS peak area ratio in the sediment matrix, and (3) the amount of $^{13}C_{12}$-TCS spiked into the sample. Figure AC-1 provides an example calibration curve for the calculations.

## Example Calculation – TCS Sediment Concentration

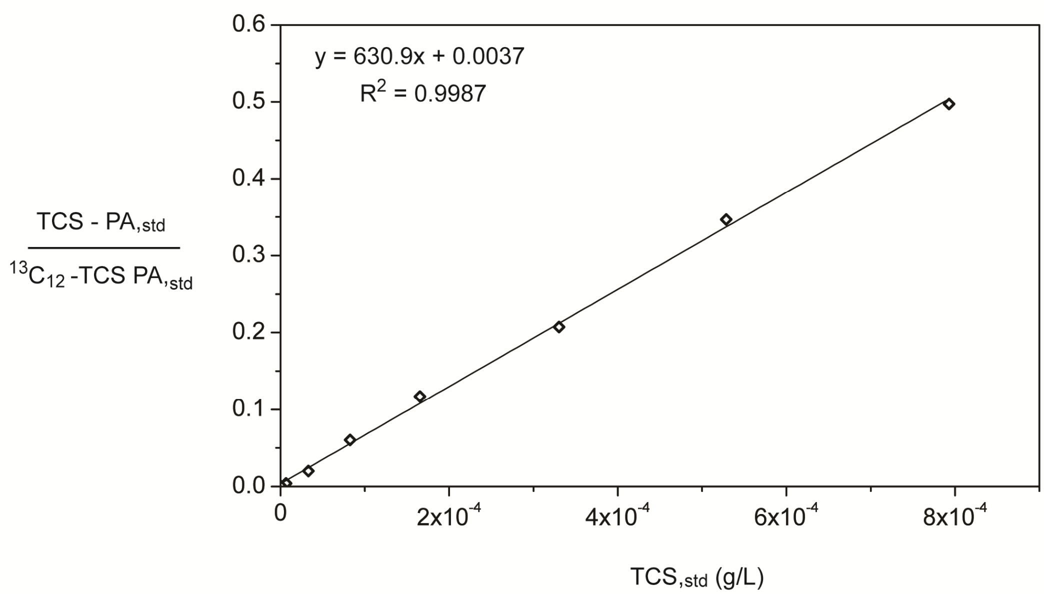



**Figure AC-1: Example TCS calibration curve. Notation: PA = peak area, std = standard.**

Equation 1 outlines the calculation of TCS mass in a sample, using isotope dilution methodology:

$$\boxed{\mathrm{TCS,_{sample}\ (g) = [RF] \times \frac{[TCS\ PA,_{sample}]}{[^{13}C_{12}\text{ - }TCS\ PA,_{sample}]} \times [^{13}C_{12}\text{ - }TCS,_{sample}\ (g)]}} \qquad (1)$$

where:

$$\mathrm{RF} = \frac{1}{\mathrm{[^{13}C_{12}\text{ - }TCS,_{std}\ (g/L)][calibration\ slope]}}$$

and:

$$\mathrm{calibration\ slope} = \frac{\mathrm{TCS\ PA,_{std}}}{\mathrm{[^{13}C_{12}\text{ - }TCS\ PA,_{std}][TCS,_{std}\ (g/L)]}}$$

Equation 1 can be expanded as follows:

$$\boxed{\begin{aligned}\mathrm{TCS,_{sample}\ (g)} &= \mathrm{\frac{[^{13}C_{12}\text{ - }TCS\ PA,_{std}][TCS,_{std}\ (g/L)]}{[^{13}C_{12}\text{ - }TCS,_{std}\ (g/L)][TCS\ PA,_{std}]} \times \frac{[TCS\ PA,_{sample}]}{[^{13}C_{12}\text{ - }TCS\ PA,_{sample}]}} \\ &\quad \times \mathrm{[^{13}C_{12}\text{ - }TCS,_{sample}\ (g)]}\end{aligned}} \qquad (2)$$

When normalized to the amount of sediment analyzed in an extract, Equation 2 provides the concentration of TCS in a given sample.

**Absolute Recovery of $^{13}C_{12}$-TCS**

The absolute recovery of $^{13}C_{12}$-TCS in sediment extracts was determined using Equation 3:

$$\boxed{{}^{13}\mathrm{C}_{12}\text{-TCS Recovery} = \frac{[{}^{13}\mathrm{C}_{12}\text{ - TCS PA},_{\mathrm{sample}}]}{[{}^{13}\mathrm{C}_{12}\text{ - TCS PA},_{\mathrm{std}}\text{ (avg)}]} \times \frac{[{}^{13}\mathrm{C}_{12}\text{ - TCS},_{\mathrm{std}}\text{ (g/L)}]}{[{}^{13}\mathrm{C}_{12}\text{ - TCS},_{\mathrm{sample}}\text{ (g/L)}]} \times 100} \quad (3)$$

where: $^{13}C_{12}$-TCS PA, $_{std}$ (avg) = the average $^{13}C_{12}$-TCS PA in the calibration curve.

## Appendix D

## $^{13}C_{12}$-PCDD/F and PCDD/F Recoveries – Pace Analytical

**Table AD-1**: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Pepin sediment core.

| $^{13}C_{12}$-PCDD/F Congener | Absolute Recovery (%) | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a] 47 ± 7.4 | (n = 16) |
| $^{13}C_{12}$-2,3,7-TriCDD | 77 ± 9.1 | (n = 16) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 73 ± 7.4 | (n = 16) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 87 ± 7.2 | (n = 16) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 75 ± 7.2 | (n = 16) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 75 ± 8.6 | (n = 16) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 85 ± 9.8 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 79 ± 10.5 | (n = 16) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 74 ± 4.0 | (n = 16) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 66 ± 4.2 | (n = 16) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 75 ± 7.7 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 83 ± 13.4 | (n = 16) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 69 ± 6.0 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 61 ± 5.7 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 60 ± 6.4 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 62 ± 6.1 | (n = 16) |
| $^{13}C_{12}$-OCDD | 55 ± 6.8 | (n = 16) |

[a] Reported values are the mean ± standard deviation

**Table AD-2:** Relative PCDD/F recovery in Lake Pepin sediment (spike and recovery).

| PCDD/F Congener | Relative Recovery (%) | [b] RPD |
|---|---|---|
| 2,8-DCDD | [a] 92 | 7.3 |
| 2,3,7-TriCDD | 108 | 4.6 |
| 2,3,7,8-TCDF | 119 | 1.4 |
| 2,3,7,8-TCDD | 87 | 1.4 |
| 1,2,3,7,8-PeCDF | 110 | 2.6 |
| 2,3,4,7,8-PeCDF | 108 | 0.2 |
| 1,2,3,7,8-PeCDD | 95 | 3.8 |
| 1,2,3,4,7,8-HxCDF | 107 | 2.2 |
| 1,2,3,6,7,8-HxCDF | 107 | 1.5 |
| 2,3,4,6,7,8-HxCDF | 106 | 0.5 |
| 1,2,3,7,8,9-HxCDF | 106 | 0.2 |
| 1,2,3,4,7,8-HxCDD | 108 | 1.2 |
| 1,2,3,6,7,8-HxCDD | 117 | 0.4 |
| 1,2,3,7,8,9-HxCDD | 109 | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 108 | 3.7 |
| 1,2,3,4,7,8,9-HpCDF | 98 | 1.7 |
| 1,2,3,4,6,7,8-HpCDD | 98 | 0.3 |
| OCDF | 97 | 1.7 |
| OCDD | 98 | 1.8 |

[a] Reported values are the mean relative recovery (n = 2)

[b] RPD = relative percent difference between matrix spike replicates

**Table AD-3**: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake St. Croix sediment core.

| $^{13}C_{12}$-PCDD/F Congener | Absolute Recovery (%) | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a] 48 ± 9.4 | (n = 16) |
| $^{13}C_{12}$-2,3,7-TriCDD | 76 ± 5.8 | (n = 16) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 82 ± 5.0 | (n = 16) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 88 ± 7.1 | (n = 16) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 84 ± 4.4 | (n = 16) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 82 ± 5.4 | (n = 16) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 88 ± 6.4 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 81 ± 11.5 | (n = 16) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 79 ± 7.5 | (n = 16) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 76 ± 6.5 | (n = 16) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 71 ± 12.7 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 78 ± 5.7 | (n = 16) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 67 ± 4.3 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 50 ± 9.7 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 45 ± 12.1 | (n = 16) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 45 ± 8.6 | (n = 16) |
| $^{13}C_{12}$-OCDD | 39 ± 8.3 | (n = 16) |

[a] Reported values are the mean ± standard deviation

**Table AD-4**: Relative PCDD/F recovery in Lake St. Croix sediment (spike and recovery).

| PCDD/F Congener | Relative Recovery (%) | [b] RPD |
|---|---|---|
| 2,8-DCDD | [a] 100 | 6.8 |
| 2,3,7-TriCDD | 108 | 2.6 |
| 2,3,7,8-TCDF | 119 | 4.4 |
| 2,3,7,8-TCDD | 96 | 0.4 |
| 1,2,3,7,8-PeCDF | 111 | 1.8 |
| 2,3,4,7,8-PeCDF | 109 | 2.9 |
| 1,2,3,7,8-PeCDD | 97 | 6.2 |
| 1,2,3,4,7,8-HxCDF | 110 | 8.3 |
| 1,2,3,6,7,8-HxCDF | 111 | 4.1 |
| 2,3,4,6,7,8-HxCDF | 106 | 3.6 |
| 1,2,3,7,8,9-HxCDF | 108 | 2.3 |
| 1,2,3,4,7,8-HxCDD | 117 | 12.9 |
| 1,2,3,6,7,8-HxCDD | 115 | 8.1 |
| 1,2,3,7,8,9-HxCDD | 109 | 5.6 |
| 1,2,3,4,6,7,8-HpCDF | 109 | 5.2 |
| 1,2,3,4,7,8,9-HpCDF | 103 | 10.9 |
| 1,2,3,4,6,7,8-HpCDD | 102 | 6.7 |
| OCDF | 100 | 5.3 |
| OCDD | 107 | 9.0 |

[a] Reported values are the mean relative recovery (n = 2)

[b] RPD = relative percent difference between matrix spike replicates

**Table AD-5**: Absolute $^{13}C_{12}$-PCDD/F recovery in the East Lake Gemini sediment core.

| **$^{13}C_{12}$-PCDD/F Congener** | **Absolute Recovery (%)** | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a] 48 ± 3.3 | (n = 8) |
| $^{13}C_{12}$-2,3,7-TriCDD | 80 ± 3.7 | (n = 8) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 76 ± 3.9 | (n = 8) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 89 ± 6.0 | (n = 8) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 80 ± 5.4 | (n = 8) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 81 ± 5.2 | (n = 8) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 91 ± 5.2 | (n = 8) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 85 ± 5.3 | (n = 8) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 76 ± 3.0 | (n = 8) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 69 ± 4.8 | (n = 8) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 79 ± 3.9 | (n = 8) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 90 ± 4.9 | (n = 8) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 73 ± 3.5 | (n = 8) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 63 ± 4.0 | (n = 8) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 61 ± 4.7 | (n = 8) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 62 ± 4.0 | (n = 8) |
| $^{13}C_{12}$-OCDD | 56 ± 3.8 | (n = 8) |

[a] Reported values are the mean ± standard deviation

**Table AD-6**: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Winona sediment core.

| $^{13}C_{12}$-PCDD/F Congener | Absolute Recovery (%) | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a] 42 ± 6.6 | (n = 11) |
| $^{13}C_{12}$-2,3,7-TriCDD | 63 ± 5.8 | (n = 11) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 63 ± 6.4 | (n = 11) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 78 ± 6.9 | (n = 11) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 70 ± 6.7 | (n = 11) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 64 ± 5.8 | (n = 11) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 70 ± 6.1 | (n = 11) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 65 ± 5.4 | (n = 11) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 67 ± 5.5 | (n = 11) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 60 ± 5.2 | (n = 11) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 61 ± 5.4 | (n = 11) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 62 ± 4.9 | (n = 11) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 53 ± 5.6 | (n = 11) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 48 ± 4.5 | (n = 11) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 44 ± 6.5 | (n = 11) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 45 ± 5.4 | (n = 11) |
| $^{13}C_{12}$-OCDD | 38 ± 6.8 | (n = 11) |

[a] Reported values are the mean ± standard deviation

**Table AD-7**: Relative PCDD/F recovery in Lake Winona sediment (spike and recovery).

| PCDD/F Congener | Relative Recovery (%) | [b] RPD |
|---|---|---|
| 2,8-DCDD | [a] 121 | 5.8 |
| 2,3,7-TriCDD | 105 | 0.5 |
| 2,3,7,8-TCDF | 119 | 1.9 |
| 2,3,7,8-TCDD | 87 | 3.3 |
| 1,2,3,7,8-PeCDF | 108 | 0.6 |
| 2,3,4,7,8-PeCDF | 107 | 1.1 |
| 1,2,3,7,8-PeCDD | 96 | 1.5 |
| 1,2,3,4,7,8-HxCDF | 109 | 3.6 |
| 1,2,3,6,7,8-HxCDF | 105 | 0.4 |
| 2,3,4,6,7,8-HxCDF | 105 | 2.6 |
| 1,2,3,7,8,9-HxCDF | 106 | 2.8 |
| 1,2,3,4,7,8-HxCDD | 114 | 6.1 |
| 1,2,3,6,7,8-HxCDD | 115 | 3.7 |
| 1,2,3,7,8,9-HxCDD | 111 | 0.6 |
| 1,2,3,4,6,7,8-HpCDF | 111 | 0.4 |
| 1,2,3,4,7,8,9-HpCDF | 100 | 0.9 |
| 1,2,3,4,6,7,8-HpCDD | 96 | 4.4 |
| OCDF | 101 | 10.2 |
| OCDD | 75 | 5.9 |

[a] Reported values are the mean relative recovery (n = 2)

[b] RPD = relative percent difference between matrix spike replicates

**Table AD-8**: Absolute $^{13}C_{12}$-PCDD/F recovery in the Duluth Harbor sediment core.

| $^{13}C_{12}$-PCDD/F Congener | Absolute Recovery (%) | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a] 75 ± 6.5 | (n = 13) |
| $^{13}C_{12}$-2,3,7-TriCDD | 80 ± 9.8 | (n = 13) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 85 ± 4.1 | (n = 13) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 98 ± 4.7 | (n = 13) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 85 ± 2.5 | (n = 13) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 80 ± 3.5 | (n = 13) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 84 ± 6.2 | (n = 13) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 87 ± 5.6 | (n = 13) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 86 ± 6.5 | (n = 13) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 77 ± 3.0 | (n = 13) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 72 ± 4.2 | (n = 13) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 74 ± 5.6 | (n = 13) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 68 ± 5.9 | (n = 13) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 51 ± 4.3 | (n = 13) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 50 ± 5.4 | (n = 13) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 51 ± 6.1 | (n = 13) |
| $^{13}C_{12}$-OCDD | 37 ± 5.5 | (n = 13) |

[a] Reported values are the mean ± standard deviation

**Table AD-9**: Relative PCDD/F recovery in Duluth Harbor sediment (spike and recovery).

| PCDD/F Congener | Relative Recovery (%) | [b] RPD |
|---|---|---|
| 2,8-DCDD | [a] 97 | 9.2 |
| 2,3,7-TriCDD | 104 | 5.5 |
| 2,3,7,8-TCDF | 111 | 3.4 |
| 2,3,7,8-TCDD | 86 | 2.3 |
| 1,2,3,7,8-PeCDF | 112 | 2.3 |
| 2,3,4,7,8-PeCDF | 111 | 1.9 |
| 1,2,3,7,8-PeCDD | 94 | 4.5 |
| 1,2,3,4,7,8-HxCDF | 116 | 4.5 |
| 1,2,3,6,7,8-HxCDF | 111 | 2.6 |
| 2,3,4,6,7,8-HxCDF | 109 | 1.9 |
| 1,2,3,7,8,9-HxCDF | 110 | 3.1 |
| 1,2,3,4,7,8-HxCDD | 106 | 0.9 |
| 1,2,3,6,7,8-HxCDD | 120 | 0.2 |
| 1,2,3,7,8,9-HxCDD | 124 | 3.1 |
| 1,2,3,4,6,7,8-HpCDF | 116 | 6.0 |
| 1,2,3,4,7,8,9-HpCDF | 102 | 5.7 |
| 1,2,3,4,6,7,8-HpCDD | 99 | 3.4 |
| OCDF | 115 | 2.9 |
| OCDD | 111 | 0.9 |

[a] Reported values are the mean relative recovery (n = 2)

[b] RPD = relative percent difference between matrix spike replicates

**Table AD-10**: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Superior sediment core.

| $^{13}C_{12}$-PCDD/F Congener | Absolute Recovery (%) | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a]62 ± 7.3 | (n = 10) |
| $^{13}C_{12}$-2,3,7-TriCDD | 78 ± 3.8 | (n = 10) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 84 ± 3.6 | (n = 10) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 104 ± 3.7 | (n = 10) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 92 ± 3.1 | (n = 10) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 98 ± 3.0 | (n = 10) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 109 ± 3.8 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 81 ± 3.2 | (n = 10) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 87 ± 3.0 | (n = 10) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 87 ± 2.4 | (n = 10) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 95 ± 4.5 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 85 ± 5.6 | (n = 10) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 78 ± 2.8 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 80 ± 2.9 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 92 ± 4.3 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 92 ± 3.8 | (n = 10) |
| $^{13}C_{12}$-OCDD | 85 ± 3.7 | (n = 10) |

[a] Reported values are the mean ± standard deviation

**Table AD-11**: Relative PCDD/F recovery in Lake Superior sediment (spike and recovery).

| PCDD/F Congener | Relative Recovery (%) | [b]RPD |
|---|---|---|
| 2,8-DCDD | [a]101 | 8.0 |
| 2,3,7-TriCDD | 111 | 17.5 |
| 2,3,7,8-TCDF | 114 | 1.3 |
| 2,3,7,8-TCDD | 78 | 4.8 |
| 1,2,3,7,8-PeCDF | 107 | 4.2 |
| 2,3,4,7,8-PeCDF | 107 | 4.6 |
| 1,2,3,7,8-PeCDD | 90 | 5.6 |
| 1,2,3,4,7,8-HxCDF | 106 | 0.3 |
| 1,2,3,6,7,8-HxCDF | 101 | 5.6 |
| 2,3,4,6,7,8-HxCDF | 99 | 1.7 |
| 1,2,3,7,8,9-HxCDF | 100 | 4.4 |
| 1,2,3,4,7,8-HxCDD | 100 | 2.9 |
| 1,2,3,6,7,8-HxCDD | 110 | 1.4 |
| 1,2,3,7,8,9-HxCDD | 107 | 1.2 |
| 1,2,3,4,6,7,8-HpCDF | 101 | 2.4 |
| 1,2,3,4,7,8,9-HpCDF | 94 | 4.2 |
| 1,2,3,4,6,7,8-HpCDD | 90 | 2.0 |
| OCDF | 103 | 4.1 |
| OCDD | 99 | 1.4 |

[a] Reported values are the mean relative recovery (n = 2)

[b] RPD = relative percent difference between matrix spike replicates

**Table AD-12**: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Shagawa sediment core.

| $^{13}C_{12}$-PCDD/F Congener | Absolute Recovery (%) | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a] 52 ± 14.7 | (n = 12) |
| $^{13}C_{12}$-2,3,7-TriCDD | 75 ± 12.7 | (n = 12) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 69 ± 11.7 | (n = 12) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 88 ± 14.6 | (n = 12) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 74 ± 12.3 | (n = 12) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 73 ± 12.6 | (n = 12) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 82 ± 14.3 | (n = 12) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 69 ± 13.1 | (n = 12) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 74 ± 13.5 | (n = 12) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 71 ± 12.1 | (n = 12) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 76 ± 12.7 | (n = 12) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 73 ± 12.4 | (n = 12) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 65 ± 11.6 | (n = 12) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 65 ± 11.5 | (n = 12) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 70 ± 13.9 | (n = 12) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 70 ± 14.5 | (n = 12) |
| $^{13}C_{12}$-OCDD | 64 ± 12.8 | (n = 12) |

[a] Reported values are the mean ± standard deviation

**Table AD-13**: Relative PCDD/F recovery in Lake Shagawa sediment (spike and recovery).

| PCDD/F Congener | Relative Recovery (%) | [b] RPD |
|---|---|---|
| 2,8-DCDD | [a] 116 | 6.8 |
| 2,3,7-TriCDD | 112 | 1.4 |
| 2,3,7,8-TCDF | 124 | 1.9 |
| 2,3,7,8-TCDD | 86 | 1.7 |
| 1,2,3,7,8-PeCDF | 115 | 0.4 |
| 2,3,4,7,8-PeCDF | 113 | 1.3 |
| 1,2,3,7,8-PeCDD | 100 | 1.1 |
| 1,2,3,4,7,8-HxCDF | 116 | 0.0 |
| 1,2,3,6,7,8-HxCDF | 113 | 2.3 |
| 2,3,4,6,7,8-HxCDF | 110 | 0.5 |
| 1,2,3,7,8,9-HxCDF | 112 | 0.8 |
| 1,2,3,4,7,8-HxCDD | 108 | 5.2 |
| 1,2,3,6,7,8-HxCDD | 122 | 4.4 |
| 1,2,3,7,8,9-HxCDD | 116 | 2.0 |
| 1,2,3,4,6,7,8-HpCDF | 113 | 0.2 |
| 1,2,3,4,7,8,9-HpCDF | 101 | 1.6 |
| 1,2,3,4,6,7,8-HpCDD | 100 | 6.0 |
| OCDF | 109 | 6.4 |
| OCDD | 109 | 2.9 |

[a] Reported values are the mean relative recovery (n = 2)

[b] RPD = relative percent difference between matrix spike replicates

**Table AD-14**: Absolute $^{13}C_{12}$-PCDD/F recovery in the Lake Little Wilson sediment core.

| $^{13}C_{12}$-PCDD/F Congener | Absolute Recovery (%) | |
|---|---|---|
| $^{13}C_{12}$-2,3-DCDD | [a]76 ± 7.4 | (n = 10) |
| $^{13}C_{12}$-2,3,7-TriCDD | 79 ± 5.6 | (n = 10) |
| $^{13}C_{12}$-2,3,7,8-TCDF | 84 ± 9.3 | (n = 10) |
| $^{13}C_{12}$-2,3,7,8-TCDD | 102 ± 6.6 | (n = 10) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 86 ± 4.7 | (n = 10) |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 75 ± 11.7 | (n = 10) |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 93 ± 7.2 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 91 ± 8.0 | (n = 10) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 101 ± 8.8 | (n = 10) |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 48 ± 21.5 | (n = 10) |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 83 ± 4.9 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 69 ± 7.9 | (n = 10) |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 90 ± 8.6 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 62 ± 6.0 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 59 ± 7.0 | (n = 10) |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 50 ± 8.6 | (n = 10) |
| $^{13}C_{12}$-OCDD | 47 ± 6.8 | (n = 10) |

[a] Reported values are the mean ± standard deviation

**Table AD-15**: Relative PCDD/F recovery in Lake Little Wilson sediment (spike and recovery).

| PCDD/F Congener | Relative Recovery (%) | [b]RPD |
|---|---|---|
| 2,8-DCDD | [a]233 | 4.0 |
| 2,3,7-TriCDD | 104 | 1.3 |
| 2,3,7,8-TCDF | 115 | 2.4 |
| 2,3,7,8-TCDD | 74 | 2.2 |
| 1,2,3,7,8-PeCDF | 105 | 0.4 |
| 2,3,4,7,8-PeCDF | 104 | 0.8 |
| 1,2,3,7,8-PeCDD | 87 | 0.3 |
| 1,2,3,4,7,8-HxCDF | 108 | 0.5 |
| 1,2,3,6,7,8-HxCDF | 96 | 0.4 |
| 2,3,4,6,7,8-HxCDF | 110 | 11.2 |
| 1,2,3,7,8,9-HxCDF | 103 | 2.3 |
| 1,2,3,4,7,8-HxCDD | 98 | 14.2 |
| 1,2,3,6,7,8-HxCDD | 108 | 10.7 |
| 1,2,3,7,8,9-HxCDD | 103 | 6.6 |
| 1,2,3,4,6,7,8-HpCDF | 104 | 0.9 |
| 1,2,3,4,7,8,9-HpCDF | 91 | 0.0 |
| 1,2,3,4,6,7,8-HpCDD | 93 | 0.0 |
| OCDF | 103 | 4.5 |
| OCDD | 103 | 0.5 |

[a] Reported values are the mean relative recovery (n = 2)

[b] RPD = relative percent difference between matrix spike replicates

## Appendix E

## Core Radiometric Dating: Lead-210 ($^{210}$Pb) and Cesium - 137 ($^{137}$Cs)

### Table AE-1: $^{210}$Pb dating for the Lake St. Croix sediment core.

| Top of Interval (cm) | Base of Interval (cm) | Cum. Dry Mass (g/cm$^2$) | Unsup. Activity (pCi/g) | Error of Unsup. Act. (±s.d.) | Cum. Act. below Int. (pCi/cm$^2$) | Age: Base of Int. (yr) | Error of Age (±s.d.) | Date A.D. | Sediment Accum. (g/cm$^2$ yr) | Error of Sed. Accum. (±s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 4 | 0.3449 | 10.7482 | 0.4304 | 63.7538 | 1.81 | 2.83 | 2008.7 | 0.1900 | 0.0140 |
| 4 | 8 | 0.8063 | 10.0442 | 0.4880 | 59.1196 | 4.24 | 2.95 | 2006.3 | 0.1904 | 0.0155 |
| 12 | 16 | 1.9456 | 7.4293 | 0.3203 | 49.9999 | 9.62 | 3.23 | 2000.9 | 0.2189 | 0.0191 |
| 20 | 24 | 3.4456 | 7.5128 | 0.3692 | 38.7598 | 17.80 | 3.84 | 1992.8 | 0.1728 | 0.0184 |
| 32 | 36 | 6.1345 | 3.7362 | 0.2460 | 25.8279 | 30.83 | 3.61 | 1979.7 | 0.2297 | 0.0249 |
| 44 | 48 | 9.2211 | 2.0437 | 0.2126 | 17.9582 | 42.50 | 3.64 | 1968.1 | 0.2900 | 0.0388 |
| 56 | 60 | 12.7143 | 1.2498 | 0.1838 | 12.7341 | 53.54 | 4.05 | 1957.0 | 0.3358 | 0.0584 |
| 68 | 72 | 16.5234 | 0.8977 | 0.1611 | 8.8850 | 65.10 | 4.97 | 1945.5 | 0.3280 | 0.0707 |
| 80 | 84 | 20.3662 | 0.8728 | 0.1741 | 5.4991 | 80.51 | 7.21 | 1930.0 | 0.2154 | 0.0579 |
| 92 | 96 | 24.3010 | 0.6530 | 0.1568 | 2.6491 | 103.96 | 13.13 | 1906.6 | 0.1461 | 0.0598 |
| 104 | 108 | 28.6548 | 0.3370 | 0.1341 | 0.7461 | 144.65 | 37.85 | 1865.9 | 0.0904 | 0.0876 |
| 116 | 120 | 33.0477 | 0.0484 | 0.1492 | 0.1208 | 203.12 | 165.94 | 1807.4 | 0.0985 | 0.4763 |

| | |
|---|---|
| Supported Pb-210: | 2.1407 ± 0.1223 pCi/g |
| Number of Supported Samples: | 3 |

| | |
|---|---|
| Cum. Unsup. Pb-210: | 67.4607 pCi/cm$^2$ |
| Unsup. Pb-210 Flux: | 2.1638 pCi/cm$^2$ yr |

### Table AE-2: $^{210}$Pb dating for the East Lake Gemini sediment core.

| Top of Interval (cm) | Base of Interval (cm) | Cum. Dry Mass (g/cm$^2$) | Unsup. Activity (pCi/g) | Error of Unsup. Act. (±s.d.) | Cum. Act. below Int. (pCi/cm$^2$) | Age: Base of Int. (yr) | Error of Age (±s.d.) | Date A.D. | Sediment Accum. (g/cm$^2$ yr) | Error of Sed. Accum. (±s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 4 | 0.1550 | 15.3132 | 0.5917 | 53.7821 | 1.39 | 0.94 | 2009.3 | 0.1117 | 0.0048 |
| 8 | 12 | 0.5727 | 13.4634 | 0.5371 | 47.9863 | 5.05 | 0.99 | 2005.6 | 0.1145 | 0.0051 |
| 12 | 16 | 0.8259 | 9.0967 | 0.3374 | 45.6826 | 6.63 | 1.01 | 2004.1 | 0.1603 | 0.0069 |
| 18 | 20 | 1.0656 | 7.2508 | 0.3411 | 43.8598 | 7.94 | 1.03 | 2002.8 | 0.1902 | 0.0100 |
| 20 | 22 | 1.2143 | 6.5013 | 0.3261 | 42.8933 | 8.65 | 1.05 | 2002.0 | 0.2078 | 0.0116 |
| 30 | 32 | 2.0967 | 6.2348 | 0.2721 | 37.3007 | 13.14 | 1.13 | 1997.6 | 0.1893 | 0.0098 |
| 40 | 42 | 3.1501 | 4.9285 | 0.2651 | 31.5929 | 18.47 | 1.13 | 1992.2 | 0.2030 | 0.0122 |
| 50 | 52 | 4.3007 | 5.2137 | 0.2607 | 25.7255 | 25.07 | 1.28 | 1985.6 | 0.1573 | 0.0093 |
| 60 | 62 | 5.5392 | 3.9961 | 0.2198 | 20.2116 | 32.82 | 1.18 | 1977.9 | 0.1614 | 0.0099 |
| 70 | 74 | 6.9945 | 4.4321 | 0.2469 | 14.0000 | 44.61 | 1.40 | 1966.1 | 0.1055 | 0.0067 |

| | |
|---|---|
| Supported Pb-210: | 0.8053 ± 0.1542 pCi/g |
| Number of Supported Samples: | 3 |

| | |
|---|---|
| Cum. Unsup. Pb-210: | 56.1564 pCi/cm$^2$ |
| Unsup. Pb-210 Flux: | 1.7934 pCi/cm$^2$ yr |

**Table AE-3:** $^{210}$Pb dating for the Lake Winona sediment core.

| Top of Interval (cm) | Base of Interval (cm) | Cum. Dry Mass (g/cm$^2$) | Unsup. Activity (pCi/g) | Error of Unsup. Act. (±s.d.) | Cum. Act. below Int. (pCi/cm$^2$) | Age: Base of Int. (yr) | Error of Age (±s.d.) | Date A.D. | Sediment Accum. (g/cm$^2$ yr) | Error of Sed. Accum. (±s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 4 | 0.5716 | 3.4376 | 0.1563 | 19.2571 | 3.12 | 1.23 | 2007.6 | 0.1832 | 0.0093 |
| 4 | 8 | 1.2719 | 3.1088 | 0.1237 | 17.0799 | 6.97 | 1.30 | 2003.7 | 0.1818 | 0.0087 |
| 8 | 12 | 2.0417 | 3.4899 | 0.1862 | 14.3935 | 12.47 | 1.42 | 1998.2 | 0.1401 | 0.0083 |
| 12 | 14 | 2.4322 | 3.0827 | 0.1288 | 13.1898 | 15.27 | 1.50 | 1995.4 | 0.1392 | 0.0076 |
| 14 | 16 | 2.8204 | 3.1380 | 0.1614 | 11.9717 | 18.38 | 1.59 | 1992.3 | 0.1248 | 0.0079 |
| 20 | 22 | 4.0042 | 2.9427 | 0.1630 | 8.4126 | 29.71 | 2.04 | 1981.0 | 0.0951 | 0.0072 |
| 24 | 26 | 4.8196 | 2.7515 | 0.1438 | 6.1311 | 39.87 | 2.66 | 1970.8 | 0.0756 | 0.0066 |
| 26 | 28 | 5.2445 | 2.8396 | 0.1271 | 4.9244 | 46.91 | 3.23 | 1963.8 | 0.0604 | 0.0058 |
| 30 | 32 | 6.0921 | 2.0997 | 0.1121 | 2.9986 | 62.84 | 4.88 | 1947.9 | 0.0508 | 0.0071 |
| 32 | 34 | 6.5615 | 1.4514 | 0.0641 | 2.3173 | 71.12 | 6.27 | 1939.6 | 0.0567 | 0.0099 |
| 34 | 36 | 7.0602 | 1.1574 | 0.0466 | 1.7401 | 80.32 | 8.30 | 1930.4 | 0.0542 | 0.0123 |
| 36 | 38 | 7.5843 | 0.8124 | 0.0387 | 1.3143 | 89.33 | 10.96 | 1921.4 | 0.0582 | 0.0174 |
| 38 | 40 | 8.1047 | 0.4820 | 0.0304 | 1.0635 | 96.13 | 13.52 | 1914.6 | 0.0765 | 0.0293 |
| 40 | 42 | 8.6647 | 0.2749 | 0.0263 | 0.9095 | 101.15 | 15.80 | 1909.5 | 0.1115 | 0.0516 |
| 44 | 46 | 9.8029 | 0.2646 | 0.0265 | 0.6054 | 114.22 | 23.69 | 1896.5 | 0.0798 | 0.0532 |
| 48 | 50 | 11.0632 | 0.3046 | 0.0268 | 0.2340 | 144.75 | 61.16 | 1865.9 | 0.0330 | 0.0471 |

| | |
|---|---|
| Supported Pb-210: 0.1978 ± 0.018 pCi/g | Cum. Unsup. Pb-210: 21.2221 pCi/cm$^2$ |
| Number of Supported Samples: 3 | Unsup. Pb-210 Flux: 0.6773 pCi/cm$^2$ yr |

**Table AE-4:** $^{210}$Pb dating for the Duluth Harbor sediment core.

| Top of Interval (cm) | Base of Interval (cm) | Cum. Dry Mass (g/cm$^2$) | Unsup. Activity (pCi/g) | Error of Unsup. Act. (±s.d.) | Cum. Act. below Int. (pCi/cm$^2$) | Age: Base of Int. (yr) | Error of Age (±s.d.) | Date A.D. | Sediment Accum. (g/cm$^2$ yr) | Error of Sed. Accum. (±s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 2 | 0.5809 | 3.3972 | 0.1766 | 28.8504 | 2.12 | 1.57 | 2008.6 | 0.2734 | 0.0167 |
| 2 | 4 | 1.2771 | 3.3137 | 0.1625 | 26.5435 | 4.80 | 1.64 | 2005.9 | 0.2601 | 0.0156 |
| 4 | 6 | 2.1365 | 3.0028 | 0.1630 | 23.9629 | 8.09 | 1.73 | 2002.7 | 0.2617 | 0.0171 |
| 8 | 10 | 4.1734 | 2.3712 | 0.1378 | 18.8419 | 15.81 | 1.94 | 1994.9 | 0.2638 | 0.0191 |
| 10 | 12 | 5.1894 | 1.9331 | 0.1100 | 16.8780 | 19.34 | 2.09 | 1991.4 | 0.2874 | 0.0217 |
| 12 | 14 | 6.1535 | 1.6272 | 0.1218 | 15.3092 | 22.47 | 2.24 | 1988.3 | 0.3077 | 0.0283 |
| 16 | 18 | 8.1187 | 1.5510 | 0.1002 | 12.2243 | 29.70 | 2.66 | 1981.0 | 0.2605 | 0.0245 |
| 18 | 20 | 9.0667 | 1.4454 | 0.1076 | 10.8541 | 33.52 | 2.93 | 1977.2 | 0.2483 | 0.0264 |
| 22 | 24 | 10.9643 | 1.1798 | 0.0969 | 8.4934 | 41.39 | 3.58 | 1969.4 | 0.2387 | 0.0302 |
| 24 | 26 | 11.9326 | 1.0367 | 0.0923 | 7.4896 | 45.43 | 4.01 | 1965.3 | 0.2397 | 0.0337 |
| 28 | 30 | 13.9559 | 1.0520 | 0.0926 | 5.3687 | 56.12 | 5.44 | 1954.6 | 0.1744 | 0.0300 |
| 30 | 32 | 14.9859 | 0.9970 | 0.0815 | 4.3418 | 62.94 | 6.65 | 1947.8 | 0.1511 | 0.0300 |
| 34 | 36 | 17.1446 | 0.6514 | 0.0797 | 2.7620 | 77.47 | 10.07 | 1933.3 | 0.1484 | 0.0444 |
| 36 | 38 | 18.2038 | 0.7364 | 0.0638 | 1.9820 | 88.12 | 13.95 | 1922.6 | 0.0994 | 0.0374 |
| 40 | 42 | 20.3218 | 0.5127 | 0.0600 | 0.7824 | 117.97 | 34.73 | 1892.8 | 0.0626 | 0.0529 |
| 42 | 44 | 21.5748 | 0.2482 | 0.0573 | 0.4714 | 134.24 | 57.41 | 1876.5 | 0.0770 | 0.1089 |

| | |
|---|---|
| Supported Pb-210: 0.7726 ± 0.0509 pCi/g | Cum. Unsup. Pb-210: 30.824 pCi/cm$^2$ |
| Number of Supported Samples: 5 | Unsup. Pb-210 Flux: 0.9878 pCi/cm$^2$ yr |

**Table AE-5:** $^{210}$Pb dating for the Lake Superior sediment core.

| Top of Interval (cm) | Base of Interval (cm) | Cum. Dry Mass (g/cm$^2$) | Unsup. Activity (pCi/g) | Error of Unsup. Act. (±s.d.) | Cum. Act. below Int. (pCi/cm$^2$) | Age: Base of Int. (yr) | Error of Age (±s.d.) | Date A.D. | Sediment Accum. (g/cm$^2$ yr) | Error of Sed. Accum. (±s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1 | 0.2670 | 11.1537 | 0.4206 | 29.4076 | 3.10 | 2.31 | 2007.6 | 0.0862 | 0.0054 |
| 2 | 3 | 0.8768 | 10.1771 | 0.3825 | 23.0623 | 10.90 | 2.66 | 1999.8 | 0.0754 | 0.0054 |
| 4 | 5 | 1.6224 | 6.8575 | 0.2829 | 17.4123 | 19.93 | 3.07 | 1990.8 | 0.0850 | 0.0073 |
| 6 | 7 | 2.4250 | 5.0320 | 0.2468 | 13.0340 | 29.23 | 3.74 | 1981.5 | 0.0868 | 0.0094 |
| 9 | 10 | 3.7590 | 2.2372 | 0.1538 | 9.0168 | 41.06 | 3.21 | 1969.7 | 0.1326 | 0.0140 |
| 11 | 12 | 4.6989 | 2.1241 | 0.1535 | 6.9940 | 49.22 | 3.91 | 1961.5 | 0.1097 | 0.0137 |
| 14 | 15 | 6.0382 | 1.5597 | 0.1405 | 4.6616 | 62.25 | 5.25 | 1948.5 | 0.0997 | 0.0168 |
| 16 | 17 | 6.9793 | 1.3668 | 0.1354 | 3.3320 | 73.03 | 7.13 | 1937.7 | 0.0832 | 0.0181 |
| 18 | 19 | 7.9482 | 0.8562 | 0.1174 | 2.3859 | 83.76 | 9.65 | 1927.0 | 0.0941 | 0.0284 |
| 19 | 20 | 8.4457 | 0.5467 | 0.1168 | 2.1139 | 87.64 | 10.82 | 1923.1 | 0.1280 | 0.0477 |
| 22 | 23 | 9.9900 | 0.2671 | 0.1074 | 1.5652 | 97.29 | 14.05 | 1913.5 | 0.1905 | 0.1081 |
| 24 | 25 | 11.0012 | 0.3761 | 0.1179 | 1.2133 | 105.47 | 17.94 | 1905.3 | 0.1081 | 0.0643 |
| 27 | 28 | 12.4561 | 0.4046 | 0.1131 | 0.6387 | 126.08 | 33.49 | 1884.7 | 0.0563 | 0.0534 |
| 29 | 30 | 13.4291 | 0.2486 | 0.1076 | 0.3601 | 144.48 | 58.92 | 1866.3 | 0.0524 | 0.0857 |
| 30 | 32 | 14.4053 | 0.1426 | 0.1012 | 0.2209 | 160.17 | 94.95 | 1850.6 | 0.0622 | 0.1496 |

Supported Pb-210: 1.131 ± 0.0904 pCi/g
Number of Supported Samples: 3

Cum. Unsup. Pb-210: 32.3862 pCi/cm$^2$
Unsup. Pb-210 Flux: 1.031 pCi/cm$^2$ yr

**Table AE-6:** $^{210}$Pb dating for the Lake Shagawa sediment core.

| Top of Interval (cm) | Base of Interval (cm) | Cum. Dry Mass (g/cm$^2$) | Unsup. Activity (pCi/g) | Error of Unsup. Act. (±s.d.) | Cum. Act. below Int. (pCi/cm$^2$) | Age: Base of Int. (yr) | Error of Age (±s.d.) | Date A.D. | Sediment Accum. (g/cm$^2$ yr) | Error of Sed. Accum. (±s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 2 | 0.1268 | 15.9131 | 0.5688 | 38.3117 | 1.65 | 1.16 | 2009.8 | 0.0769 | 0.0033 |
| 4 | 6 | 0.4370 | 13.4765 | 0.2741 | 33.9610 | 5.52 | 1.23 | 2005.9 | 0.0810 | 0.0028 |
| 8 | 10 | 0.8125 | 11.6901 | 0.2458 | 29.4168 | 10.13 | 1.33 | 2001.3 | 0.0814 | 0.0031 |
| 12 | 14 | 1.2176 | 10.4672 | 0.2209 | 25.0567 | 15.28 | 1.47 | 1996.2 | 0.0777 | 0.0033 |
| 16 | 18 | 1.6301 | 9.5049 | 0.3403 | 21.0383 | 20.90 | 1.66 | 1990.6 | 0.0721 | 0.0040 |
| 20 | 22 | 2.0497 | 8.2273 | 0.3641 | 17.4577 | 26.89 | 1.91 | 1984.6 | 0.0693 | 0.0046 |
| 24 | 26 | 2.4630 | 6.6243 | 0.3027 | 14.5603 | 32.72 | 2.19 | 1978.7 | 0.0716 | 0.0054 |
| 30 | 32 | 3.1014 | 5.8806 | 0.2676 | 10.6532 | 42.75 | 2.84 | 1968.7 | 0.0597 | 0.0054 |
| 32 | 34 | 3.3130 | 5.1465 | 0.1910 | 9.5644 | 46.21 | 3.13 | 1965.3 | 0.0611 | 0.0059 |
| 36 | 38 | 3.7621 | 3.1404 | 0.1794 | 7.9540 | 52.13 | 3.61 | 1959.3 | 0.0824 | 0.0098 |
| 42 | 44 | 4.5074 | 2.0919 | 0.0949 | 6.1570 | 60.36 | 4.44 | 1951.1 | 0.0956 | 0.0131 |
| 46 | 48 | 5.0426 | 1.3995 | 0.0811 | 5.3219 | 65.04 | 5.08 | 1946.4 | 0.1226 | 0.0197 |
| 50 | 52 | 5.5861 | 0.9879 | 0.0881 | 4.7315 | 68.81 | 5.68 | 1942.7 | 0.1533 | 0.0293 |
| 52 | 54 | 5.8625 | 1.0100 | 0.0879 | 4.4523 | 70.77 | 6.03 | 1940.7 | 0.1415 | 0.0282 |
| 58 | 60 | 6.7377 | 1.0956 | 0.0822 | 3.5183 | 78.33 | 7.59 | 1933.1 | 0.1046 | 0.0247 |
| 60 | 64 | 7.3849 | 0.8744 | 0.0856 | 2.9524 | 83.96 | 9.01 | 1927.5 | 0.1149 | 0.0312 |
| 64 | 68 | 8.0402 | 0.5663 | 0.0736 | 2.5813 | 88.27 | 10.28 | 1923.2 | 0.1519 | 0.0490 |
| 72 | 76 | 9.3706 | 0.5344 | 0.0708 | 1.8597 | 98.80 | 14.20 | 1912.7 | 0.1185 | 0.0501 |
| 84 | 88 | 11.3420 | 0.3678 | 0.0713 | 1.0274 | 117.86 | 25.28 | 1893.6 | 0.0968 | 0.0708 |

Supported Pb-210: 1.2097 ± 0.0483 pCi/g
Number of Supported Samples: 3

Cum. Unsup. Pb-210: 40.3297 pCi/cm$^2$
Unsup. Pb-210 Flux: 1.2808 pCi/cm$^2$ yr

**Table AE-7:** $^{210}$Pb dating for the Lake Little Wilson sediment core.

| Top of Interval (cm) | Base of Interval (cm) | Cum. Dry Mass ($g/cm^2$) | Unsup. Activity (pCi/g) | Error of Unsup. Act. (±s.d.) | Cum. Act. below Int. ($pCi/cm^2$) | Age: Base of Int. (yr) | Error of Age (±s.d.) | Date A.D. | Sediment Accum. ($g/cm^2$ yr) | Error of Sed. Accum. (±s.d.) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 2 | 0.0896 | 24.7811 | 0.5491 | 34.8219 | 1.99 | 0.57 | 2009.5 | 0.0451 | 0.0011 |
| 4 | 6 | 0.3038 | 21.1130 | 0.4671 | 30.1203 | 6.64 | 0.58 | 2004.8 | 0.0461 | 0.0012 |
| 8 | 10 | 0.5559 | 23.1291 | 0.5204 | 24.4140 | 13.39 | 0.63 | 1998.1 | 0.0348 | 0.0009 |
| 12 | 14 | 0.8263 | 20.5690 | 0.4664 | 18.6855 | 21.98 | 0.69 | 1989.5 | 0.0304 | 0.0008 |
| 14 | 16 | 0.9664 | 19.8735 | 0.4064 | 15.9013 | 27.16 | 0.76 | 1984.3 | 0.0270 | 0.0007 |
| 18 | 20 | 1.2692 | 17.9593 | 0.5867 | 10.3258 | 41.02 | 0.93 | 1970.4 | 0.0202 | 0.0008 |
| 20 | 22 | 1.4331 | 11.9421 | 0.2293 | 8.3689 | 47.77 | 1.10 | 1963.7 | 0.0243 | 0.0008 |
| 22 | 24 | 1.6010 | 9.3088 | 0.2170 | 6.8059 | 54.41 | 1.31 | 1957.1 | 0.0253 | 0.0010 |
| 24 | 26 | 1.7720 | 6.0378 | 0.2884 | 5.7735 | 59.69 | 1.50 | 1951.8 | 0.0324 | 0.0020 |
| 28 | 30 | 2.1210 | 4.1336 | 0.2167 | 4.1784 | 70.08 | 1.57 | 1941.4 | 0.0341 | 0.0022 |
| 32 | 34 | 2.4676 | 2.1717 | 0.1252 | 3.2752 | 77.90 | 1.15 | 1933.6 | 0.0496 | 0.0031 |
| 36 | 38 | 2.8205 | 1.7410 | 0.1256 | 2.6243 | 85.01 | 1.29 | 1926.5 | 0.0496 | 0.0038 |
| 40 | 42 | 3.1823 | 1.4688 | 0.1104 | 2.0691 | 92.65 | 1.51 | 1918.8 | 0.0466 | 0.0039 |
| 42 | 44 | 3.3590 | 1.1524 | 0.0975 | 1.8655 | 95.97 | 1.64 | 1915.5 | 0.0531 | 0.0050 |
| 46 | 48 | 3.7053 | 1.1773 | 0.1029 | 1.4600 | 103.84 | 2.01 | 1907.6 | 0.0413 | 0.0041 |
| 52 | 54 | 4.2353 | 1.0908 | 0.0991 | 0.8668 | 120.59 | 3.09 | 1890.9 | 0.0274 | 0.0033 |
| 56 | 58 | 4.5905 | 0.6612 | 0.0613 | 0.5958 | 132.62 | 3.92 | 1878.8 | 0.0307 | 0.0043 |
| 60 | 64 | 5.1150 | 0.5806 | 0.0749 | 0.2828 | 156.55 | 7.56 | 1854.9 | 0.0201 | 0.0042 |
| 64 | 68 | 5.4631 | 0.3893 | 0.0510 | 0.1473 | 177.50 | 13.97 | 1834.0 | 0.0166 | 0.0055 |
| 68 | 72 | 5.8230 | 0.1587 | 0.0480 | 0.0902 | 193.25 | 21.96 | 1818.2 | 0.0229 | 0.0135 |
| 72 | 76 | 6.1939 | 0.0695 | 0.0446 | 0.0644 | 204.07 | 29.63 | 1807.4 | 0.0343 | 0.0327 |

| | |
|---|---|
| Supported Pb-210: | 1.064 ± 0.0329 pCi/g |
| Number of Supported Samples: | 1 |

| | |
|---|---|
| Cum. Unsup. Pb-210: | 37.0433 $pCi/cm^2$ |
| Unsup. Pb-210 Flux: | 1.1793 $pCi/cm^2$ yr |

**Table AE-8:** $^{137}$Cs dating for the East Lake Gemini sediment core.

| Top of Interval (cm) | Bottom of Interval (cm) | Detector | Total Pb-210 (pCi/g) | Total Supported Pb-214 (pCi/g) | Excess Pb-210 (using Pb-214) (pCi/g) | Cs-137 (pCi/g) |
|---|---|---|---|---|---|---|
| 20 | 22 | 2 | 7.90 | 0.63 | 7.27 | 0.78 |
| 40 | 42 | 2 | 5.22 | 1.08 | 4.14 | 1.46 |
| 60 | 62 | 1 | 3.75 | 1.02 | 2.73 | 2.77 |

**Table AE-9:** $^{137}$Cs dating for the Lake Winona sediment core.

| Top of Interval (cm) | Bottom of Interval (cm) | Detector | Total Pb-210 (pCi/g) | Total Supported Pb-214 (pCi/g) | Excess Pb-210 (using Pb-214) (pCi/g) | Cs-137 (pCi/g) |
|---|---|---|---|---|---|---|
| 20 | 22 | 1 | | | | 0.77 |
| 22 | 24 | 1 | | | | 0.77 |
| 24 | 26 | 1 | | | | 0.81 |
| 26 | 28 | 1 | | | | 1.17 |
| 28 | 30 | 1 | | | | 1.04 |
| 30 | 32 | 1 | | | | 1.07 |
| 32 | 34 | 1 | | | | 0.81 |
| 34 | 36 | 1 | | | | 0.83 |

**Table AE-10:** $^{137}$Cs dating for the Duluth Harbor sediment core.

| Top of Interval (cm) | Bottom of Interval (cm) | Detector | Total Pb-210 (pCi/g) | Total Supported Pb-214 (pCi/g) | Excess Pb-210 (using Pb-214) (pCi/g) | Cs-137 (pCi/g) |
|---|---|---|---|---|---|---|
| 14 | 16 | 2 | | | | 0.64 |
| 18 | 20 | 2 | | | | 0.62 |
| 22 | 24 | 2 | | | | 0.92 |
| 24 | 26 | 2 | | | | 1.00 |
| 26 | 28 | 2 | | | | 1.63 |
| 30 | 32 | 2 | | | | 1.06 |
| 34 | 36 | 2 | | | | 0.52 |
| 38 | 40 | 2 | | | | ND |

**Table AE-11:** $^{137}$Cs dating for the Lake Shagawa sediment core.

| Top of Interval (cm) | Bottom of Interval (cm) | Detector | Total Pb-210 (pCi/g) | Total Supported Pb-214 (pCi/g) | Excess Pb-210 (using Pb-214) (pCi/g) | Cs-137 (pCi/g) |
|---|---|---|---|---|---|---|
| 26 | 28 | 1 | | | | 2.76 |
| 28 | 30 | 1 | | | | 3.18 |
| 30 | 32 | 1 | | | | 3.41 |
| 32 | 34 | 1 | | | | 3.45 |
| 34 | 36 | 1 | | | | 3.41 |
| 38 | 40 | 1 | | | | 1.37 |
| 42 | 44 | 1 | | | | 0.67 |
| 46 | 48 | 1 | | | | 0.5 |
| 50 | 52 | 1 | | | | 0.29 |
| 60 | 64 | 1 | 1.190 | 1.260 | | 0.30 |
| 72 | 76 | 1 | small peak | 1.150 | | ND |
| 84 | 88 | 1 | small peak | 1.230 | | ND |

**Table AE-12:** $^{137}$Cs dating for the Lake Little Wilson sediment core.

| Top of Interval (cm) | Bottom of Interval (cm) | Detector | Total Pb-210 (pCi/g) | Total Supported Pb-214 (pCi/g) | Excess Pb-210 (using Pb-214) (pCi/g) | Cs-137 (pCi/g) |
|---|---|---|---|---|---|---|
| 60 | 64 | 2 | | 0.950 | | ND |
| 68 | 72 | 2 | | 0.670 | | ND |
| 76 | 80 | 2 | | 0.250 | | ND |

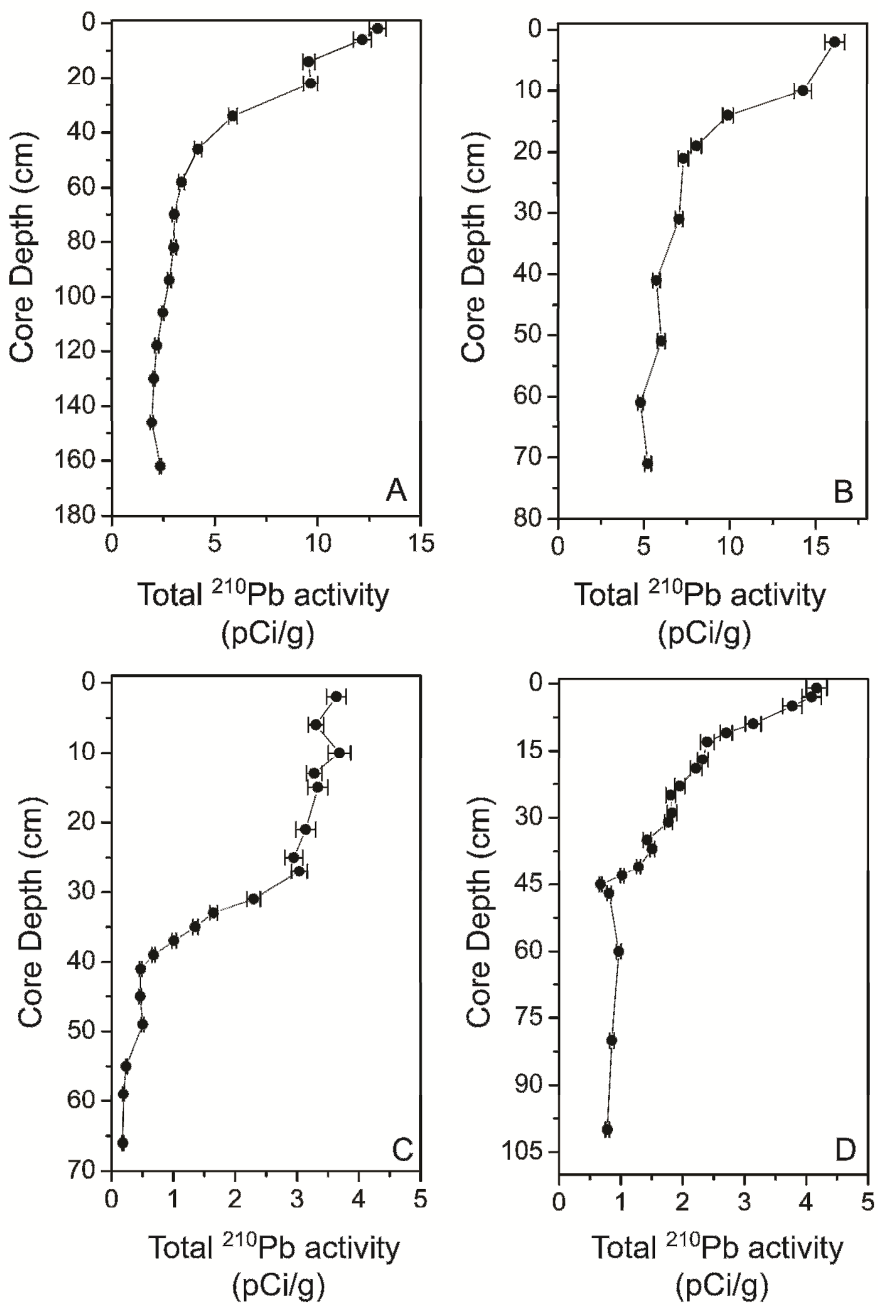



**Figure AE-1:** Total $^{210}$Pb activity in the Lake St. Croix (A), East Lake Gemini (B), Lake Winona (C), and Duluth Harbor (D) cores. Error bars represent one standard deviation in $^{210}$Pb activity.

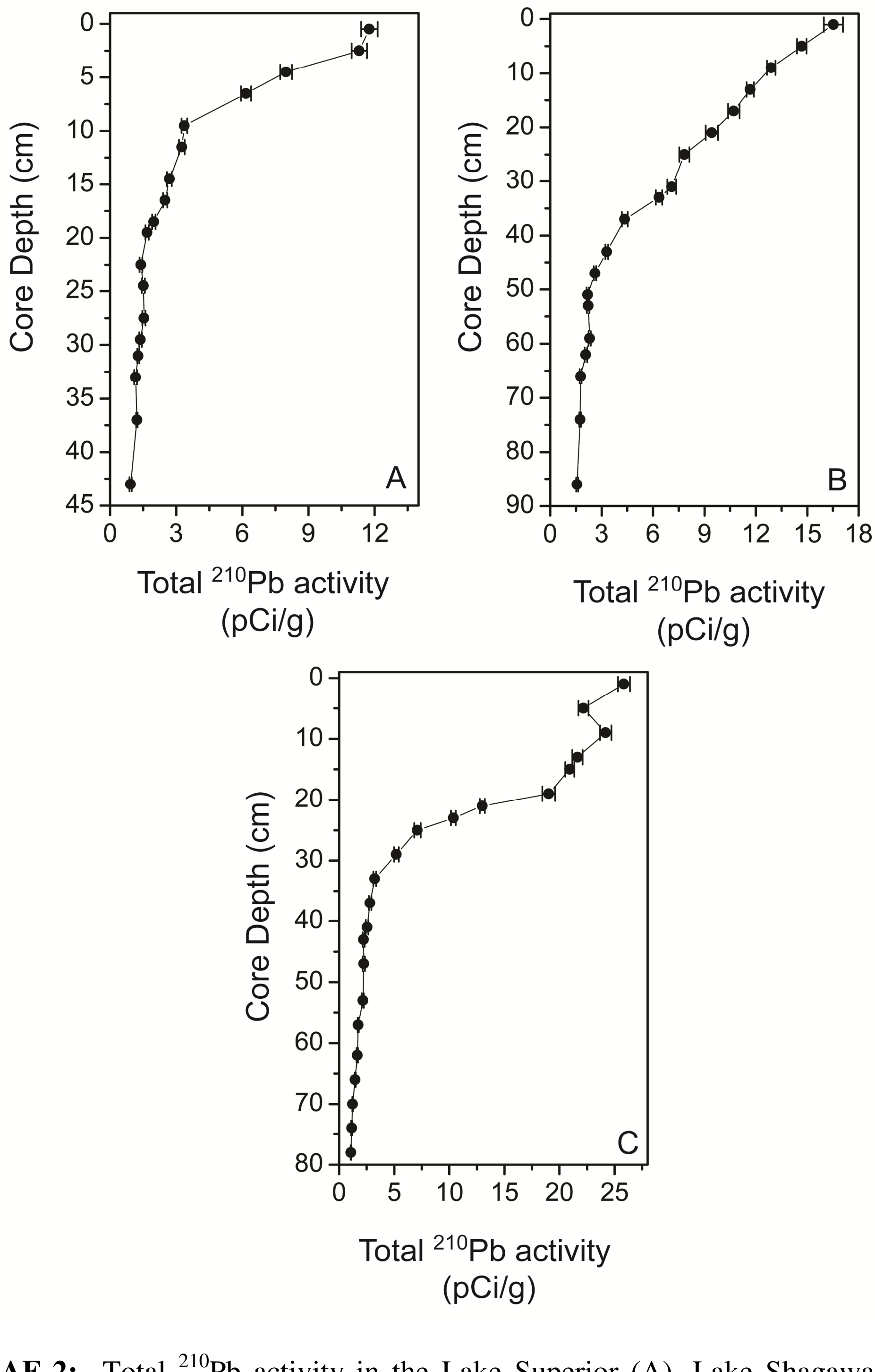



**Figure AE-2:** Total $^{210}$Pb activity in the Lake Superior (A), Lake Shagawa (B), and Lake Little Wilson (C) cores. Error bars represent one standard deviation in $^{210}$Pb activity.

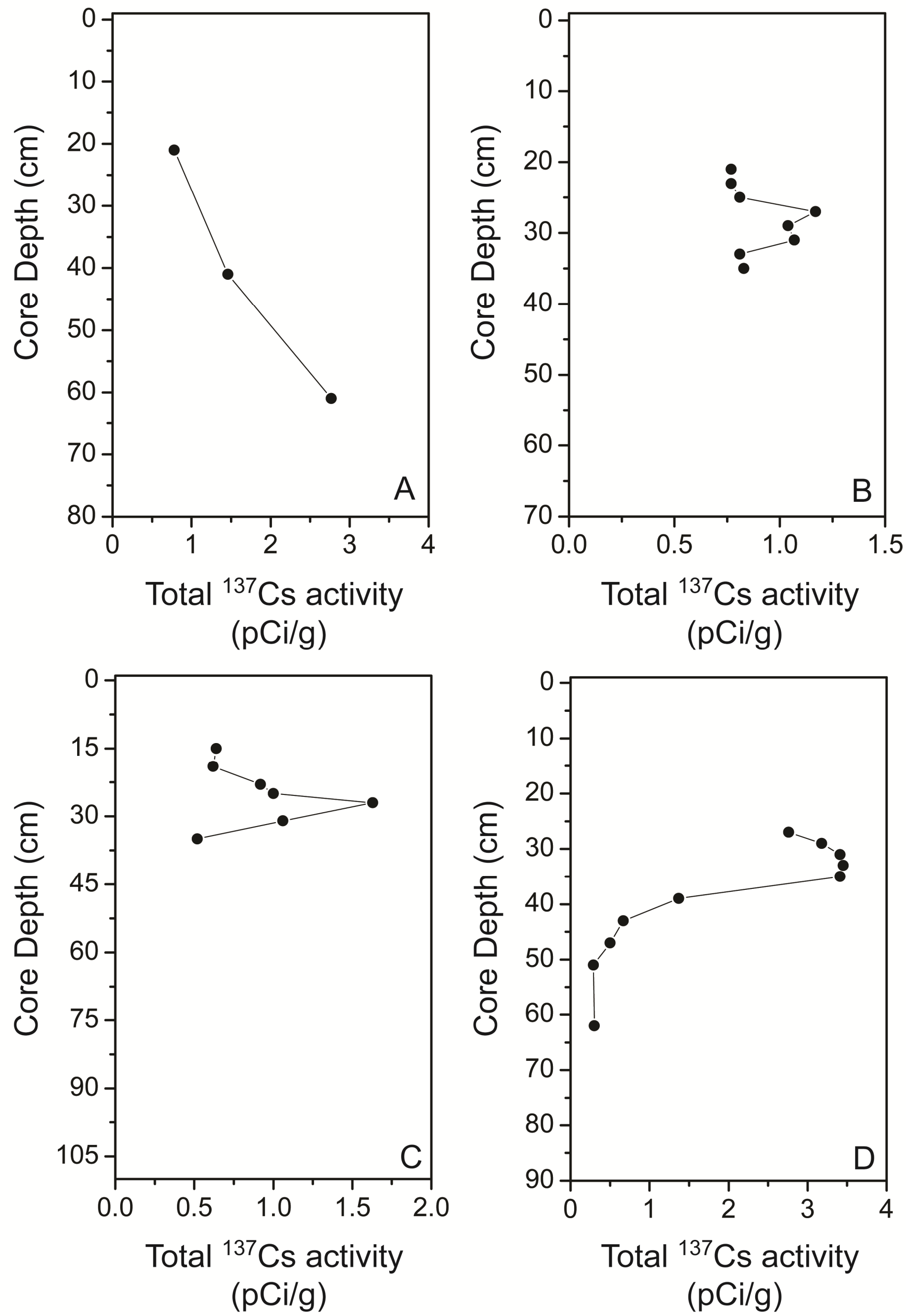



**Figure AE-3:** Total $^{137}$Cs activity in the East Lake Gemini (A), Lake Winona (B), Duluth Harbor (C), and Lake Shagawa (D) cores.

**Table AE-13: Sediment focusing factors for the Lake Pepin sediment core.**

| Radiometric Dating Interval | Focusing Factor |
|---|---|
| 1996-2008 | 0.25 |
| 1990-1996 | 0.59 |
| 1980-1990 | 0.57 |
| 1970-1980 | 0.66 |
| 1960-1970 | 0.66 |
| 1950-1960 | 0.85 |
| 1940-1950 | 0.93 |
| 1930-1940 | 1.39 |
| 1910-1930 | 1.26 |
| 1890-1910 | 1.19 |
| 1860-1890 | 1.29 |
| 1830-1860 | 1.61 |
| <1830 | 1.32 |

**Table AE-14: Sediment focusing factors for the Lake St. Croix sediment core.**

| Radiometric Dating Interval | Focusing Factor |
|---|---|
| 1990-2001 | 0.74 |
| 1980-1990 | 0.77 |
| 1970-1980 | 0.68 |
| 1960-1970 | 0.59 |
| 1950-1960 | 0.41 |
| 1940-1950 | 0.51 |
| 1930-1940 | 0.56 |
| 1910-1930 | 0.77 |
| 1890-1910 | 0.80 |
| 1870-1890 | 0.99 |
| 1850-1870 | 0.83 |
| <1850 | 0.53 |

**Table AE-15: Sediment focusing factors for East Lake Gemini, Lake Winona, Duluth Harbor, Lake Superior, Lake Shagawa, and Lake Little Wilson.**

| Sediment Core | Focusing Factor |
|---|---|
| East Lake Gemini | 3.59 |
| Lake Winona | 1.35 |
| Duluth Harbor | 1.98 |
| Lake Superior | 2.06 |
| Lake Shagawa | 2.56 |
| Lake Little Wilson | 2.36 |

**Notes on Focusing Factor Calculations:**

For non-riverine lake systems in this study (East Lake Gemini, Lake Winona, Duluth Harbor, Lake Superior, Lake Shagawa, Lake Little Wilson), a sediment focusing factor (FF) was determined by taking the ratio of the observed, unsupported $^{210}Pb$ flux in each core to the $^{210}Pb$ flux expected from atmospheric deposition to the lake (Equation 4).

$$FF = \frac{\text{unsupported } ^{210}\text{Pb flux (pCi cm}^{-2}\text{ yr}^{-1})}{0.5 \text{ pCi cm}^{-2}\text{ yr}^{-1}} \tag{4}$$

where:

$0.5 \text{ pCi cm}^{-2} \text{ yr}^{-1}$ = an approximate atmospheric $^{210}Pb$ flux to lakes in MN [119].

FF values greater that 1 signify areas of deposition, or sediment focusing to deeper parts of a lake. FF values less than 1 suggests that the core site may be erosional on a transient basis. Because TCS, CTDs, and PCDDs are hydrophobic and rapidly partition to sediment, one should expect that sediment focusing factors will be representative of analyte focusing in a given lake.

**Lake Pepin and Lake St. Croix**

In riverine systems, like Lake Pepin and Lake St. Croix, a significant amount of $^{210}Pb$ is deposited upstream of these depositional environments. Therefore, the unsupported $^{210}Pb$ flux recorded in these sediment cores cannot be directly compared to the atmospheric deposition of $^{210}Pb$ at the surface of these lakes.

To mitigate this issue, multiple sediment cores were collected in each lake in previous studies [94,120]. The sedimentation rates for these cores were integrated over the lake area to provide whole-lake sedimentation rates over time. The FF values for Lake Pepin (Table AE-13) and Lake St. Croix (Table AE-14) were determined by taking the ratio of the core-specific sediment flux to the whole-lake sediment flux at different time intervals (Equation 5).

$$FF = \frac{\text{core - specific sediment flux (g cm}^{-2}\text{ yr}^{-1})}{\text{whole - lake sediment flux (g cm}^{-2}\text{ yr}^{-1})} \tag{5}$$

**Correcting Analyte Accumulation Rates for Sediment Focusing**

Analyte accumulation rates presented in Figures 3-5 to 3-12, 3-13, and 3-15 are all normalized to their core-specific focusing factors. This normalization accounts for sediment focusing at each core site and provides insight into whole-lake analyte accumulation rates.

## Appendix F

## TCS and CTD Derived PCDDs – % By Mass and TEQ

**Table AF-1:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Pepin PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2009 | 112.10 | 652.50 | 17.18 | 0.221 | 5.912 | 3.74 |
| 2005 | 133.20 | 534.10 | 24.94 | 0.252 | 5.048 | 4.99 |
| 2002 | 145.30 | 621.40 | 23.38 | 0.283 | 6.084 | 4.65 |
| 1997 | 64.40 | 352.20 | 18.29 | 0.131 | 3.609 | 3.63 |
| 1992 | 87.10 | 295.90 | 29.44 | 0.142 | 2.611 | 5.44 |
| 1989 | 62.70 | 428.50 | 14.63 | 0.105 | 4.217 | 2.49 |
| 1983 | 127.10 | 1019.70 | 12.46 | 0.191 | 7.681 | 2.49 |
| 1980 | 105.80 | 1158.20 | 9.13 | 0.158 | 8.167 | 1.93 |
| 1974 | 61.00 | 831.60 | 7.34 | 0.088 | 6.460 | 1.36 |
| 1971 | 77.10 | 3130.40 | 2.46 | 0.123 | 24.206 | 0.51 |
| 1964 | 3.61 | 700.12 | 0.52 | 0.013 | 5.072 | 0.25 |
| 1961 | 4.19 | 1054.90 | 0.40 | 0.015 | 8.066 | 0.18 |
| 1958 | 4.12 | 1076.48 | 0.38 | 0.012 | 8.283 | 0.14 |
| 1953 | 1.77 | 195.57 | 0.91 | 0.004 | 1.383 | 0.30 |
| 1944 | 0.83 | 58.08 | 1.43 | 0.001 | 0.677 | 0.12 |
| 1891 | 0.79 | 44.01 | 1.80 | 0.001 | 0.198 | 0.40 |

**Table AF-2:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake St. Croix PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2007.5 | 36.50 | 567.70 | 6.43 | 0.059 | 3.608 | 1.64 |
| 2002.3 | 40.21 | 864.01 | 4.65 | 0.069 | 5.447 | 1.27 |
| 1996.9 | 33.24 | 914.04 | 3.64 | 0.053 | 5.406 | 0.99 |
| 1992.8 | 18.26 | 781.64 | 2.34 | 0.030 | 4.541 | 0.65 |
| 1989.5 | 28.92 | 1008.92 | 2.87 | 0.046 | 6.499 | 0.71 |
| 1983.0 | 18.49 | 1881.39 | 0.98 | 0.032 | 4.478 | 0.71 |
| 1979.7 | 15.62 | 744.02 | 2.10 | 0.021 | 4.906 | 0.43 |
| 1976.8 | 14.61 | 1275.21 | 1.15 | 0.020 | 8.205 | 0.24 |
| 1971.0 | 13.65 | 1172.20 | 1.16 | 0.020 | 7.974 | 0.24 |
| 1968.1 | 18.26 | 1474.52 | 1.24 | 0.030 | 10.582 | 0.28 |
| 1965.3 | 13.23 | 1586.50 | 0.83 | 0.024 | 11.974 | 0.20 |
| 1961.2 | 3.36 | 1447.26 | 0.23 | 0.008 | 11.819 | 0.07 |
| 1957.0 | 1.79 | 1358.09 | 0.13 | 0.004 | 12.819 | 0.03 |
| 1947.0 | 1.93 | 615.43 | 0.31 | 0.009 | 7.218 | 0.13 |
| 1930.0 | 1.30 | 82.00 | 1.59 | 0.001 | 1.078 | 0.12 |
| 1865.0 | 0.96 | 12.50 | 7.68 | 0.001 | 0.334 | 0.29 |

**Table AF-3:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the East Lake Gemini PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2008.4 | 282.69 | 419.59 | 67.37 | 0.307 | 1.904 | 16.12 |
| 2004.9 | 424.90 | 715.40 | 59.39 | 0.469 | 3.128 | 14.99 |
| 2002.8 | 374.40 | 800.50 | 46.77 | 0.414 | 4.523 | 9.15 |
| 1996.3 | 911.00 | 1480.40 | 61.54 | 1.010 | 5.737 | 17.61 |
| 1992.2 | 413.60 | 601.00 | 68.82 | 0.446 | 2.375 | 18.78 |
| 1985.6 | 1192.72 | 1770.09 | 67.38 | 1.298 | 5.533 | 23.46 |
| 1977.9 | 960.00 | 1479.00 | 64.91 | 1.050 | 4.754 | 22.09 |
| 1966.1 | 1419.00 | 2405.70 | 58.98 | 1.590 | 8.521 | 18.66 |

**Table AF-4:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Winona PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2008 | 4581.00 | 8268.80 | 55.40 | 6.210 | 19.381 | 32.04 |
| 2004 | 6314.00 | 10968.00 | 57.57 | 8.240 | 25.120 | 32.80 |
| 1998 | 5932.00 | 11177.00 | 53.07 | 8.020 | 27.087 | 29.61 |
| 1995 | 6028.00 | 11151.00 | 54.06 | 8.080 | 26.776 | 30.18 |
| 1992 | 5932.00 | 11338.00 | 52.32 | 8.020 | 27.610 | 29.05 |
| 1981 | 5197.00 | 11117.00 | 46.75 | 6.970 | 28.720 | 24.27 |
| 1971 | 4390.00 | 10892.00 | 40.30 | 6.100 | 28.707 | 21.25 |
| 1964 | 3570.00 | 9728.00 | 36.70 | 5.100 | 27.205 | 18.75 |
| 1948 | 2077.00 | 11206.00 | 18.53 | 2.770 | 31.786 | 8.71 |
| 1930 | 324.60 | 4855.90 | 6.68 | 0.456 | 16.226 | 2.81 |
| 1915 | 303.90 | 1849.80 | 16.43 | 0.429 | 23.774 | 1.80 |

**Table AF-5:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Duluth Harbor PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2009 | 381.10 | 4115.50 | 9.26 | 0.571 | 33.149 | 1.72 |
| 2006 | 413.80 | 4256.00 | 9.72 | 0.628 | 37.362 | 1.68 |
| 2003 | 432.70 | 3299.00 | 13.12 | 0.637 | 31.475 | 2.02 |
| 1995 | 313.30 | 2727.00 | 11.49 | 0.523 | 25.155 | 2.08 |
| 1991 | 187.40 | 3877.00 | 4.83 | 0.434 | 34.569 | 1.26 |
| 1988 | 186.00 | 5545.00 | 3.35 | 0.510 | 48.683 | 1.05 |
| 1981 | 173.60 | 4812.00 | 3.61 | 0.476 | 44.275 | 1.08 |
| 1977 | 209.00 | 6176.00 | 3.38 | 0.470 | 54.191 | 0.87 |
| 1969 | 228.00 | 7637.00 | 2.99 | 0.660 | 71.136 | 0.93 |
| 1965 | 157.30 | 7392.00 | 2.13 | 0.493 | 72.714 | 0.68 |
| 1955 | 22.50 | 8419.80 | 0.27 | 0.117 | 72.313 | 0.16 |
| 1923 | 33.60 | 12585.00 | 0.27 | 0.192 | 140.875 | 0.14 |
| 1893 | 23.10 | 17807.20 | 0.13 | 0.157 | 363.404 | 0.04 |

**Table AF-6:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Superior PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2006 | 37.35 | 223.70 | 16.70 | 0.077 | 3.062 | 2.50 |
| 1998 | 66.40 | 503.30 | 13.19 | 0.151 | 7.602 | 1.99 |
| 1988 | 26.40 | 314.20 | 8.40 | 0.075 | 4.501 | 1.67 |
| 1979 | 56.40 | 1284.70 | 4.39 | 0.177 | 14.728 | 1.20 |
| 1968 | 18.90 | 1652.80 | 1.14 | 0.081 | 21.986 | 0.37 |
| 1958 | 16.00 | 1362.90 | 1.17 | 0.075 | 23.661 | 0.32 |
| 1946 | 22.20 | 1679.90 | 1.32 | 0.105 | 51.044 | 0.21 |
| 1935 | 6.75 | 178.05 | 3.79 | 0.031 | 6.046 | 0.51 |
| 1911 | 2.63 | 7.63 | 34.47 | 0.008 | 0.211 | 3.94 |
| 1880 | 14.10 | 59.09 | 23.86 | 0.058 | 2.480 | 2.35 |

**Table AF-7:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Shagawa PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2009 | 517.80 | 1444.90 | 35.84 | 0.678 | 10.179 | 6.66 |
| 2005 | 509.70 | 1550.00 | 32.88 | 0.687 | 12.555 | 5.47 |
| 2000 | 396.80 | 1260.00 | 31.49 | 0.548 | 10.173 | 5.39 |
| 1995 | 136.20 | 404.00 | 33.71 | 0.192 | 3.385 | 5.67 |
| 1989 | 148.30 | 880.40 | 16.84 | 0.223 | 7.022 | 3.18 |
| 1983 | 171.50 | 933.20 | 18.38 | 0.275 | 8.290 | 3.32 |
| 1976 | 85.60 | 708.10 | 12.09 | 0.154 | 6.471 | 2.38 |
| 1971 | 96.20 | 755.60 | 12.73 | 0.170 | 6.929 | 2.45 |
| 1964 | 59.10 | 690.40 | 8.56 | 0.105 | 7.313 | 1.44 |
| 1957 | 36.60 | 677.60 | 5.40 | 0.069 | 9.184 | 0.75 |
| 1945 | 22.40 | 146.40 | 15.30 | 0.044 | 2.814 | 1.56 |
| 1933 | 24.60 | 111.50 | 22.06 | 0.048 | 1.842 | 2.61 |

**Table AF-8:** Percent of TCS and CTD derived PCDDs, by mass and TEQ, of the Lake Little Wilson PCDD pool.

| Approximate Date | TCS Derived PCDDs (pg/g) | Total PCDDs (pg/g) | % By Mass | TCS Derived PCDDs (pg TEQ/g) | Total PCDDs (pg TEQ/g) | % By TEQ |
|---|---|---|---|---|---|---|
| 2007 | 18.60 | 455.21 | 4.09 | 0.024 | 7.429 | 0.32 |
| 1998 | 35.90 | 1171.51 | 3.06 | 0.053 | 16.352 | 0.32 |
| 1984 | 38.03 | 975.10 | 3.90 | 0.056 | 17.087 | 0.33 |
| 1967 | 19.94 | 568.81 | 3.51 | 0.028 | 9.120 | 0.31 |
| 1954 | 24.30 | 484.78 | 5.01 | 0.036 | 8.849 | 0.41 |
| 1944 | 15.00 | 207.60 | 7.23 | 0.015 | 3.369 | 0.45 |
| 1934 | 24.34 | 180.40 | 13.49 | 0.027 | 3.588 | 0.76 |
| 1925 | 24.00 | 58.80 | 40.82 | 0.024 | 0.813 | 2.95 |
| 1900 | 19.00 | 37.50 | 50.67 | 0.019 | 0.260 | 7.31 |
| 1873 | 49.00 | 92.40 | 53.03 | 0.049 | 0.295 | 16.63 |