IX. RESEARCH PROJECTS:

Environment and Natural Resources Trust Fund

Research Addendum for Peer Review

Project Manager Name: William Arnold

Project Manager Email Address: arnol032@umn.edu

Project Title: Evaluation of Dioxins in Minnesota Lakes

Project number: 009-A2

1. Abstract

It is now well established that a plethora of pharmaceuticals and personal care products enter the environment via discharge of treated wastewater. While there has been much attention paid to the potential biological effects of antibiotics and hormones in surface waters, other previously unanticipated impacts also warrant attention. The common antibacterial compound triclosan is present in wastewater discharges. When exposed to sunlight, this compound and its chlorinated derivatives (which form via exposure to chlorine in tap water or during wastewater disinfection) undergo a cyclization reaction to form chlorinated dibenzo-*p*-dioxins. Dioxins have long been known to arise from incineration processes and are among the most toxic contaminants known. Dioxins are also suspected carcinogens and are bioaccumulative. Thus, the production of dioxins from triclosan is of obvious concern. The goal of this research project is to quantify the fraction of dioxins present in Minnesota lakes that are attributable to triclosan and its chlorinated derivatives. Historical trends will be determined by analyzing the triclosan and dioxins present in sediment cores as a function of depth. This research will allow determination of the risk posed by triclosan derived dioxins and if any action in response to this risk is required.

2. Background

Triclosan is the primary antibacterial ingredient in liquid handsoaps and various other consumer products. Given that the compound is washed down the drain during the normal course of use, it is not surprising that triclosan is detected in influent wastewater, effluent wastewater, and surface waters around the world [1-6]. Recent studies have shown that chlorinated derivatives of triclosan (formed in tap water or upon disinfection of wastewater effluent via reaction with chlorine; [7-9]) are present in wastewater influent and effluents [10-12]. Methylated versions of these chlorinated triclosan derivatives have also been found [10, 11].

Dioxins are an infamous class of pollutants that are toxic, carcinogenic, and endocrine disrupting. They accumulate in sediments and bioaccumulate in fish. Dioxins are linked to birth defects, developmental abnormalities, and other disorders. Dioxins pose a risk to the health of aquatic species and their predators (including humans). Known sources

of dioxins are combustion/incineration processes, manufacture of vinyl chloride, chlor alkali (electrolysis) processes, and bleaching in pulp and paper mills. The latter three processes release dioxins into surface waters. Technological improvements have dramatically decreased the loads of dioxins to the environment over the past twenty years. Dioxins, however, are still released to air, water, and land. A previously unrecognized potential source of dioxins to the environment, however, is the triclosan discharged in wastewater effluents.

It has long been recognized that 2-hydroxy-2'-chlorodiphenylethers (a class of which triclosan is one member) are precursors to dioxins [13-21]. Indeed, cyclization of such precursors has been a favored synthetic route to dioxins. In the specific case of triclosan, almost certainly the 2-hydroxy-2'-chlorodiphenylether produced in the greatest amount, there have been studies examining both the thermal [15, 20, 21] and photochemical [16-19] versions of this transformation. Thermal cyclization of triclosan occurs above 320 ºC, a temperature relevant to combustion [15]. The photochemical cyclization of triclosan has been carried out by a number of laboratories, including ours, and occurs readily at ambient temperatures under sunlight conditions in pure water and natural water [16-19]. The dioxin product that arises from cyclization of triclosan, 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD), is essentially non-toxic to guinea pigs, chick embryos, or Japanese medaka embryos [22-24]. Because the toxicity of dioxins increases dramatically with increasing chlorine substitution, particularly at the β-positions, a route to higher chlorinated dioxins from triclosan is clearly of concern.

In our past research (sponsored by the National Science Foundation), we have demonstrated that such reactions occur under environmental conditions and lead to the presence of dioxins in natural waters. These results are briefly summarized here. In influent wastewater, approximately 3000 ng/L of triclosan and 10-25 ng/L of each of the chlorinated triclosan derivatives are present (**Table 1;** line 1). Biological wastewater treatment removes ~90% of these compounds (**Table 1;** line 2). The wastewater is then treated with chlorine, and some of the triclosan is chlorinated by free chlorine during wastewater disinfection, again yielding chlorinated triclosan derivatives (**Table 1**; [25]). Note that the sum of chlorinated triclosan derivatives formed during chlorination is equal to the mass of triclosan lost upon chlorination (difference in triclosan between lines 2 and 3). Thus, even though the wastewater treatment process reduces the amount of triclosan, there is a significant load of triclosan and chlorinated triclosan derivatives to the environment, especially considering this wastewater treatment plant discharges nearly 700 _million_ liters per day to the Mississippi River.

Table 1. Triclosan and triclosan derivatives in wastewater influent at effluent at the St. Paul Metro Treatment Plant

Sample	Concentration $\pm$ standard deviation (ng/L)			
triclosan		4-Cl-triclosan	6-Cl-triclosan	4,6-Cl-triclosan
Secondary influent	2,840 $\pm$ 20	8 $\pm$ 3	24 $\pm$ 1	14 $\pm$ 15
Pre-chloriation effluent	212 $\pm$ 8	<LOQ	3 $\pm$ 2	3 $\pm$ 2
Post-chlorination effluent	183 $\pm$ 5	4 $\pm$ 1	6 $\pm$ 4	21 $\pm$ 8

Furthermore, in surface waters triclosan and the chlorinated triclosan derivatives undergo photolysis when exposed to sunlight to form chlorinated dioxins in 1-3% yield via the reaction pathways shown in Figure 1 [16-19].

Even small conversion yields of triclosan and its chlorinated derivatives leading to production of these dioxins could result in a large environmental impact. We calculate a lower limit on the mass of triclosan released into US surface waters to be 22 metric tons/year. We arrive at this value using 3 mg/day as the per capita influent mass of triclosan for wastewater treatment plants. This is the value measured for Columbus, OH in 1997 by McAvoy and co-workers [12], who also found similar values for four nearby smaller communities (3 – 5 mg/capita/day). The annual load of triclosan is roughly estimated by multiplying the per capita release by the US population (300 M people) and the removal efficiency of the wastewater treatment processes (approx. 75% of plants are activated sludge giving 96% removal; 25% other processes that are less efficient at removing triclosan, 85% removal;[12]). Assuming a 3% conversion of triclosan its derivatives to the corresponding dioxins, our worst-case estimate is that dioxins derived from triclosan may be equivalent to 10% of all currently known dioxin releases to air, land, and water on a toxicity basis.
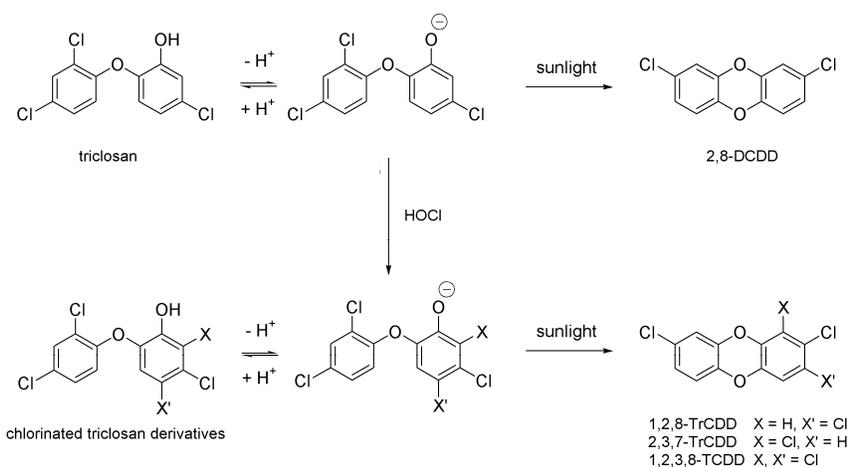

Figure 1. Formation of tri- and tetra-chlorinated dioxins via chlorination (during wastewater treatment) and photolysis (after wastewater discharge) of triclosan.

3. Hypothesis

Our central hypothesis is that photolysis of triclosan and chlorinated triclosan derivatives will lead to the accumulation of specific dioxin congeners in sediments of wastewater impacted water bodies. We also expect that these specific dioxin congeners will be absent from lakes receiving only "background" (i.e., atmospheric) loading of dioxins. We also hypothesize the concentrations of these specific dioxin congeners will increase with time (i.e., be absent in deep portions of sediment cores and have highest concentrations in surface sediment) reflecting increasing triclosan usage over the past 50 years.

4. Methodology

A record of triclosan use and photochemical dioxin production will be present in the sediments in depositional zones downstream of wastewater effluent discharge points. The selected wastewater impacted sites to be sampled are Lake Pepin, Lake St. Croix, Lake Superior (and/or the Duluth/Superior Harbor), Lake Winona near Alexandria, and Shagawa Lake near Ely We will also obtain a core at a control site that is not impacted by wastewater (either from a lake in the Boundary Waters Canoe Area or from Lake Itasca). Duplicate cores will be collected by a piston or box-type corer. Cores will be dated using lead-210 and cesium-137 methods and other chemical markers as described in Dr. Engstrom's recent work [26]. Briefly, ^{210}Pb will be analyzed by polonium isotope-dilution, alpha spectrometry following high-temperature distillation; dates will be calculated from the stratigraphic profile of excess ^{210}Pb according to the constant rate of supply (c.r.s.) model. Cesium-137 will be analyzed by low-background gamma spectrometry, and the peak and onset of ^{137}Cs will be used as dating markers (1963 and c. 1950, respectively) for atmospheric radiocesium release by above-ground nuclear testing. 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 mass of sediment contained between dated points in the core section. Dr. Engstrom has all of the required equipment and facilities to collect and date sediment cores.

After dating, cores will be sectioned, and each section will be homogenized and the moisture content determined gravimetrically by drying a subsample in an oven until constant weight is achieved. For triclosan analysis, wet samples with a mass corresponding to 1-10 g dry weight (based on the measured moisture content) from each core section will be spiked with $^{13}C_{12}$-triclosan as an isotope dilution internal standard. A single un-spiked blank sample of clean sand will be processed and analyzed to ensure that there is no triclosan contamination. Two recovery standards will be spiked with $^{13}C_{12}$-triclosan and of triclosan. The samples will be extracted into methanol using the accelerated solvent extraction system. The extracts are concentrated and centrifuged to remove particulate matter. The supernatant is then transferred to a new vial by gas-tight syringe and its exact volume recorded. From each supernatant, 1.00 mL is dissolved in 25 mL of water adjusted to pH 4. These solutions are the cleaned up using solid-phase extraction followed by silica gel. For the solid phase extraction, pre-washed Oasis HLB solid phase extraction cartridges are used. Dissolved organic matter will be washed from the cartridges using a 50:50 methanol water mixture, followed by elution of the target analytes with methanol and then 90:10 MTBE:methanol (v/v). The eluate is then concentrated, cleaned up on a silica column (eluted with ethyl acetate), solvent exchanged into 50:50 acetonitrile:water (v/v), and concentrated again to a final volume of ~ 30-40 μL. This gives detection limits of <1 ng triclosan per g sediment [25]. Analysis of the samples will be performed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) in negative mode electrospray ionization (available in the U of MN Cancer Center on an hourly basis).

For dioxin analysis, a 1-10 g dry weight sample of each homogenized core section will be spiked with nineteen $^{13}C_{12}$-labeled di- through octa-chlorodibenzo-p-dioxin and furan isomers as isotope dilution internal standards and analyzed following a version of U.S. EPA Method 1613B [27] expanded to analyze for di- and tri- chlorodibenzo-p-dioxin and

furans. Method blank and laboratory spike samples are prepared with the extraction batch to demonstrate freedom from laboratory contamination and to provide precision and accuracy information for the analysis. Each sample is extracted with toluene using a Soxhlet/Dean Stark apparatus. The extracts are spiked with $^{37}Cl_4$-2,3,7,8-tetrachlorodibenzo-p-dioxin as a cleanup standard, concentrated, and washed by shaking with concentrated sulfuric acid. Each extract is then cleaned up using silica and aluminum oxide columns. The eluate is then solvent exchanged into hexane and added to a column containing 18% activated carbon on Celite. Potentially interfering compounds are washed through each column in the forward direction and then the analytes are eluted off the column in the reverse direction. The sample is then concentrated to a final volume of 40 μL. The dioxin levels are then determined using high-resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). These extractions and analyses will be performed by a laboratory with expertise in dioxin analysis (Pace Analytical Services, Minneapolis, MN) with whom we have an existing relationship for such analyses.

From the data derived from analyses above, the concentrations (mass per mass) and accumulation rates (mass per area per time) of triclosan and the dioxins will be calculated. Because we will measure the specific dioxins derived from triclosan and chlorinated triclosan-derivatives (Figure 1) as well as the total amounts of all di- through octa-chlorinated dioxins and chlorinated furans, we will be able to calculate the fraction of dioxins in each time range within the sediment core that are attributable to triclosan release. Because triclosan was introduced in the 1960s, sediments of age greater than 50 years should have negligible amounts of triclosan derived dioxins.

5. Results and Deliverables

This research is broken into two tasks/results: 1) the collection and dating of sediment cores; and 2) the determination of triclosan and dioxin concentrations. For the first result, the deliverable is the set of dated sediment cores for wastewater impacted lakes and a control site. The second deliverable is an accounting of the triclsoan and dioxin concentrations in the collected sediment cores. We expect that triclosan concentrations in the sediments will increase with time (i.e., the more recently the sediment was deposited, the higher the concentration will be) paralleling increasing triclosan use by consumers over the past five decades. We also expect that the specific dioxins derived from triclosan will increase in concentration over time, paralleling increases in triclosan concentrations. Comparing the distribution of the expected triclosan-derived dioxins at the different sites will also provide information about how wastewater treatment techniques and practices (e.g., the use of chlorination) impacts the loads of specific triclosan-derived dioxin congeners.

 For other, higher chlorinated dioxin congeners and for chlorinated furans, we anticipate concentrations to be highest in sediment samples dating from the 1970s with concentrations decreasing over time as combustion/incineration processes (which are the major source of higher chlorinated dioxns and furans) have been improved. For each sediment sample, we will calculate the contribution of the total dioxin load that can be attributed to triclosan. This will provide the information necessary to evaluate if the

dioxins derived from triclosan and its derivatives pose a threat to aquatic ecosystems and fish consumers.

6. Timetable

The research tasks outlined above will be accomplished according to the following schedule. Shaded regions are continuous efforts and X's mark discreet events.

	Year 1				Year 2			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Result 1: Core collection and dating								
Core collection	▓	▓						
Core dating and determination of sediment deposition rates		▓	▓	▓	▓	▓		
Data analysis			▓	▓	▓	▓		
Product delivery	X			X				
Result 2: Measurement of triclosan and dioxins in sediment cores								
Triclosan extractions	▓	▓	▓	▓				
Triclosan concentration measurements		▓	▓	▓				
Dioxin extractions			▓	▓	▓	▓		
Dioxin concentration measurements				▓	▓	▓	▓	
Data analysis	▓							▓
Product delivery		X						X
Reporting	X		X		X		X	

6

7. Budget

The requested funds from LCCMR total $264,000. See attached sheets for cost breakdown. The justificaiton is as follows.

Staff or Contract Services. Over the two year project, Dr. Arnold will devote 10% (1.25 months per year) of time to the project (total salary and fringe benefits of $38,132). The responsibilities of the principal investigator includes experimental design, product coordination, data analysis, student guidance, and report/product preparation. Two graduate student researchers pursuing M.S. or Ph.D. degrees will conduct the day-to-day experiments described above. A 50% appointment is considered full time for students (and includes tuition payment and health insurance), and funds for two 43.75% appointments for two academic years and 50% time for one summer is budgeted ($111,868). The remaining 7.5% appointment in the academic year will be supplied by teaching assistantships (TAs) or funding from other research grants.

Contracts: A sum of $37,000 is for a contract to the Science Museum of Minnesota. These funds will pay 4% of Dr. Engstrom's salary and fringe benefits per year of the project ($12,000) and for core collection and dating costs, including laboratory supplies and instrument time ($25,000)

Equipment. 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. Given the number of samples expected to generated by the project, it is more economical to purchase an instrument rather than pay fees to an outside contractor to process the samples to be analyzed for triclosan.

Supplies. A total of $14,000 is requested for laboratory supplies (glassware, chemicals, analytical reagents/consumables, gloves, data storage media, laboratory notebooks, laboratory safety equipment). Dioxin standards and isotopically labelled triclosan are expected to be a significant portion of these costs.

Travel expenses: A total of $3,000 is requested for in-state travel to collect core samples and to attend in-state conferences.

Other. Additional funds totaling $25,000 dollars are requested for analytical services, specifically instrument time on liquid chromatograph-tandem mass spectrometers and dioxin extraction and analyses.

8. Credentials

Drs. Arnold and Engstrom are nationally-known researchers with expertise on the fate and transport of anthropognic organic chemicals (including solvents, pesticides, and pharmaceuticals) and use of lake sediment records to understand long-term environmental change, particularly the effects of human activities on water quality, atmospheric chemistry, and biogeochemical processes on a global scale,respectively. Dr. Arnold will be responsible for the determination of triclosan and dioxin concentrations. Dr. Engstrom will focus on collection and dating of the sediment cores. Both Drs. Arnold and Engstrom will be responsible for supervising the graduate student researchers.

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PROFESSIONAL EXPERIENCE

9/2005-present	**Associate Professor**, Department of Civil Engineering, and Member of the Graduate Faculty in Water Resources Science and in Stream Restoration Science and Engineering, *University of Minnesota*, Minneapolis, Minnesota
8/2006-6/2007	**Visiting Researcher**, Eawag, The Swiss Federal Institute for Environmental Science and Technology
8/08-present	**Associate Fellow**, University of Minnesota Institute on the Environment
9/07-present Digital	**Associate Fellow**, University of Minnesota Supercomputing Institute for Simulation and Advanced Computation
9/1999-9/2005	**Assistant Professor**, Department of Civil Engineering, and Member of the Graduate Faculty in Water Resources Science, *University of Minnesota*, Minneapolis, Minnesota

EDUCATION

1999	**Ph.D.** The Johns Hopkins University, Baltim ore, MD, Department of Geography and Environmental Engineering.
1995	**M.S.** Yale University, New Haven, CT, Department of Chemical Engineering.
1994	**S.B.** Massachusetts I nstitute of Technolo gy, Cambri dge, MA, Chemical Engineering, Minor in Chemistry.

RESEARCH INTERESTS
Fate and abiotic transfor mations of anthropogenic chemicals in natural and engineered aquatic systems, including
- Redox reactions at metal and mineral surfaces
- Photochemistry in surface waters and for water treatment
- Disinfection by-product degradation and formation
- Reactive membrane systems

SELECTED HONORS AND AWARDS
2005   Excellence in review award from *Environmental Science and Technology*
2003   1st Place   Montgomery-Watson-Harza Cons ulting Engineers/AEESP Master's   Thesis Award for Jennifer L. Packer's Thesis

2003   Bonestroo, Rosene, Anderlik an   d Associat es Undergraduate Faculty Award   (for
       excellence in teaching, advising, and mentoring of students)
2003   MFES Minnesota Young Engineer/Science & Technology Professional of the Year
2003   ASCE Minnesota Section Young Engineer of the Year

PROFESSIONAL AFFILIATIONS
American Chemical Society (En vironmental Ch emistry Di vision), American Geophysical Union
(Hydrology Section) **,** American Society of Civil Engineers, Associa   tion of Environmental
Engineering and Scie   nce Professors, American Water   Works A   ssociation, Licensed
Professional Engineer (Minnesota)

SELECTED RELEVANT PEER-REVIEWED PUBLICATIONS (48 total)
Five most closely related to the proposed project:
1. Steen, P.O.; Grandbois, M., McNeill, K.; **Arnold, W.A.** 2009. Photochemical formation of halogenated dioxins from hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and chlorinated derivatives (OH-PBCDEs). *Environmental Science and Technology* 43, 4405-4411.
2. Buth, J.M., Grandbois, M., Vikesland, P.J., McNeill, K., **Arnold, W.A.** 2009. Aquatic photochemistry of chlorinated triclosan derivatives: potential source of polychlorodibenzo-p-dioxins. *Environmental Toxicology and Chemistry,* available online: http://dx.doi.org/10.1897%2F08-490.1
3. Buth, J.M., **Arnold, W.A.**, McNeill, K. 2007. Unexpected Products and Reaction Mechanisms of the Aqueous Chlorination of Cimetidine *Environmental Science and Technology,* 41(17), 6228 -6233. http://dx.doi.org/10.1021/es070606o
4. Latch, D. E.; Packer, J. L.; Stender, B. L.; VanOverbeke, J; **Arnold, W.A.**, McNeill, K., 2005. Aqueous photochemistry of triclosan: Formation of 2,4-dichlorophenol, 2,8-dichlorodibenzo-*p*-dioxin and oligomerization products, *Environmental Toxicology and Chemistry* 24, 517-525.
5. Latch, D.E.; Packer, J.L.; **Arnold, W.A.**; McNeill, K., 2003. Photochemical conversion of triclosan to 2,8-dichlorodibenzo-*p*-dioxin in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry,* 158, 63-66.

Five other publications:
1. Surdo, E.M., Cussler, E.L., **Arnold, W.A.** 2009. Sorptive and reactive scavenger-containing sandwich membranes as contaminant barriers. *Journal of Environmental Engineering-ASCE*, 135(2), 69-76.
2. Hofstetter, T., Neumann, A., **Arnold, W.A..** Bolotin, J., Hartenbach, A., Cramer, C.J.; Schwarzenbach, R.P. 2008. Substituent effects on nitrogen isotope fractionation during abiotic reduction of nitroaromatic compounds, *Environmental Science and Technology,* 42(6), pp. 1997-2003.
3. **Arnold, W.A.**, Bolotin, J., von Gunten, U., Hofstetter, T.B. 2008. Evaluation of functional groups responsible for chloroform formation during water chlorination using compound specific isotope analysis, *Environmental Science and Technology,* 42, 7778–7785.
4. Werner,   J.J.; **Arnold, W.A.**; McNeill, K., 2006. Water hardness as a photochemical parameter: tetracycline photolysis as a function of calcium concentration, magnesium concentration, and pH, *Environmental Science and Technology*, 40(23), 7236-7241.
5. Chun, C.L.; Penn, R.L.; and **Arnold, W.A.**, 2006. Kinetic and microscopic studies of reductive transformations of organic contaminants on goethite. *Environmental Science and Technology,* 40, 3299-3304.

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Professional Preparation

B.A.   1971   University of Minn., Duluth (Zoology, minor: chemistry) Magna cum Laude
      1971-73 University of Wisconsin, Madison (Zoology: Limnology)
M.S.   1975   University of Minnesota, Duluth (Zoology, minor: Botany)
Ph.D.   1983   University of Minnesota, Minneapolis (Ecology)

Appointments

1999-   Director, St. Croix Watershed Research Station, Science Museum of Minn.
1995-99   Sr. Scientist, St. Croix Watershed Research Station, Science Museum of Minn.
1990-   Adjunct Professor, Dept. of Geology and Geophysics, University of Minnesota
2004-   Adjunct Professor, Water Resources Science, Univ. of Minnesota
1983-95   Research Associate, Limnological Research Center, Univ. of Minnesota

Publications

(i) Project Related

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

Balogh, S.J., **D.R. Engstrom**, J.E. Almendinger, C. McDermott, J. Hu, Y.H. Nollet, M. L. Meyer, and D. K. Johnson. 2009. A sediment record of trace metal loadings in the upper Mississippi River. *Journal of Paleolimnology* 41: 623-639.

Engstrom, D.R., E.B. Swain, and S.J. Balogh. 2007. History of mercury inputs to Minnesota lakes: influences of watershed disturbance and localized atmospheric deposition. *Limnology and Oceanography* 52: 2467-2483.

Biester, H., R. Bindler, A. Martinez-Cortizas, and **D.R. Engstrom**. 2007. Modeling the past atmospheric deposition of mercury using natural archives. *Environmental Science and Technology* 41: 4851-4860.

Triplett, L.D., **D.R. Engstrom**, D.J. Conley, and S.M. Schellhaass. 2008. Silica fluxes and trapping in two contrasting natural impoundments of the upper Mississippi River. *Biogeochemistry* 87: 217-230.

(ii) Other Significant

Bookman, R., C.T. Driscoll, **D.R. Engstrom**, and S.W. Effler. 2008. Local to regional emission sources affecting mercury fluxes to New York lakes. *Atmospheric Environment* 42: 6088-6097.

Lindberg, S.E., O.R. Bullock, R. Ebinghaus, **D.R. Engstrom**, X. Feng, W.F. Fitzgerald, N. Pirrone, E.M. Prestbo, and C. Seigneur. 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* 36: 19-32

Engstrom, D.R. 2007. Fish respond when the mercury rises. *Proceedings of the National Academy of Sciences* 104: 16394-16395.

Milner, A.M., C.L. Fastie, F.S. Chapin, **D.R. Engstrom**, and L.C. Sharman. 2007. Interactions and linkages among ecosystems during landscape evolution. *Bioscience* 57: 327-247.

Engstrom, D.R., Schottler, S.P., Leavitt, P.R., and Havens, K.E. 2006. A re-evaluation of the cultural eutrophication of Lake Okeechobee, Florida, using multiproxy sediment records. *Ecological Applications* 16: 1194-1206.

Synergistic Activities

Executive Committee: *International Paleolimnology Association*, 2006-present

Panel Chair, Sediment-core work group: *Multimedia Measurements of Mercury in the Great Lakes Region*, La Crosse, WI, November 2008 (and ongoing)

Invited Expert, *National Mercury Monitoring Workshop*, USEPA and other Federal Agencies, Annapolis, MD, May, 2008.

Expert Panel Member: *International Workshop on Environmental Mercury Pollution*, Madison WI 2005-06

Member: *Lake Pepin-Mississippi River TMDL Science Advisory Panel,* 2006-present

9. Dissemination and Use

Findings will be disseminated and archived via reports to LCCMR, peer-reviewed publications, and presentations at conferences. We will also, when appropriate, disseminate results via the media. The audience is not only the scientific community, but also the public and policymakers. The information derived from this research will show the extent to which specific dioxins present in Minnesota lakes are derived from triclosan. If necessary, this information can be used to craft a voluntary or regulatory solution if the risks posed by the dioxins are deemed unacceptable.

Sediment samples will be freeze-dried for potential future analyses. Extracts will also be labeled and archived (frozen) for potential future analyses.

10. References

1. 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. *Environmental Science and Technology* 2002, *36*, (6), 1202-1211.
2. Lindstrom, A.; Buerge Ignaz, J.; Poiger, T.; Bergqvist, P.-A.; Muller Markus, D.; Buser, H.-R., Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. *Environmental science and technology* 2002, *36*, (11), 2322-9.
3. Nakada, N.; Kiri, K.; Shinohara, H.; Harada, A.; Kuroda, K.; Takizawa, S.; Takada, H., Evaluation of Pharmaceuticals and Personal Care Products as Water-soluble Molecular Markers of Sewage. *Environ. Sci. Technol.* 2008.
4. Sabaliunas, D.; Webb, S. F.; Hauk, A.; Jacob, M.; Eckhoff, W. S., Environmental fate of Triclosan in the River Aire Basin, UK. *Water Research* 2003, *37*, (13), 3145-3154.
5. Singer,   H.; Mueller, 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. *Environmental Science and Technology* 2002, *36*, (23), 4998-5004.
6. Tixier, C.; Singer Heinz, P.; Canonica, S.; Muller Stephan, R., Phototransfomation of ticlosan in surface waters: a relevant elimination process for this widely used biocide--laboratory studies, field measurements, and modeling. *Environmental science & technology* 2002, *36*, (16), 3482-9.
7. Onodera, S.; Ogawa, M.; Suzuki, S., Chemical changes of organic compounds in chlorinated water. 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* 1987, *392*, 267-75.
8. Rule, K. L.; Ebbett, V. R.; Vikesland, P. J., Formation of Chloroform and Chlorinated Organics by Free-Chlorine-Mediated Oxidation of Triclosan. *Environmental Science and Technology* 2005, *39*, (9), 3176-3185.
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