2010 Project Abstract
For the Period Ending June 30, 2012

PROJECT TITLE: Evaluation of Dioxins in Minnesota Lakes
PROJECT MANAGER: William Arnold
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2010, Chp. 362, Sec. 2, Subd. 5f

APPROPRIATION AMOUNT: $264,000

Overall Project Outcome and Results

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.

Project Results Use and Dissemination

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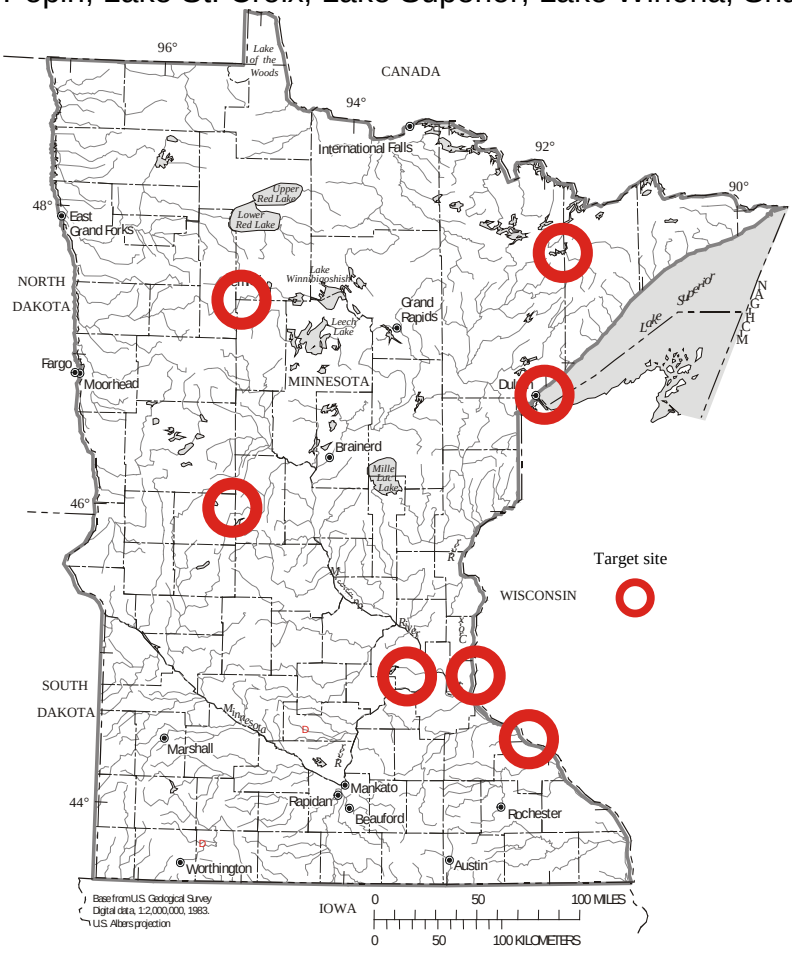
Location: University of Minnesota, Hennepin County, Minneapolis, 55455 and St. Croix Watershed Research Station, Washington County, Marine on St. Croix, 55047. Lake Pepin, Lake St. Croix, Lake Superior, Lake Winona, Shagawa Lake, and Lake Itasca.



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**