

# **Toxic Cyanobacteria and Harmful Algal Blooms in Lake Ontario**

Prepared by Gregory Boyer, SUNY-ESF, Syracuse NY 13210 (glboyer@esf.edu)

## **Description of the issue and its significance to Lake Ontario:**

Bloom-forming algae and the toxins they produce are causative agents for human and animal illness/mortality as well as a litany of environmental-, legal-, and recreational-related problems (Codd, 2005). Most often, cyanobacteria toxins have been associated with the poisoning of birds and livestock. However, several high profile cases of human intoxication have occurred in recent years. In the United States, adverse human affects have included severe gastroenteritis in Pennsylvania (Lippy and Erb, 1976) and recently Nebraska, Massachusetts, Vermont and New York have all closed recreational and swimming beaches in the last few years due to toxic cyanobacterial blooms. Other worries include chronic exposure to cyanobacteria toxins in untreated drinking water leading to liver damage, possible carcinogenesis and tumor growth promotion.

Fortunately, the effects due to cyanobacteria toxins in the Great Lakes ecosystem have been limited primarily to wildlife and animal fatalities. During 1999 and 2000, large die-offs of waterfowl occurred in Lake Erie and Lake Huron. These deaths were associated with type E or C avian botulism. While the connection with toxic cyanobacteria is tenuous, microcystin-producing cyanobacteria may sensitize the birds to avian botulism (Murphy et al., 2000). The connection between an anatoxin-a producing bloom in Lake Champlain and dog fatalities is more direct. In 1999 and again in 2000, toxic outbreaks of a toxic cyanobacteria resulted in the deaths of several dogs, first from anatoxin-a, and then from microcystin intoxication (Boyer et al, 2004). Microcystins bioaccumulate (but probably not bioconcentrate) in bivalve and fish tissue (Magalhaes et al., 2001), but the significance of this route of exposure is still unknown. The recent resurgence in *Microcystis* blooms in Saginaw Bay and western Lake Erie is of concern due to the widespread use of these waters for recreation, fishing and drinking water.

## **Current scientific knowledge that exists for Lake Ontario:**

Toxic cyanobacterial blooms are well established in the western basin of Lake Erie (Brittain et al., 2000, Rinta-Kanto et al 2005) and in the Saginaw Bay for Lake Huron (Vanderploeg et al., 2001). In addition, there have also been a number of studies on Lake Erie and Lake Ontario by NOAA's MERHAB-LGL program and by Environment Canada. The locations of these toxic blooms are summarized in Figure 1.



Figure 1. Location of toxin cyanobacteria blooms in the Great Lakes. (Adapted from Watson et al., 2006)

Environment Canada has conducted an extensive survey of the Bay of Quinte Region of Lake Ontario in 2003 and again in 2005. This survey showed that microcystin levels in the middle reaches of the Bay routinely exceeded the Health Alert Guideline (HCG) values for microcystins in drinking water (Figure 2). Similar studies conducted in the embayments along the New York shore have also shown a widespread potential for toxic *Microcystis* (e.g. the genetic signatures for toxin biosynthetic genes are present; Hotto et al., submitted), but there is a relatively low conversion of this genetic signatures into actual toxin production (Makarewicz et al., 2006, submitted). The one exception to this was the 2003 bloom of *Microcystis* in the eastern basin near Oswego where surface water concentrations near the Oswego County water drinking water intakes exceeded the World Health Organizations HCG values of  $1 \mu\text{g L}^{-1}$  (Boyer 2006, in press).

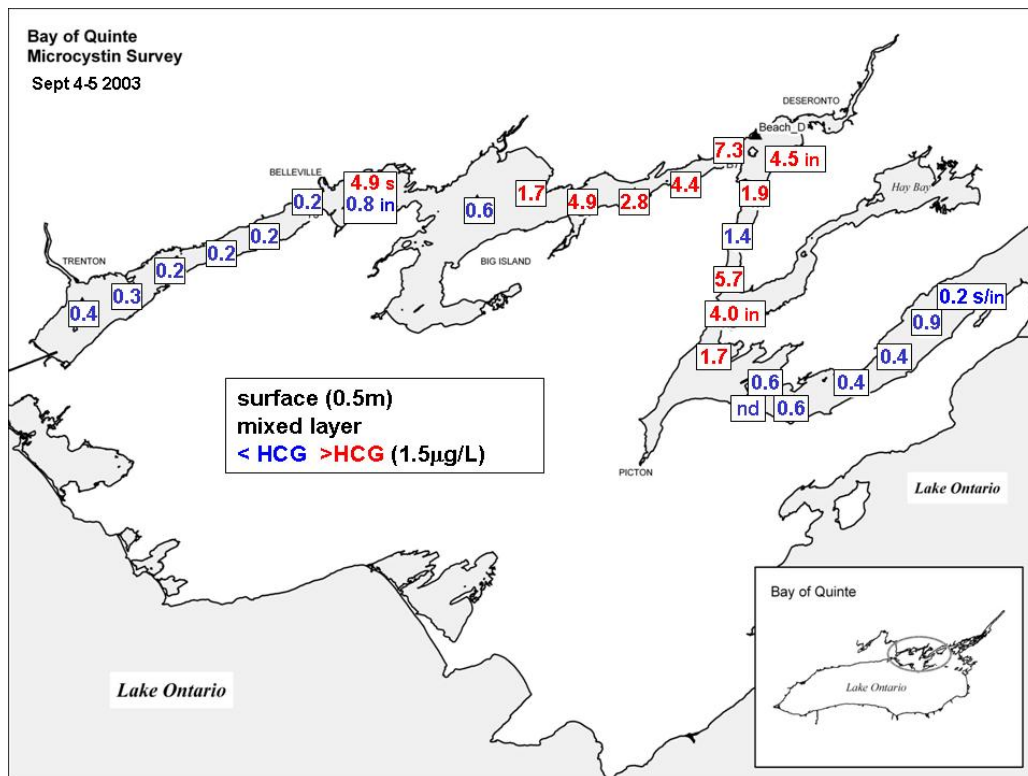


Figure 2. Bay of Quinte microcystin survey by Environment Canada 2003. Microcystin concentrations are given in  $\mu\text{g}$  Microcystin LR equivalents per liter.

Less is known about the production of cyanobacterial toxins in the offshore waters of Lake Ontario. A survey of offshore waters conducted in 2003 as part of the MERHAB-LGL monitoring program suggested a toxic bloom occurred in the waters off Toronto in the western basin in July (Boyer, unpublished). Whether this bloom moved through the lake-wide circulation patterns and contributed to the August bloom in the eastern basin, or represented an independent bloom event unconnected to the blooms in the eastern basin, remains to be determined.

Even less is known about the distribution of the other cyanobacterial toxins in Lake Ontario. The neurotoxin anatoxin-a has been identified in low concentrations in the near shore sites and

embayments along the NY shore in 2003 and 2004, in waters off of Toronto in 2004, and in selected stations near Oswego in 2001. Other cyanobacterial toxins such as cylindrospermopsin and the paralytic shellfish toxins have not been identified in Lake Ontario waters, in agreement with their limited distribution in the more oligotrophic waters of the North Eastern United States.

### **Identification of the data / information gaps that should be addressed in 2008:**

To date there have been no whole-lake systematic surveys looking at the temporal and spatial distribution of toxic cyanobacterial blooms in Lake Ontario. Current and past studies have either looked at occurrence of the blooms in the embayments easily reached by land-based vehicles or small boats, or have relied on single one-time cruises conducted as part of the Environment Canada Taste and Odor program in late summer. While this gives a snapshot image of the blooms in Lake Ontario, we have little to no information on the occurrence of toxic cyanobacterial blooms in open waters early in the season, and on the contribution and movement of water from the embayments and rivers to the offshore waters. Suggested information gaps that should be addressed in 2008 include:

1. A detailed mapping of the spatial (whole Lake) and temporal (throughout the season) distribution of toxic cyanobacterial blooms in Lake Ontario.
2. A basic understanding on the impact of the embayments and Niagara River on the growth and distribution of toxic cyanobacteria in the offshore waters. Are these acting as a potential source of seed populations or providing essential nutrients that promote the growth of toxic populations in offshore waters?
3. A basic understanding of the physiological, biological and chemical factors limiting growth of toxic organisms and toxin production in this system. Included in this may be looking at factors that result in a shift in populations between toxic and nontoxic cell types (Welker et al 2003, Rinto-Kanto et al., 2005).
4. What is the occurrence and distribution of other toxins besides microcystins? These will be more difficult to identify since they tend to occur at other times of the season and in populations that may be less likely to form high biomass blooms.

### **Monitoring proposed for 2008 and potential coordination and partners:**

MERHAB-LGL was a 5-yr project and due to terminate in Fall 2008. It is uncertain if we will monitor Lake Ontario during that last summer using MERHAB funding. Plans are underway for a continuation of that project; however the field aspects of those future projects have yet to be decided. A main limitation for those programs is access to large ships suitable for offshore sampling with sufficient temporal resolution to determine population shifts. This was best addressed in the International Field Year on Lake Erie by multi-agency partnerships. Potential partners include USEPA (RV *Lake Guardian*), Environment Canada (CCGS *Limnos*), members of the NY Great Lakes Research Consortium located along Lake Ontario (Buffalo, Brockport, Oswego, ESF, Clarkson), New York Sea Grant and the Lake Ontario LAMP.

### Other factors to be considered for the 2008 cooperative monitoring plan:

Key for the understanding of microbial contaminants such as toxic cyanobacterial blooms in Lake Ontario is to obtain the needed ancillary data to properly interpret the results. This is often overlooked when designing monitoring plans. This should include a full nutrient workup on both the inshore and offshore waters, size fractionated chlorophyll (0.2, 2 and 20 $\mu$ ), DOC levels, accessory pigments such as phycocyanin and a general distribution of taxonomic species.

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**Waterborne Pathogen and *E. coli* Contamination – Issue Paper**

Issue and significance

Waterborne pathogens can pose significant threats to drinking water supplies, recreational water, irrigation water, as well as to aquatic ecosystems and biodiversity. While outbreaks of waterborne disease do not appear to be commonly reported around Lake Ontario, the incidence of such disease is notoriously under-reported, and existing pathogen detection and disease reporting mechanisms are poorly developed.

High numbers of *E. coli* can be found in many Lake Ontario tributaries and nearshore waters indicating the presence of fecal pollution, and the potential occurrence of a variety of waterborne pathogens. *E. coli* contamination at many Lake Ontario beaches continues to result in numerous beach postings, and the loss of recreational opportunities.

Waterborne pathogens can have significant human and animal health impacts. A *Cryptosporidium* drinking water outbreak in Milwaukee (1993) on Lake Michigan contributed to about 40 deaths and 400,000 illnesses. There have also been outbreaks of waterborne disease in areas surrounding Lake Ontario in recent years. A drinking water outbreak of *E. coli* O157:H7 in Walkerton, Ontario (2000) resulted in 7 deaths and 2,300 illnesses. A recreational water outbreak of *E. coli* O157:H7 in Montreal, Quebec (2001) resulted in the hospitalization of at least 4 children. An outbreak of *Legionella pneumophila* in Toronto, Ontario (2005) associated with contaminated air cooling water resulted in 23 deaths and 112 illnesses. A new Viral Hemorrhagic Septecemia (VHS) virus and a toxin from *Clostridium botulinum* have recently contributed to disease outbreaks in Lake Ontario fish and wildlife.

Pathogen contamination of aquatic ecosystems can occur from a range of sources including fecal pollution associated with municipal wastewater effluents, stormwater outfalls, septic tanks, agricultural wastes, and wildlife droppings. Other waterborne pathogens such as *Legionella pneumophila* may not be associated with sources of fecal pollution. Waterborne pathogens may pose growing threats in the future due to increasing human and livestock population densities, urbanization and changing land drainage, aging municipal wastewater infrastructure, changing patterns of water use, extreme weather events and flooding, and an inadequate knowledge of the sources, occurrence, concentrations, survival and transport of waterborne pathogens in aquatic ecosystems.

### Current knowledge

As one contributor, Environment Canada's National Water Research Institute has conducted waterborne pathogen research in Lake Ontario dating back to the 1970s. More recently, efforts have focused on studying the occurrence of *E. coli* and waterborne pathogens in nearshore recreational waters and evaluating microbial source tracking techniques. Considerable water quality work has been undertaken around Hamilton Harbour to better understand the occurrence and sources of *E. coli* in sand and beach waters. Antibiotic resistance analyses have indicated the presence of multiple antibiotic resistant *E. coli* in recreational waters (Can. J. Microbiol. 2005, 51:501-505). Extensive microbial source tracking studies have been conducted to determine the source of *E. coli* contaminating beaches around the City of Toronto. The studies have pointed to the importance of bird droppings (gulls and geese) as the most prominent source of *E. coli* contamination at some beaches. Other studies have applied a new DNA microarray tool to discover an unexpectedly high number of *E. coli* pathotypes in Hamilton Harbour, including *E. coli* pathotypes associated with urinary tract infections (Appl. Environ. Microbiol. 2006, 72: 4200-4206). Similar *E. coli* pathotype results were found in the Detroit River corridor, particularly near municipal wastewater outfalls (Appl. Environ. Microbiol. 2007, 73: 477-484). A preliminary study conducted in 2006 at a beach in Hamilton Harbour detected *Campylobacter* species in sand and adjacent beach water, although pathogen levels seemed low.

### Information/data gaps

- Synthesis of existing information/data on occurrence of *E. coli* and waterborne pathogens in Lake Ontario and its tributaries.
- Knowledge about the occurrence of bacterial, protozoan, and viral pathogens in Lake Ontario source waters used for drinking and recreation.
- Knowledge about the significance of pathogen loadings and transport from Lake Ontario tributaries, wastewater effluents, and other sources.
- Better understanding of waterborne pathogen exposures and the actual incidence of waterborne disease around Lake Ontario

### Monitoring plans for 2008

- Continue ongoing collaboration with the City of Toronto to apply microbial source tracking techniques to determine the source of fecal pollution responsible for beach postings, and to identify key sources of human sewage contamination.
- Potential new partnership to investigate waterborne pathogens at Lake Ontario drinking water intakes with Larry Moore and Collaborative Study to Protect Lake Ontario Drinking Water.

Tom Edge, Ph.D.

National Water Research Institute, Environment Canada

# Integrating Multimedia Mercury Measurements for the Great Lakes

By  
Dave Evers, Biodiversity Research Institute  
and  
Jon Dettling, Great Lakes Commission

## **Synopsis**

Mercury poses a significant threat to human and wildlife health within the Great Lakes basin. Measurements of environmental mercury concentrations are needed to better understand mercury dynamics in the basin and to parameterize models being developed of mercury fate and exposure. While there is a clear need for additional data collection, pre-existing measurement data might be used in many cases to answer critical questions as well as to provide a historical context of mercury contamination prior to recent regulatory actions. Unfortunately, mercury measurement information is scattered into many discrete data holding by individual research labs, government agencies and elsewhere. In addition, data from differing collection efforts is rarely in a format to allow easy inter-comparison. A collaborative project is suggested here to overcome these constraints by integrating a wide variety of dispersed mercury data holding for the region and to provide interpretation of the combined data in an effort to answer many critical mercury questions. This work would leverage a significant commitment made in recent years to a similar effort in the neighboring region of northeastern North America (extending from New York State to the Canadian maritime provinces). The database constructed there would be extended geographically to include the Great Lakes region and the combined dataset would be used to the research team to examine patterns and relationships in the data and provide data for use in modeling activities.

## **Problem Statement**

The U.S. EPA estimates that hundreds of thousands of children are born each year at risk of health impairments due to maternal methylmercury exposure. Among the more than 3000 fish advisories in place nationally in 2004, more than 75% are within the eight Great Lakes states and the five Great Lakes themselves are each under lake-wide advisories against eating certain fish due to mercury-related health concerns. In addition, piscivorous wildlife species within the Great Lakes region have been demonstrated to suffer health impacts at environmentally relevant methylmercury exposure levels. Mercury contamination in the Great Lakes environment is clearly among the chief human and wildlife health concerns and federal and state governments within the region have taken or contemplated aggressive policy measures in attempt to alleviate these risks.

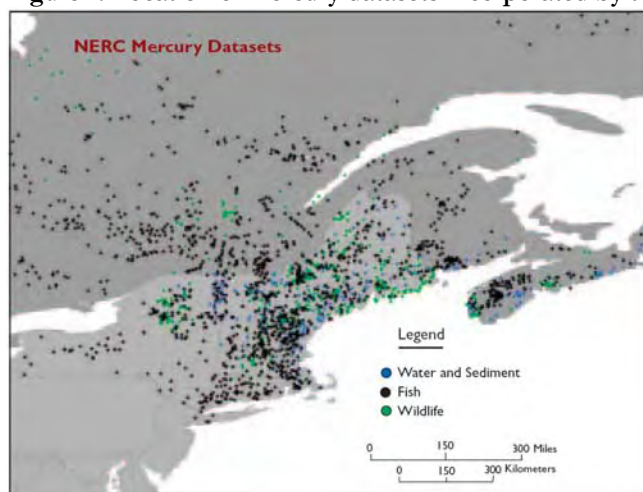
Although health implications of mercury have been clearly identified, the environmental processes governing mercury cycling and exposure remain poorly understood. The processes that determine mercury loading to ecosystems, availability to microorganisms, conversion to methylmercury and accumulation within aquatic food chain can only be very roughly approximated. While guesses and assumptions can be made regarding the linkage between mercury releases and exposures, accurate quantification of these processes is not yet possible. Better understanding requires combination of process-level investigations and modeling with robust environmental data collection efforts. While many thousands of environmental mercury data points have been collected over past decades throughout the Great Lakes basin at a cost of many millions of dollars, this body of data is not available to answer the large-scale ecosystem questions for which it would be useful. While programs exist to collect data within a given medium and jurisdiction, integration of past data across media

and jurisdictions is needed to take full advantage of past data collection efforts. By leveraging these substantial past investments in data collection, the proposed project will produce an integrated multi-media mercury dataset for the whole of the Great Lakes basin. This dataset will be exploited by leaders in the field of mercury science to answer critical questions regarding mercury patterns and processes.

### **The Northern States Research Cooperative's Mercury Research Group**

Beginning in 2001, a group of scientists and others of varied backgrounds was assembled with an aim of compiling a comprehensive database of mercury measurements in Northeast North America and interpreting the resulting dataset with a variety of techniques. The criterion for participation was simply the ability to contribute data to the regional database. The study area is shown in figure 1, along with the spatial distribution of the datasets that were included. Although New York state and eastern Ontario were included within the study geography none of the Great Lakes themselves (nor Lake Champlain) was included within the study. Over the course of several years, more than 50 scientists contributed data and technical expertise to the project.

**Figure 1: Location of mercury datasets incorporated by the NSRC mercury research group**



The project operated through a series of annual workshops at which the project contributors would convene to work on the technical aspect of data sharing and to brainstorm methods for interpreting the compiled regional database. The project work was divided into a number of separate teams: air/deposition; water and watershed; sediments; algae; invertebrates; fish; birds; mammals; and database management and GIS mapping. This work resulted in an unprecedented database of multimedia mercury measurements from across the Northeastern U.S. and eastern Canada and supported the production of numerous research articles, published within a special issue of the journal *Ecotoxicology* ([Volume 14, Issues 1-2, March 2005](#)) and elsewhere.

Results include the estimation of total (wet+dry) annual mercury deposition across the region, regional time trends of mercury in lake sediments, spatial trends of mercury and methylmercury in lake and river waters, differences and distributions of fish mercury concentrations among species and habitat types, quantifying mercury transfers in the food chain. Figures 2 through 7 illustrate some of these results. This research has led to numerous policy-relevant outcomes relating to addressing the mercury issue in the Northeast and provide a framework for the expansion suggested here.

Figure 2: Total annual mercury deposition (wet + dry) for northeastern North America (from Miller et al., 2005)

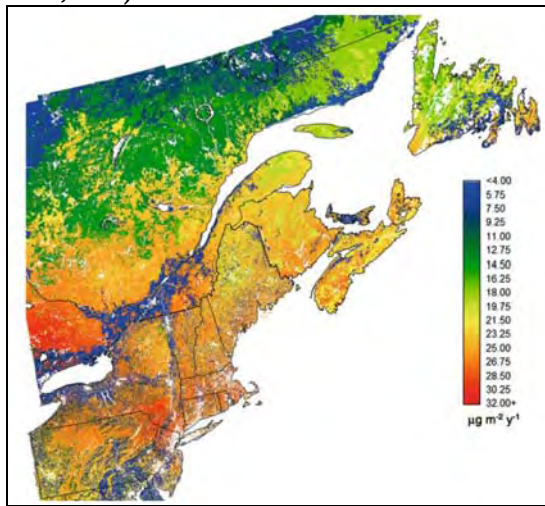


Figure 3: Temporal trend of mercury concentrations in sediments from northeastern North America (from Evers, 2005)

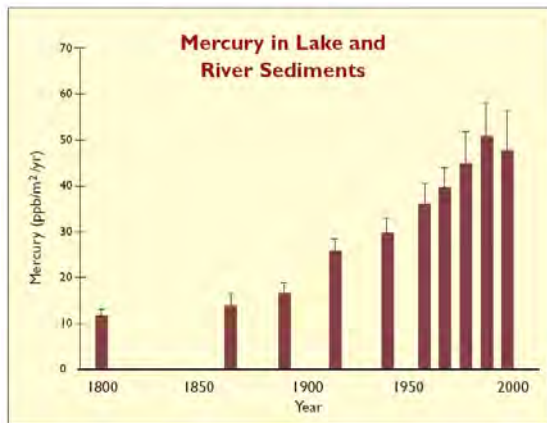


Figure 4: Spatial pattern of total mercury in lake and river waters (from Dennis et al., 2005)

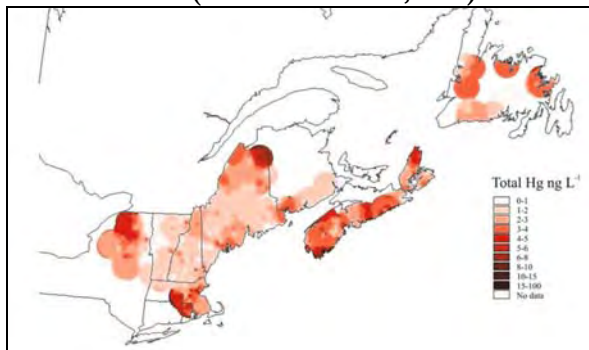


Figure 5: Mercury in Yellow Perch and Brook Trout by habitat type (from Evers, 2005)

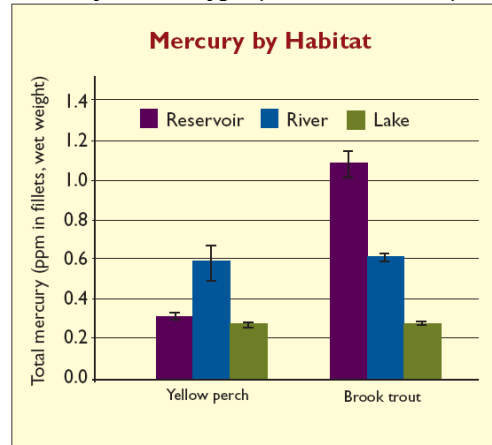


Figure 6: Mercury concentration distributions in various fish species (from Evers, 2005)

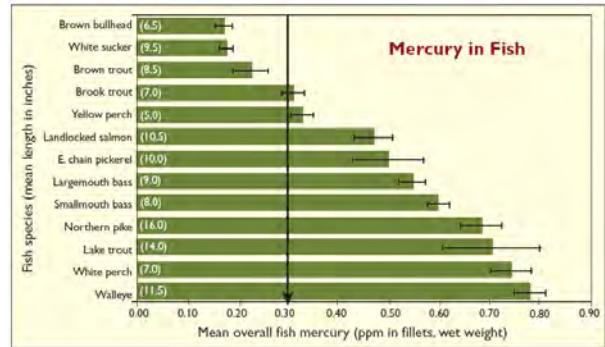
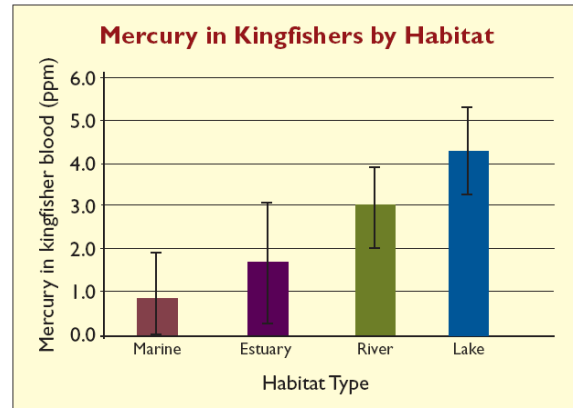


Figure 7: Mercury in Kingfisher blood by habitat type (From Evers, 2005)



## **Expansion to the Great Lakes**

The proposed project will leverage not only the work done between 2001 and 2006 under the Northern States Research Cooperative's Mercury Research Group, but also the vast prior investment in mercury measurements from across the Great Lakes basin. Building upon the tools and framework developed under the NSRC project, we suggest that the NSRC data based be expanded to include the Great Lakes region (encompassing the full province of Ontario and the states Pennsylvania, Ohio, Michigan, Indiana, Illinois, Wisconsin and Minnesota). This will be done through a community-derived scientific effort that will apply this database in developing important informational products and in answering vital scientific questions regarding mercury cycling in the Great Lakes basin and in the lakes themselves. The project will include a large consortium of university-based and government scientists from across the region. In addition to a core team of leaders for each environmental compartment, outreach will be made to identify those holding mercury measurement data and to encourage their participation in the project. As found in the NSRC initiative, it is anticipated that the dual benefits for policy development and scientific assessments will result in very high participation among the scientific and governmental communities.

The identification, comparison and integration of datasets will take place through a series of workshops and collaborative work via teleconferences and internet communications. During the year following the initial workshop, project leaders and participants will work to identify additional data components and overcome any technical or institutional issues that may arise for adequate data documentation and integration. Beginning the second year of the project, a second workshop will be held at which scientific leaders from across the region will be engaged in employing the dataset to answer critical scientific and policy-relevant questions regarding mercury deposition, processing within the Great Lakes ecosystem and impacts. The informational tools available to address these questions will be unprecedented on a basin-wide level. Among the questions that will be examined through this approach are:

- What are the spatial and temporal patterns in the total (dry plus wet) mercury deposition over the Great Lakes basin and to the lakes themselves.
- What are the differences in mercury loading between the Great Lakes and the numerous small lakes in the surrounding basin?
- What spatial patterns exist in mercury and methylmercury concentrations in waters, fish, piscivorous birds and other wildlife? What factors might explain these patterns?
- Where do concentrations exceed wildlife or human health thresholds? Do mercury "hotspots" or highly sensitive eco-regions exist within the Great Lakes basin?
- What is the contribution of watershed and wetlands to total and methyl mercury to the aquatic ecosystems in the basin?
- What processes govern mercury methylation and cycling in the Great Lakes, and how do those processes differ from the small lakes?
- And many others.

Tangible outcomes of the project will include the database itself and a series of peer-reviewed publications detailing the application of the data in addressing the questions listed above. In addition, the proposed project will lay a groundwork for further work, including parameterization and validation of models and continued use in scientific assessment and tracking of trends.

## **NIAGARA RIVER UPSTREAM/DOWNSTREAM MONITORING PROGRAM:**

The Niagara River has a significant influence on Lake Ontario. It is responsible for more than 83% of the total tributary inflow to the lake (Eadie and Robertson 1976), 85% of the total input water budget, and about 50% of all incoming fine grained sediment (Kemp and Harper 1976). Because of this influence, Environment Canada established a monitoring station in 1975 at the mouth of the Niagara River at Niagara-on-the-Lake (NOTL) to estimate the annual chemical loads and changes/trends in these loads from the river to Lake Ontario. A second station was established at the head of the Niagara River at Fort Erie (FE) in October 1983, to estimate the loads of chemicals to the river from Lake Erie.

This Upstream/Downstream Program, as it became known, was a key component of the Niagara River Long Term Monitoring Plan recommended by the Niagara River Toxics Committee (NRTC 1984). It was formally incorporated into the Niagara River Declaration of Intent (DOI) signed by the Four Parties (Environment Canada, the United States Environmental Protection Agency (Region II), the Ontario Ministry of the Environment, and New York State Department of Environmental Conservation) in February, 1987. Thus, what had begun as an Environment Canada initiative, became a component of the Niagara River Toxics Management Plan (NRTMP). The overall goal of the NRTMP is to achieve significant reductions of toxic chemical pollutants in the Niagara River. Specifically, results from the Upstream/Downstream program are intended to determine whether concentrations of specified chemicals at NOTL are statistically different from concentrations at FE, and to assess trends over time.

Concentrations and loads have been summarised in annual data reports for the first 11 years of the program. At the end of that first series of annual reports, the first trend report summarising changes in contaminants over the 1986 – 1997 period was released by Environment Canada (Williams et al. 2000). Program reports now summarise chemical data collected over a two-year period (April 1 - March 31) and include the raw data and the annual mean concentrations and loads estimated by the Maximum Likelihood Estimation (MLE) method (El-Shaarawi 1989) for all the parameters measured at both the FE and NOTL stations.

The Upstream/Downstream Program measures the concentrations of trace organic contaminants in water and suspended solids and trace metals in whole water at the head of the Niagara River at Fort Erie (FE) and at the mouth of the River at Niagara-on-the-Lake (NOTL). A complete list of chemicals measured, and the analytical detection limits used for the 1999-2000 and 2000-2001 data sets are provided in Table 1.

In addition to the parameters in Table 1, Environment Canada has also collected and analysed Niagara River water and sediment for new and emerging contaminants such as Acid Pharmaceuticals and Personal Care Products.

Table 1. Practical Detection Limits for 1999-2000 and 2000-01 Data

<b>Organics</b>	<b>Water (ng/L)</b>	<b>Solids (ng/g)</b>	<b>Organics</b>	<b>Water (ng/L)</b>	<b>Solids (ng/g)</b>
1,3-Dichlorobenzene	0.285	6.44	Fluoranthene	0.17	33.9
1,4-Dichlorobenzene	0.234	7.47	Pyrene	0.17	62.9
1,2-Dichlorobenzene	0.214	6.70	Benzo(a)anthracene	0.01	43.5
1,3,5-Trichlorobenzene	0.009	0.92	Chrysene/Triphenylene	0.03	39.4
1,2,4-Trichlorobenzene	0.011	2.08	Benzo(b+k)fluoranthene	0.03	70.4
1,2,3-Trichlorobenzene	0.006	0.35	Benzo(a)pyrene	0.01	33.7
1,2,3,4-Tetrachlorobenzene	0.005	0.34	Indeno(1,2,3-c,d)pyrene	0.02	29.1
Pentachlorobenzene	0.005	0.30	Dibenzo(a,h)anthracene	0.02	10.9
Hexachlorobenzene	0.005	0.29	Benzo(g,h,i)perylene	0.02	20.5
Hexachlorobutadiene	0.003	0.12			
Hexachlorocyclopentadiene	0.004	0.31			
				<b>Whole Water (ug/L)</b>	<b>Solids (ug/g)</b>
Heptachlor	0.010	0.66	<b>Metals</b>		
Aldrin	0.010	0.37	Aluminum	2.0	
Octachlorosytrene	0.004	0.19	Antimony	0.01	
p,p'-DDE	0.011	0.37	Arsenic	0.1	
p,p'-TDE (p,p'-DDD)	0.030	1.35	Barium	0.05	
o,p'-DDT	0.033	0.57	Boron	0.1	
p,p'-DDT	0.043	1.02	Beryllium	0.002	
Photomirex	0.040	0.44	Cadmium	0.005	
Mirex	0.014	0.66	Cobalt	0.002	
α-BHC	0.031	0.24	Chromium	0.02	
γ-BHC	0.031	0.18	Copper	0.02	
Heptachlor Epoxide	0.015	0.75	Gallium	0.002	
γ-Chlordane	0.006	0.42	Lanthanum	0.001	
α-Endosulfan	0.012	0.57	Iron	1.0	
α-Chlordane	0.036	0.49	Lithium	0.02	
Dieldrin	0.032	0.67	Manganese	0.005	
Endrin	0.030	0.97	Molybdenum	0.01	
β-Endosulfan	0.010	0.62	Nickel	0.05	
Endrin Aldehyde	0.027	1.07	Lead	0.005	
Methoxychlor	0.070	4.62	Rubidium	0.002	
TCPCB	0.211	14.6	Selenium	0.1	
2-Methylnaphthalene	0.12	5.23	Silver	0.005	
1-Methylnaphthalene	0.08	3.26	Strontium	0.05	
Naphthalene	0.33	5.27	Tellurium	0.001	
Acenaphthylene	0.09	8.05	Uranium	0.001	
Fluorene	0.07	5.5	Vanadium	0.01	
Phenanthrene	0.12	32.2	Zinc	0.05	
Anthracene	0.02	16.2	<b>Mercury in susp. solids</b>		0.004
2-Chloronaphthalene	0.01	3.0			
Atrazine	6.04	20.5			
Metolachlor	0.82	46.3			

# **The Presence of Pharmaceuticals, Pesticides and Endocrine Disrupting Compounds in Great Lakes Water**

Saad Jasim, Walkerton Clean Water Centre

## **Introduction**

The occurrence and fate of pharmaceutically active and personal care products (PPCPs) in surface waters originating from urban sources is one of the leading emerging issues in environmental chemistry. At least 80 PPCPs (e.g., analgesics, antibiotics, antiepileptics, antidepressants, and blood lipid regulators) have been identified in outflows from sewage treatment plants (STPs) and surface waters worldwide [1, 2]. However, many PPCPs remain unidentified. Moreover, little is known regarding the fate, characterization and quantification at drinking water intakes.

Although pharmaceuticals at such low concentrations may seem rather benign, we do not know the effect of a complex mixture of compounds from sewage effluent and overflows. Preliminary analysis indicated that trace levels of some of these compounds were detected in incoming rivers that connected to the Great Lakes [3,4].

Pharmaceuticals are most likely to appear in surface waters from sewage discharges as a product of their human use and consequent excretion [5,6] and are discharged continuously into the environment in highly populated areas [7]. Reports have shown that as much as 50% to 90% of an administered drug can be excreted in original form or a similar biologically active form [8,9]. In sewage treatment plant (STP) discharges, PPCPs and EDCs may be present as a result of incomplete removal during treatment, from combined sewage and stormwater overflows (CSOs), illicit connections, or leaking septic systems. Other point source contamination can result from pharmaceutical manufacturers [7]. Agricultural practices can constitute a significant contribution to

nonpoint sources of PPCPs and EDCs. Veterinary antibiotics were detected in surface water supplies in proximity to large-scale hog confinement operation in Iowa [10]. Some pharmaceuticals have also been shown to leach through subsoil and into groundwater [11].

### **Health Effects (Human and Ecological)**

Since medical drugs are designed with a specific mode of action, it is expected that they may have a variety of effects on non-target receptors and can possibly cause adverse effects in a target organism [10]. Antibiotic resistance is the issue receiving the most attention of all the PPCPs, especially since a large portion of antibiotics leaves the body and end up in receiving waters [10]. We do not know what threshold levels are toxic, especially in complex mixtures. It is speculated that EDCs may be responsible for declining sperm counts and decreased sperm motility and function in the human population [12, 13]. EDCs may cause adverse effects including hormone dependent cancers, reproductive tract disorders, and reduction in reproductive fitness [14].

Effects on wildlife have been documented from PPCPs in surface waters. In Lake St.Clair, upstream from Windsor's intake, male fish have been found to have eggs [15]. This gonadal intersex is suspected to have occurred from exposure to endocrine disrupting chemicals. Studies in the United Kingdom and United States in the 1990s indicated reproductive abnormalities in fish living below wastewater treatment plants [16].

Antidepressant drugs of the class serotonin reuptake inhibitors (SSRIs) are known to be potent spawning inducers in aquatic invertebrates at environmentally relevant

concentrations such as low ppb levels [17]. Ecological consequences (e.g., population, community, ecosystem-wide effects) of this are not yet known.

Routine screening being done on EDCs may not be fully adequate in predicting ecosystem and human health effects because the effects may not be manifested until after long, chronic exposures. For example, the metamorphosis of fertilized frog eggs was inhibited by low levels of perchlorate after a 70-day exposure, but not after the 14-day exposure recommended by the Endocrine Disrupter Screening and Testing Advisory Committee's (EDSTAC) method for testing EDCs [8]. Furthermore, in a realistic scenario, aquatic organisms would be exposed to EDCs during entire life cycles.

#### **Planned Activities:**

The Walkerton Clean Water Centre and other organizations (Ontario Ministry of the Environment, University of Windsor, AWWARF), are considering a study to evaluate the presence of these compounds in Great Lakes water, and evaluate the possible formation of by-products from oxidation reaction of treatment processes used for water, or wastewater treatment for effluents which are discharged to fresh water sources.

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## **Nutrient Status of the Coastal Zone of Lake Ontario**

**Joseph C. Makarewicz**  
**Department of Environmental Science and Biology**  
**SUNY Brockport, Brockport, NY 14420**

Embayment, shoreside and stream water in New York coastal waters have greater sediment loads, have higher nutrient levels (TP, TKN, nitrate), have greater amounts of Cyanobacteria and algae, and have higher levels of cyanotoxins than offshore waters. Coastal New York phosphorus levels generally exceed the NYSDEC Ambient Water Quality Guideline for phosphorus. In the Province of Ontario, TP levels do not generally exceed the Provincial Water Quality Objective (10/20  $\mu\text{gP/L}$ ). However, there are many locations in the coastal zone such as embayments, river mouths and locations near the shoreline where TP will periodically, if not frequently exceed 10 or 20  $\mu\text{g/L}$ . There are spatial differences along the New York coastal zone. Sediment loads, nutrient concentrations and Cyanobacteria appear to be higher in the streams, embayments and at shoreside sites compared to offshore sites west of the Genesee River. In general, water quality of the coastal zone is generally poorer than water from the offshore zone.

Other coastal ecosystem impairments include an over abundance of aquatic weeds, shoreline erosion, invasive species, and habitat destruction. Dreissenids have altered nutrient cycling and increased water clarity resulting in a rebound of the benthic green alga *Cladophora*. It is possible that the pods or mats of algae, often several meters in diameter floating into beaches, are associated with *Cladophora* scouring during wind events and seasonal die-back. Public beaches are often closed or posted due to elevated levels of fecal pollution indicators and poor water quality. Elevated levels of fecal indicator may result from factors other than strictly poor water quality in a conventional sense (e.g. beach sediments, gulls).

Structure and function of the coastal zone are influenced by the proximity of the shoreline, localized sources of meso-scale variability (e.g., tributaries, land-use in the watershed, embayments, geology, effluent pipes) and variations in the current regime (wind direction, upwellings, etc.). Current regime, in turn, controls transport and distribution of temperature, nutrients, contaminants, and planktonic organisms, as well as bottom shear stress and erosion potential. Environmental integrity and sustainable use of coastal habitats are threatened by anthropogenic forces including rapid population growth - especially in the Greater Golden Horseshoe region (Lake Ontario's western basin). One hypothesis suggests that the high levels of nutrients observed along the New York coastal zone from the Niagara River to the Genesee River may be related to land use within the "Golden Horseshoe" area of Canada.

Coastal zone waters receive large amounts of anthropogenic inputs, and associated ecological responses likely reflect the character of the adjacent watersheds. Such responses in water

quality and plankton in the coastal zone may foreshadow lake ecosystem change. In conclusion, portions of the coastal zone continue to be plagued by cultural eutrophication with high nutrient levels leading to the unwanted growth of Cyanobacteria and *Cladophora* and other water quality problems. Until the significance of habitat extension and internal nutrient supply mediated by dreissenids is evaluated using growth models and experimentation, it will be difficult to demonstrate that further controls on point and non-point P sources will have the desired effect of substantially reducing nearshore growth of *Cladophora*. The principal nutrient of concern, phosphorus, comes from a variety of point and non-point sources, including domestic animal waste, fertilizers, soil loss, combined sewer effluent, leaky septic systems, and sewage treatment plant effluent.

## **Issue Paper for Lake Ontario Contaminant Monitoring & Research Workshop:**

### **Contaminants in Drinking Water – Canadian Studies**

#### **Issue/significance**

On October 19, 2006, the Clean Water Act, 2006 became law. This legislation ensures communities are able to protect their drinking water supplies through a preventative approach.

In support of that legislation the Ontario Ministry of the Environment funds technical studies necessary to support the development of source protection plans.

Lake Ontario has 33 intakes (20 water systems) from the Niagara River to the Bay of Quinte. Together these water systems provide drinking water to critical businesses and institutions and approximately 6 million people.

A research collaborative has been established to identify and evaluate both local and lakewide hazards. This collaborative includes the municipalities from Niagara Region to Prince Edward County as well as the conservation authorities and a wide range of scientists and consultants. (More information on the partners of the collaborative is provided at the end of this issue paper.)

In 2006, the Ontario Ministry of the Environment funded \$595,000 for Phase 1 of the "Collaborative Study to Protect Lake Ontario Drinking Water". In 2007, the Collaborative was allocated over \$2M in technical studies funding by the Ministry for Phase 2. This will allow for the setup, testing, and application of numerical models in the Western Basin of Lake Ontario to define vulnerable zones for each intake, and the undertaking of the Issues Evaluation and Threats Inventory and Water Quality Risk Assessment. The work will also include intensive hydrological work on priority watersheds to better understand the potential impacts from those tributaries on drinking water intakes, specifically during storm events.

The Mission of this collaborative is:

*To ensure the long-term, proactive and strategic protection of Lake Ontario-based drinking water supplies.*

#### **Current knowledge - drinking water intake vulnerability:**

Extensive data exists related to the chemistry of the water entering the drinking water intakes on Lake Ontario. Some Ecoli test data also exists. Plant operators also track intake turbidity and temperature and see the impacts of heavy rainfall events and the upwelling/downwelling that marks Lake Ontario along the north shore. Through the Ontario Water Works Research Consortium (OWWRC), the forerunner of the new research collaborative, there was intensive work from 1999 to 2006 on the chemistry,

physics and biology of Lake Ontario to explain the periodic taste and odour events at the water intakes in the western basin of Lake Ontario.

### **Data/information gaps 2008**

Identification of gaps is part of the current study. However, a few critical gaps were clear at the beginning of the study. The ones that need to be addressed in 2008 include:

- Improved data on actual pathogens, including their presence during heavy runoff events (very little monitoring data exists)
- Improved winter data (especially contaminants and the physics that can deliver contaminants to intakes)
- Improved information on watershed loadings and the hazards that exist in the watersheds. This includes the need for improved flow data on the watersheds.
- Need to identify and, to the extent possible quantify, all significant hazards along the shore since intakes far from a hazard can be impacted by that hazard.

### **Planned work for 2008**

#### **Identification of key threats to drinking water intakes (and the source of those threats)**

- a) Priority watershed tributaries will have refined loading calculations including loadings during peak events.
- b) Key threats along the whole of these watersheds, such as manure storage areas, CSOs, storm drains, wastewater bypasses and treated industrial/municipal wastewater discharges will be identified and quantified as practical.
- c) Threats like gas stations and dry cleaners within the watershed or the sewershed – stormwater/CSOs- will be identified within the 2 hour time of travel to each intake.
- c) Significant discharges directly to the lake will also be identified and quantified as practical. This work will be done for the whole study area.

#### **Identification of significant issues at the drinking water intakes (and the source of those issues)**

- a) Review and analysis of existing data for each water intake. Research, as practical, the sources of the contaminants found.
- b) Use data from the intakes (present and historical) and compare with the Ministry of the Environment's threats database lookup tables when available to establish priority issues.
- c) Gaps in the information will be identified.

#### **Refinement of intake protection zones (IPZ-2's) for each intake**

The IPZ-2s delineated in Phase 1 will be refined in the Phase 2 research.

- a) Improve lakewide circulation input to the current modeling of IPZ-2s.

- b) Detailed statistical assessment of boundary conditions to refine current IPZs.
- c) Consideration of other data gaps identified in Phase 1 research and more focus on the extreme conditions such as maximum flows in tributaries and sewers, winter conditions, the presence of a strong thermal bar and potentially the presence of strong upwelling/downwelling in Lake Ontario.

**Special studies planned for 2007/08 are:**

- Development (and implementation) of a pathogen monitoring plan\*; and,
- Development of an effective approach for the management of extensive and dispersed data/information.

\* Tom Edge from Environment Canada is addressing plans for pathogen monitoring. This may be a key area for cooperation in 2008

**Partners:**

**Collaborative Study to Protect Lake Ontario Drinking Water:**

Municipal partners in the Collaborative Study to Protect Lake Ontario Drinking Water include:

Region of Durham  
City of Toronto  
Region of Peel (lead municipality and Chair of Steering Committee)  
Region of Halton  
City of Hamilton  
Niagara Region  
Town of Cobourg  
Municipality of Port Hope, and  
Prince Edward County.

The Collaborative's Conservation Authority (CA) partners include representatives from:  
CTC (Central Lake Ontario CA, Toronto and Region CA, Credit Valley CA)  
Trent Conservation Coalition (Kawartha Conservation, Crowe Valley CA, Ganaraska Region CA, Lower Trent Conservation, Otonabee)  
Halton-Hamilton (Conservation Halton, Hamilton Region CA)  
Quinte Conservation (Moir River, Prince Edward Region, Napanee Region), and  
Niagara Peninsula CA

The Collaborative has retained the Ontario Clean Water Agency to provide project coordination and project management. The studies, including modeling, are being conducted by scientists at Environment Canada and by a consulting team led by Stantec Engineering.

More information is available at [www.owwrc.com](http://www.owwrc.com)

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**Prepared:**

Laurence F. (Larry) Moore PhD

Coordinator: Collaborative Study to Protect Lake Ontario Drinking Water

March 22, 2007

## **New contaminants in Lake Ontario: siloxanes, perfluoros, organophosphates, and halogenated phenolics**

Derek Muir, Mehran Alaei, Bill Lee and Brian Scott

Water Science and Technology Directorate, Aquatic Ecosystem Research Protection Division,  
Environment Canada, Burlington ON L7R 4A6

### **1. Brief description of the issue and its significance to Lake Ontario**

There are about 30,000 chemical substances in wide commercial use (>1 t/y), however, very few are measured in environmental media, and their emissions and fate are unknown. The work of various programs e.g. U.S. EPA's HPVC Challenge and TSCA screening, the OECD's HPVC program and the Environment Canada's categorization of the Domestic Substances List (DSL) are gradually making available more information on individual chemicals. These data can be used to help prioritize chemicals for future monitoring. In the followup to the DSL categorization, the Chemical Management Plan (CMP), Environment Canada and Health Canada have identified about 4000 chemicals that may be persistent, bioaccumulative and toxic and that require further assessment and have listed 318 as high priority for gathering environmental exposure data because of predicted persistence, or bioaccumulation, and toxicity. Among the 318 substances are siloxanes, halogenated phenolics and many organophosphates. Perfluorinated carboxylic acids e.g. PFOA, are being assessed by the USEPA and Environment Canada and are included in both environmental and human monitoring programs in the US and Canada.

### **2. Summary of the extent of current scientific knowledge that exists for Lake Ontario**

**Cyclic siloxanes:** Three compounds with short names D4, D5 and D6 (named for 4, 5 or 6 methyl siloxanes in a ringed structure) are very widely used. Applications include fuel additives, surface treatment, cleaning/washing agents, filler, impregnation material, adhesives, binding agents, paints, laquers, varnishes, reprographic agents, softeners, surface active agents. Preliminary air measurements for D4-D6 have been conducted within the Great Lakes region (S. Backus, Environment Canada, Burlington presented at IAGLR 2006) and these suggest the cyclic siloxanes are present at  $\mu\text{g}/\text{m}^3$  concentrations near urban areas. The first studies of siloxanes in Lake Ontario water and sediments were conducted in 2006. Preliminary results show detectable concentrations of D4-D6 in Toronto harbour but near or at detection limits in mid-lake sediments. Analytical problems prevented measurement in lake water or air.

**Organophosphates:** These compounds are used as flame retardants and are mainly tri-substituted e.g. tributyl phosphate. Related compounds (generally dialkyl substituted) are used as insecticides but are not considered here. Scott et al (Can J Water Poll Res 1996) showed that tri-n-butyl-phosphate (TBP), tris(2-chloroethyl)phosphate (TCEP) and tris(chloroisopropyl)phosphate (TCPP) were present in water entering Lake Ontario (Fort Erie and Niagara-on-the-Lake) at concentrations ranging from 0.2-38 ng/L. Recently Andresen et al (Environ Toxicol Chem 2007) detected TBP in the range of 0.3 to 3.2 ng/L and TCEP/TCPP in the range of 2.1 to 3.5 ng/L in western Lake Ontario. About 10-fold higher concentrations were found in Hamilton Harbour. Scott et al (1996) also detected TBP, TCEP and TCPP in rain samples from Toronto, implying that atmospheric inputs of these compounds could be significant.

**Halogenated phenolics:** Hydroxy-PCBs and hydroxy-PBDEs have recently been measured in Lake Ontario waters and in precipitation in the region (Ueno et al. ES&T 2007 in press; Ueno et al. Environment Canada unpublished data). Total concentrations of OH-PCBs in water ranged from 0.87 to 130  $\mu\text{g}/\text{L}$  and from 230 to 990  $\mu\text{g}/\text{g}$  in particulate organic matter. OH-PCBs were higher in rain than in snow samples implying higher concentrations during the summer months are due to oxidation of airborne PCBs which are higher at elevated temperatures. OH-PCBs have also

been measured in lake trout blood plasma from Lake Ontario (Campbell et al. ES&T 2003) and in brown bullheads from Areas of Concern. Also detectable in the fish are tetra- and pentachlorophenol, hydroxy-heptachloro-sytrene and the bactericide, triclosan (Campbell et al 2003; Muir et al. Environment Canada unpublished data 2007). Triclosan and methyl triclosan were detected in lake water from western Lake Ontario at 1 ng/L and 0.1 ng/L, respectively (Andresen et al. 2007). Methyl triclosan is a volatile metabolite of triclosan formed in sediments and sewage treatment plants.

**Perfluoroalkyl acids (PFAs):** In comparison with the other classes of substances, there has been a lot of work on PFAs in Lake Ontario biota, municipal waste effluents, sediments, precipitation, and open lake waters. Volatile precursors of the PFAs (perfluorosulfonamido alcohols and fluorotelomer alcohols) has been monitored in air in Toronto. The measurements show that PFOA and PFOS are the predominant PFAs in lake water while PFOS and longer chain perfluoro-carboxylates predominate in the food web. Stock et al (ES&T submitted) have recently developed a mass balance for PFAs in Lake Ontario. They found that losses to sediment were a significant removal pathway for PFOS. Previous mass balance estimates (Boulanger et al. EST 2005) had not measured this pathway. Lake Ontario lake trout have relatively high concentrations of PFOS, averaging 46 ng/g (in whole fish); only lake trout from Lake Erie had higher concentrations (Furdui et al. ES&T 2007). PFOS was shown to be increasing in Lake Ontario lake trout (Martin et al. ES&T 2004) however that study involved archived fish for the period 1980 to 2001. A followup study using post-2001 samples is planned to determine if PFOS concentrations are declining with the removal of the perfluorooctane-related products from the market in 2001.

### **3. Identification of the data / information gaps that should be addressed in 2008**

**Siloxanes:** Current concentrations in air, water, sediments and biota. The record of historical inputs based on sediment cores. Mass balance estimates.

**Organophosphates:** Expanded list of OP flame retardants to include more on Environment Canada's priority lists. Concentrations in air, precipitation and water.

**Halogenated phenolics:** Concentrations of triclosan, methyl triclosan, and other antimicrobials e.g. triclocarban, in open lake waters. Broader suite of brominated phenolics e.g. bromophenols, TBBPA.

**PFAs.** Temporal trends in biota, precipitation and lake water

**Other compounds:** There is a lack of environmental measurement data for many other medium and high production volume chemicals that have predicted PB&T characteristics based on the Canadian DSL categorization, the USEPA screening of TSCA, and other ongoing studies (e.g. Muir and Howard ES&T 2006).

### **4. Monitoring that your agency is proposing for 2008 and potential coordination and partners**

We plan to conduct the following work in cooperation with Environment Canada colleagues and University and industry partners. We will be requesting a one week cruise on the lake (Limnos) and possibly access to other cruises to get some seasonal data e.g. spring, summer, fall, for selected media (e.g. zooplankton, water).

**Siloxanes:** Measurement of concentrations in air, water, sediments and biota. The record of historical inputs based on sediment cores. Mass balance estimates. We are collaborating with Dow-Corning on this study and will begin our own work (led by M. Alaei) in 2007.

**Organophosphates:** Expanded measurements of OP flame retardants in air, precipitation and water to include more on Environment Canada's priority lists. Led by D. Muir and B. Scott.

**Halogenated phenolics:** Studies of bioaccumulation of triclosan, methyl triclosan, and brominated phenolics e.g. bromophenols in open lake waters and AOCs. Broader suite of TBBPA. Led by D. Muir, M. Alae

**PFAs.** Temporal trends in biota, precipitation and lake water. Led by B. Scott.

**Metals:** Subject to discussion with other groups we may determine platinum group elements, and priority metals under the Environment Canada CMP (Co, V, Se, Ag) in selected media. Led by D. Muir and H. Wong

**Other compounds:** Additional work on brominated flame retardants that are not currently monitored but are probably present in existing extracts from conventional POPs analysis is also being considered. We are also interested in determining if pharmaceuticals and personal care products are persisting in open lake waters. (B. Lee).

#### **5. Other factors to be considered for the 2008 cooperative monitoring plan**

Lack of funding for ship time and inability to convert operating to salary dollars within Environment Canada may severely impact our ability to conduct field work, to make measurements, and prepare reports in a timely manner.

## **DEVELOPMENT OF A MERCURY MULTI COMPARTMENTAL MODEL FOR LAKE ONTARIO**

Elsie Sunderland, USEPA and John McDonald, IJC

### **Background and significance to Lake Ontario**

Over the past several years, the International Joint Commission, working with the USEPA, NOAA and Environment Canada, and several interested state and provincial parties, in particular the Ontario Ministry of the Environment, has tracked and supported the development of models simulating the behaviour of mercury in the environment.

The first stage of this effort was dedicated to the development and verification of the NOAA-HYSPLIT atmospheric deposition model. The results of this work can be seen in the International Air Quality Advisory Board segments of the 1999/2001 and 2001/2003 Great Lakes Priority Reports available on the International Joint Commission website.

More recently, the project focus has moved toward an attempt to develop a linked sequence of models to track the fate of mercury from its initial release into the larger environment and its subsequent distribution into waterbodies, sediments, followed by bioaccumulation and ultimate uptake by humans.

Several experts and members of the public interested in this initiative participated in a workshop at the IJC Biennial Forum in Kingston Ontario in June 2005 to explore progress to date and the challenges remaining in the development of this multi-compartment model.

A second meeting was held in Niagara Falls in January 2006 with a variety of experts to review recent developments in the evolution of this model and to consider further advice and guidance from the expert community on the challenges inherent in its application to the Lake Ontario basin. A mix of formal presentations and extensive discussion were pursued at this workshop, with the intent of developing a methodology for managing these challenges and continuing the evolution of a Lake Ontario Mercury Model.

### **Current state of knowledge**

Presently, working versions of models are available for all media. Presently, these models have been only “loosely coupled” for Lake Ontario as they continue to be refined and updated with new knowledge and monitoring data. The resolution of these models and their predictive capability are limited by a number of inherent uncertainties in the science and the availability of monitoring data for the Lake Ontario region.

#### **(a) Source-receptor modeling**

A number of uncertainties in emissions inventories, including limited speciated measurements of mercury releases, are among the greatest challenges for evaluating source-receptor modeling to date. In addition, lack of speciated mercury measurements and event based sampling has limited the degree to which source-receptor modeling for mercury conducted by NOAA’s Air Resource Laboratory can be evaluated and constrained using empirical measurements.

(b) Watershed and water body modeling

In 2006, a preliminary survey of total and methylmercury concentrations in the water and sediments of Canadian waters was conducted by the Ontario Ministry of the Environment to support modeling efforts. Prior to these sampling efforts, no data on methylmercury concentrations in the water and sediments of Lake Ontario were available. These data are being incorporated into the water body model for Lake Ontario being developed using EPA's WASP model framework. This modeling effort is expected to complement the Lake Ontario mercury fate and bioaccumulation model developed by Atkinson and DePinto in 2005 for EPA Region 2. Comparison of model results should reveal key areas of uncertainty for future research and data collection. One ongoing limitation of the current modeling effort is the degree to which the modeling team has been able to characterize watershed cycling in the Lake Ontario drainage basin as well as the influence of changing land use patterns on mercury accumulation in fish and ultimately human exposure in the region.

(c) Human exposure modeling

A preliminary case-study analysis of mercury exposure in Oswego County, NY has been completed using the MENTOR-SHEDS modeling system. In addition, the New York City Health Department recently conducted a probabilistic survey of blood mercury concentrations in the NY region ("NY HANES") and found elevated levels relative to national means, particularly in various ethnic populations (study is forthcoming). EPA Region 2 is currently building on these results to investigate sources of exposure for women of childbearing age in the New York and New Jersey Region, including a detailed analysis of fish mercury levels in various seafood markets. The data will contribute to the modeling team's ability to link changes in concentrations of various sport-fish species in Lake Ontario to overall human mercury exposure in the region and evaluate risks to the most highly exposed individuals.

**Data gaps to be addressed in 2008, proposed monitoring work and potential collaboration and partners**

The Ontario Ministry of the Environment is presently moving forward with plans to expand collection of mercury deposition data in the Lake Ontario region and is considering enhancing these monitoring efforts to include a research program on watershed cycling of mercury in the Lake Ontario Drainage basin. The U.S. EPA continues to support the development of watershed and water body models for mercury cycling in freshwater systems. Similarly, NOAA's Air Resources Laboratory will continue to actively model source-receptor relationships for mercury. Ultimately, coordination of modeling and monitoring efforts could better enable models to predict effects of changing land use, climate, water chemistry, and food web structure on mercury accumulation and exposure for humans and wildlife in the Lake Ontario region.

**CYANOBACTERIAL AND ALGAL METABOLITE IMPAIRMENT IN LAKE ONTARIO:  
TASTE-ODOUR - CURRENT STATUS, MONITORING AND MANAGEMENT**  
Sue Watson, NWRI Environment Canada

**Background**

Algal<sup>1</sup> blooms have been an issue in the Great Lakes for over half a century (Bierman et al. 1984; Munawar & Munawar 1996; 2000), and linked to more than half of the listed beneficial use impairments in the designated Areas of Concern (AOCs) in these lakes. Considerable research and remediation has focussed on the excess biomass produced by these blooms, but recently there has been increasing concern with noxious algal<sup>2</sup> metabolites (NAMs) released by this biomass, which cause taste and odour (T&O) or are toxic to humans and other organisms. NAMs are often far less apparent than the cells that produce them; nevertheless they can have pervasive ecological and socio-economic impacts, affecting the integrity, aesthetics and safety of surface waters used for drinking and recreation, and tourist and aquaculture industries. The most problematic of these compounds are generally highly stable, are not removed by boiling or conventional water treatment, and can persist and bioaccumulate in surface waters leaving beach and recreational areas, small water users and fisheries industries particularly vulnerable.

Taste and odour and restrictions to drinking water consumption is one of the 14 beneficial use impairments (#9) listed under the Great Lakes Water Quality Agreement (GLWQA) for Areas of Concern (AOCs). Cyanobacterial toxins were identified far more recently as a potential threat in freshwaters, although human and animal poisonings from bloom-laden waters have been reported for many centuries. Because little was known about these toxins when the GLWQA was drawn up, they were not recognized as a threat or considered as delisting criterion however, given the potential ecological and socio-economic threats to ecosystem and human health in both treated drinking water supplies and other important zones of potential exposure (e.g. inshore areas, beaches) we argue that not only should RAP and Lakewide monitoring Program (LaMP) targets be re-evaluated to specifically include these compounds, but adopt a broader focus beyond treated drinking water supplies. Much of our research in the Great Lakes in collaboration with SUNY ties in both odour and toxic compounds, but this paper will focus on T&O (Watson et al. submitted).

Drinking water suppliers in Lake Ontario and other Great Lakes have attempted to control T&O and toxins via water treatment, and RAPs have targeted them by using broad-scale nutrient-biomass models (e.g. TP-chla; Bierman et al. 1984; N:P; Vollenweider 1968; Reynolds 2003) to control phytoplankton biomass, with the assumption that production is a direct function of this biomass. However, this approach is often unsuccessful, for a number of reasons:

- i) Not all bloom-forming taxa produce T&O and among those that do, production can vary among populations, or under different growth and environmental conditions
- ii) plankton are not the only sources (subsurface/deep layer, benthic and littoral communities can be major sources, particularly in clear, shallow or lotic systems),
- iii) biosynthesis and release may be discontinuous or externally induced.
- iv) T&O outbreaks often show little relationship to total algal standing stock.
- v) Broad scale nutrient-biomass models are based on seasonal averages which may miss and/or over-weight biomass peaks and declines, surface scums, deep layer maxima and other aggregations. In particular, most among-lake models cannot predict the *biomass maxima* where outbreaks are potentially of most concern. The models do not resolve the underlying range in structure and biomass of algal communities which determine the risk, concentration and nature of T&O compounds. These are governed by: i) the capacity of the cells for production; ii) growth and spatial/temporal dynamics; iii) triggers and feedback that modify production; iv) the properties of the compounds and their fate in the environment (e.g. Watson 2004). Furthermore, the widespread assumption that N:P ratios 'control' cyanobacteria, based on the fact that many of these taxa are N-fixers, is debated and often misapplied; in most systems P is the major factor driving these blooms (e.g. Downing et al. 2001)
- vi) Surface-waters contain a diverse mix of metabolites and algal species, but their relative and absolute abundances may show little relationship. Species produce compounds which differ in potency, toxicity

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<sup>1</sup> For simplicity, in this paper, 'algae' is used to denote both eukaryotic algal taxa and Cyanobacteria

and/or stability. Cell production (chemistry, timing, internal/external storage and release) varies among and within species, and with growth and environment (Watson 2003; Jüttner and Watson in press). This means that odour outbreaks may show little direct relationship to measures of ambient nutrients or algal biomass – as seen in Lake Ontario where recent erratic episodes of T&O and toxins have increased despite the remedial reduction in P levels and frequent lack of visible surface blooms (e.g. Watson et al. 2007 a,b). Hydrological and physical vectors may transport metabolites away from cells, or move planktonic, metabolite-containing cells over considerable distances; for example, downwelling plays a key role in the timing and severity of odour events detected by N.W. Lake Ontario municipalities (Rao et al. 2003).

- vii) Although often used interchangeably, the two most common measures of standing stock, chl<sub>a</sub> and biomass (biovolume), are correlated poorly and *neither is a robust measure of the risk or nature of these metabolites*.
- viii) In the Great Lakes invasive species such as dreissenids have significantly altered inshore-offshore exchange and recycling processes assumed by traditional models. As a result, some remedial efforts have not only failed to achieve a stable reduction of algal biomass, but have been followed by outbreaks of noxious or toxic species. Hamilton Harbour continues to develop summer algal blooms with erratic outbreaks of noxious and sometimes toxic cyanobacteria despite significant nutrient reduction. Severe and persistent cyanobacteria outbreaks have been reported recently in other remediated AOCs and elsewhere in the Great Lakes. The Bay of Quinte has undergone a shift towards a predominance of hepatotoxic cyanobacteria such *Microcystis aeruginosa*, which can produce toxin levels in recreational areas and water treatment plant intakes which exceed the Health Canada guideline (1.5 g L<sup>-1</sup> total microcystin). At the same time, outbreaks of T&O, produced by different species, continue to occur (Watson et al. 2007c). Similar outbreaks are reported from Saginaw Bay and outside Oswego Harbour. *This has led to a general perception that noxious cyanobacteria outbreaks in the Great Lakes are increasing, but in fact it is not clear to what extent the apparent increased frequency of these blooms in the Great Lakes and other waterbodies represent greater vigilance as harmful algal blooms are more publicised*.
- ix) Cyanobacteria are the only known group of freshwater phototrophs to produce toxins (cyanotoxins; below), and are also the most frequent sources of odour compounds (Jüttner and Watson in press), but other organisms such as actinomycetes and fungi may contribute to T&O, particularly during spring runoff or as integral components of biofilms. In fact, historically, there has been a misconception throughout most of the water industry that these taxa are primarily responsible for most T&O, largely based on the fact that the two most problematic odour compounds (geosmin and MIB) were first identified from actinomycete cultures (Gerber 1963; Jüttner and Watson in press) However, the distribution and abundance of these heterotrophic taxa in Lake Ontario, and their relative importance as T&O producers, remains uncharacterized (Zaitlin and Watson 2006; Zaitlin et al. 2003).
- x) T&O and toxin and odour production by these taxa are neither concurrent nor well predicted by traditional models. Cyanobacteria differ among species and strains in their NAM chemistry and production dynamics, and can form surface scums, deep maxima, biofilms or benthic mats, all of which can be a source of these metabolites. Actinomycetes tend to be associated with particulate material, mussel beds, macrophytes or biofilms (Zaitlin et al. 2003). Producers and metabolites can become spatially and temporally decoupled, as in the upper Saint Lawrence River where annually high levels of odour in the water are produced by biofilms on shoreline substrates, mussels and macrophytes, not suspended cells (Ridal et al. 2007; Watson et al. 2004).

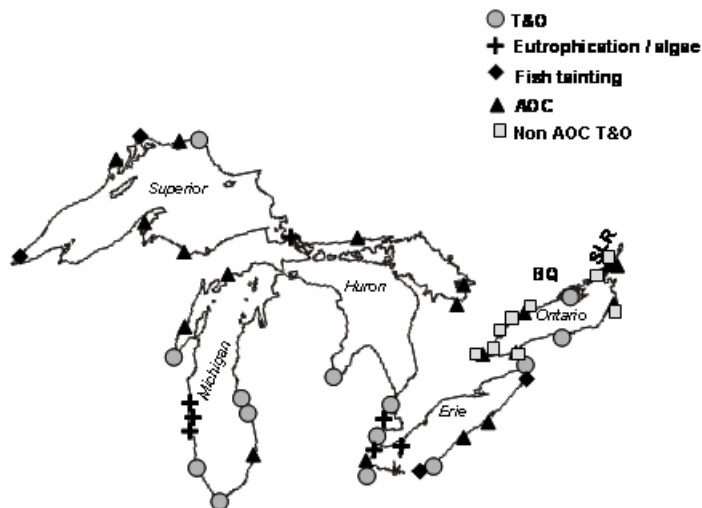
Two earthy/muddy/musty terpenoids, geosmin and 2-methylisoborneol, account for a large number of reported drinking water odour in Lake Ontario. These are highly potent (detectable at <10 ng L<sup>-1</sup>), stable, and resist conventional water treatment. Their production by a number of common Cyanobacteria<sup>2</sup> varies even among closely related taxa and cannot be predicted from simple microscopic examination. Most production is retained within the cells with some external release during growth, depending on the species and environment; the bulk release occurs at senescence, death, or during

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<sup>2</sup> they are also produced by some actinomycetes and fungi

grazing or treatment. In contrast, pungent thiols are continually excreted over growth by select species of *Microcystis aeruginosa* (a potent toxin-producing species), while the musty-tobacco smelling  $\gamma$ -cyclocitral is generated only at cell damage/death by all *Microcystis* spp., thus representing a good biomarker for the presence of this genus. Both thiols and  $\gamma$ -cyclocitral are short-lived in the water and rapidly lost by volatilization and chemical/photooxidative breakdown; therefore more difficult to monitor (e.g. Watson 2003).

Many areas of the Great Lakes are prone to outbreaks of noxious algal metabolites (Fig. 1). A recent survey of 59 Canadian and US water facilities drawing water from the Great Lakes and serving some 5 million consumers found that almost 20% of the plants experience annual T&O, while a further 27% report erratic outbreaks (Moore and Watson 2007). For the most part, these water treatment plant (WTP) data are based on non-quantitative measures similar to those used by RAPs to assess T&O (see below), such as informal records of customer complaints and plant operator notes, although some are qualified by odour descriptors ('fishy', earthy-muddy', 'sewage', 'chlorine') and timing (i.e. seasonality). Most of affected utilities draw water from, or near to, AOCs (i.e. the more densely populated regions of the lower Great Lakes), with the majority of outbreaks experienced during the summer or fall - during peak biological activity.



**Fig. 1:** Areas in Gt. Lakes with **recorded** outbreaks of T&O in the past 5 years (adapted from Watson et al. submitted).

A far more quantitative 2000-2002 MOE assessment of municipal drinking water supplies between 2000 and 2002 included concentrations of several potent VOCs (trichloroanisoles, methoxypyrazines, geosmin and MIB) in raw and treated water. The survey included plants drawing water from the Great Lakes including some AOCs (e.g. Sarnia, Hamilton Harbour, the Bay of Quinte and the St Lawrence River). Even though samples often did not coincide with the high risk summer-fall period for T&O, a significant number showed geosmin or MIB levels in treated water that exceeded the OTCs of  $\sim 2\text{-}3\text{ ng L}^{-1}$ . In many cases it is likely that the limited observation period and infrequent measures ( $\sim 2\text{-}3\text{ x}$  a year) underrepresented the actual impairment. An ongoing detailed study of T&O in the Western basin of Lake Ontario since 1998 shows late summer geosmin peaks in both the Lake and at WTP intakes which occur every year, but which have only exceeded the OTC in 1998, 1999 and 2004 (Watson et al. 2007).

**Overall there are few data available to evaluate the actual level of impairment by T&O in the Great Lakes, and a conspicuous absence of systematic records.** The few studies have been carried out, however, show that this impairment is highly complex and cannot be assessed using scattered incidental reports. It is seasonal and can show erratic patterns. In Western Lake Ontario, 5 years of multidisciplinary research by the Ontario Waterworks Research Consortium was required to characterize the complex mechanisms behind erratic geosmin outbreaks (Moore and Watson 2007). This study demonstrated the importance of climate and large-scale water movement in highly dispersed offshore pelagic T&O production and transport to drinking water intakes. In the St. Lawrence River (SLR)-Cornwall AOC, a similar research effort traced annual geosmin and MIB events to shoreline algal biofilms in the extensive and complex littoral zone which generate sufficient metabolite production to cause severe T&O along a 200 km stretch of shoreline (Ridal et al. 2007; Watson and Ridal 2004). Nevertheless, because “the source of the problem is natural, and originates outside the AOC (as does the drinking water intake for Cornwall) and because technological solutions appeared to be implemented”, drinking water T&O is not listed in the Cornwall AOC (but is listed in the SLR-Massena AOC). These examples highlight the problems with the current BUI delineation within the boundaries of the AOCs, the seemingly arbitrary interpretation of this restriction applied by different RAPs, and the question as to whether NAM impairments in these large and complex source waters are more effectively targeted on a broader scale, for example, through LaMPs, or multidisciplinary collaborative associations such as the OWWRC.

The definition of IBU#9 places a disturbing onus on the drinking water industry to ‘fix’ source-water impairment. This approach is inherently unsustainable and beyond the resources of many municipalities. It requires that WTPs maintain or upgrade treatment technology to stay ahead of newly identified and existing threats, and to constantly monitor source and treated water for changes in the level of impairment. In both the SLR and Niagara AOCs T&O is ‘externally derived’ and therefore not a listed impairment, yet municipalities in these AOCs have incurred substantial costs to install granular activated carbon (GAC) systems - which for the SLR, has been unable to fully alleviate the problem.

**The RAP evaluation procedure was (and still is) faced with the lack of uniform standards or guidelines defining acceptable target levels.** In Canada, there are no national drinking water standards and only highly subjective guidelines in different provinces. Ontario has an ‘aesthetic’ guideline stating that treated drinking water should be ‘inoffensive’ In the USA, some state agencies and larger municipal suppliers have adopted the US-EPA secondary maximum contaminant level (SMCL) for T&O, which is ambiguous and non-mandatory, based on target SMCLs for six inorganic minerals, pH, total dissolved solids (TDS), ‘foaming agents’ and corrosivity, together with ‘odour’ assessed at less than 3 TON<sup>3</sup>. TON is an inadequate measure of odour. Many utilities (and RAPs) use customer complaints as an indication of exceedences – a haphazard approach to the problem, since there are often no formal and consistent records of complaints logged by WTPs, and customers cannot always be relied on to report incidences, or to remain unbiased by media coverage (i.e. the ‘snowball effect’).

Despite the lack of historical data, taste and odour (including that derived from industrial contaminants) was included by the IJC in two of the original listed impairments: in drinking water (BUI#9) and tainting fish/wildlife flavour (BUI#2). Nevertheless, the criteria and methods used to define and evaluate these two BUIs have generally underrepresented the scope and severity of this impairment across the AOCs and Great Lakes (and still do). Although approximately 30% of AOCs have listed T&O/restriction of drinking water consumption as an impairment (BUI#9), we estimate the number of affected sites to be higher, because the original BUI definition:

- i) considers only **treated drinking water from municipal supplies** drawn from, or contaminated by, sites within the boundaries of the AOCs. It entirely disregards the often-significant T&O impairment of water drawn by small or remote communities, or individual users not on municipal supplies; many of whom do not have access even to ‘standard treatment’. In fact some AOCs have no public drinking water supply drawn from the source water, and thus no formal WTP reports exist on the status of this IBU - for example the Black and Cuyuga River AOCs (Erie).
- ii) considers only **‘persistent’ outbreaks** (i.e. lasting more than a few days) which are not removed using ‘standard treatment’ (i.e. coagulation, settling, disinfection) (IJC, 1989).

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<sup>3</sup> SMCL of three times the Threshold Odour Number (TON).

- iii) does not recognize the **impacts on other sectors** – such as impairment of beaches and recreational waters during the growth and decay of algal (and other) biota, and the impacts on the tourist and fishing industries.

**Several other BUIs potentially include off flavour or odour impairments, but have not addressed this issue.** Over 70% of all AOCs list ‘undesirable algae/eutrophication’ as an impairment (BUI#8), which is often associated with T&O (and toxins) in the source water or beach and recreational areas. The definition of BUI#2 (impairment of fish and wildlife flavour) focuses on industrial contaminants such as phenols, but overlooks tainting from biological metabolites such as geosmin and MIB, long known to cause significant fish and shellfish tainting in aquaculture operations, a growing industry in some areas of the Great Lakes. Algal metabolites can contribute to the degradation of aesthetics (BUI#11) in these and other areas such as recreational zones. Algal VOCs can also impose increased costs to agricultural, drinking water, food/beverage and tourist industries (BUI#12).

**To evaluate T&O as an impairment, many RAPs have relied on sporadic measures of treated municipal drinking water, customer complaints (if recorded) and incidental reports, or in the absence of any data, on proxy measures** (phosphorus (i.e. TP) and algal biomass *anticipated* from measures of TP, chemical treatment doses, disinfection by-products of high natural organic material (NOM), consumer complaints) with the assumption that these are correlated with odour. *None of these factors is consistently related to odour production by cells, or to the final metabolite levels in source or treated waters.*

**Above all, effective NAMs management needs adopt a multi-level approach to provide a basis for immediate and longer term proactive management of these events in the face of the continued anthropogenic disturbance and constantly changing aquatic resource.** The large-scale biomass-nutrient models used for bloom abatement in many AOCs could provide a better gauge of the annual or seasonal risk if maximum, rather than mean biomass relationships are used. The major factors which favour NAMs producers (vs. non-producers), and trigger or modify production need to be identified to predict short-term changes in NAMs biosynthesis, release and distribution in source waters.

**With the exception of a few recent studies, NAMs remains an uncharacterized impairment in many AOCs despite the progress toward meeting other BUIs** Current methods of assessing impairment are ambiguous and difficult to evaluate. For T&O, alternative methods to define and measure the levels of impairment would greatly facilitate the RAP delisting process. These include regular measurement of compounds which are the most common sources of T&O, and use of odour threshold concentrations as the quantitative target levels. Where possible, monitoring might involve the application of new genetic techniques to detect the presence of potential odour producers in surface waters (Gill et al in prep). In the absence of sufficient resources to carry out such chemical analyses, sensory techniques are inexpensive and can be systematically used by trained operators at WTPs to monitor T&O (Rashash et al. 1997).

**Toxins should also be systematically investigated in high risk areas.** This should be carried out using regular monitoring at recreational areas and intake protection zones, combined with mid-late summer spatial surveys for toxins during high risk periods.

In 1991, the IJC delisting principles for IBU#9 were defined as: 1) densities of disease causing organisms or concentrations of hazardous or toxic chemicals or radioactive substances which do not exceed human health objectives, standards or guidelines; 2) absence of taste and odor problems; and 3) when treatment needed to make raw water suitable for drinking does not exceed the standard treatment used in comparable portions of the Great Lakes which are not degraded (i.e. settling, coagulation, disinfection) (IJC, 1991). These principles were designed to be consistent with the GLWQA and account for jurisdictional standards, yet also to be practical and sensitive to increased cost as a measure of impairment. In reality these criteria have been difficult to apply in a consistent manner, largely because of the lack of standards, defined, measureable targets and high degree of subjectivity in assessing T&O and other drinking water impairment. Where cyanotoxins are considered, an increasing number of areas in the Great lakes, including some of the more eutrophic AOCs may fail to meet the first criterion. It is apparent that a broad interpretation by some RAPs has provided ‘loopholes’ which allow this issue to be

considered not impaired. For example, this can occur if it can be demonstrated that the impairment is not a local issue but typical of lakewide conditions *and that sources within the AOC are controlled*. Similarly, if it is demonstrated that the impairment is due to natural rather than human causes or that it originates from outside the AOC boundaries. This is a short-sighted and narrow approach to an impairment which needs to be addressed directly in the face of the growing concern with the quality and safety of drinking water supplies.

We propose a multi stage approach to these impairments in AOCs (and other source waters):

- 1) Evaluate original listing for each AOC from all documented sources;
- 2) Evaluate current status of these issues using field measures of odour compounds, algal taxa and toxin levels in (i) all AOCs on one or more occasions during high risk summer period; (ii) selected AOCs with listed algal-related impairments over the growing season (inshore-offshore, benthic and pelagic sites)
- 3) Identify major drivers and sources, and integrate these data with (i) concurrent physico-chemical and nutrient data; (ii) WTP data, systematic customer complaint records and community surveys; using a standard format and odour descriptors to differentiate problems derived from treatment processes (notably chlorine) from those originating in the source water; (iii) Develop and recommend restoration action

#### **Planned activities in Lake Ontario, 2007:**

1. **W Lake Ontario:** ongoing AEMR monitoring for source water quality, biota (inc. pathogens; see papers by T. Edge and L. Moore) and T&O (weekly; inshore-offshore stations 750, 752)
2. **Bay of Quinte:** ongoing biweekly AEMR monitoring for water quality, toxins (microcystins) and biota at 4 stations (in collaboration with Project Quinte); June-Oct (includes a detailed spatial survey at high risk late summer period); some T&O where resources permit
3. **Lakewide survey, Lake Ontario/Bay of Quinte/Upper St Lawrence River** Annual late summer (Aug-Sept) AEMR/OWWRC/SUNY Lake Ontario/SLR survey of water quality, biota, T&O and toxins (with Boyer)
4. **SLR (Cornwall), and work with Cornwall WTP:** Ongoing AEMR/SLREIS (J. Ridal; St Lawrence River Institute for Environmental Science) /Clarkson (M. Twiss) monitoring of water quality and T&O
5. **Hamilton Harbour:** Ongoing weekly AEMR monitoring of water quality and biota and sporadic monitoring of toxins (station 1001)

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## **Contaminants in Lake Ontario Wildlife: The Herring Gull Egg Contaminants Monitoring Program (1974-2006), and studies of Tree Swallows, Snapping Turtles and Mink**

### **1. The issue and its significance to Lake Ontario**

The issue is: what are the current concentrations and temporal and spatial trends in contaminants in aquatic wildlife which use Lake Ontario? This includes both legacy contaminants and newly identified and current use contaminants. The significance of this issue to Lake Ontario lies, in part, with the fact that fish-eating birds share the top predator position in the aquatic ecosystem with humans; they both consume the lake's fish. The contaminants that are found in birds are also found in humans who consume fish from Lake Ontario. In light of that, it is in our best interest to know as much as possible about patterns of occurrence of contaminants in fish and their effects.

### **2. Extent of current scientific knowledge that exists for Lake Ontario.**

The Canadian Wildlife Service has a wealth of information on current concentrations and spatial and temporal trends of legacy contaminants (PCBs, DDE, mirex, HCB, Hg, OCS, etc.) in Herring Gull eggs from Lake Ontario and all the Great Lakes. Its present monitoring program was initiated in 1974 and has been maintained annually since that time. Three sites are monitored in Lake Ontario: Hamilton Harbour, Toronto Harbour and Snake Island, near Kingston. Samples of the temporal and spatial data are included here as Figures 1 and 2. Several CWS researchers have also recently concluded their part of a multi-disciplinary Fish and Wildlife Health Effects study of contaminants in/near Areas of Concern (AOCs) on the lower Great Lakes. A large part of the CWS work focused on Herring Gulls, snapping turtles and mink in Lake Ontario AOCs. One component of that study, for example, searched for vitellogenin, an egg yolk protein, in male Herring Gulls as an indicator of endocrine disruption (Dr. Laird Shutt). In addition, pathways of contaminant transfer to gulls are being investigated by Dr. Craig Hebert using food web tracers, e.g. stable isotopes and fatty acids. Also, within the last 2-3 years, Dr. Rob Letcher (CWS-NWRC-Ottawa) has developed a program for tracking new contaminants. His work, which includes Herring Gull eggs from Lake Ontario, involves brominated flame retardants (including 38 BDE congeners and 17 non-PBDE BFRs), current use pesticides (e.g. chloro-s-triazines and chlorophenoxy herbicides), halogenated phenolics, etc. Several of these are on the DSL lists. There are limited contaminants data for other fish-eating bird species which nest on islands/peninsulas in Lake Ontario, e.g. Double-crested Cormorants, Great Black-backed Gulls, Caspian Terns, Black-crowned Night-herons, etc. These mainly date from the 1970s and 1980s. CWS is also assessing health effects and measuring contaminants (pharmaceuticals) in a passerine bird, the Tree Swallow, in Hamilton Harbour (Dr. Kim Fernie). CWS has also had a program to monitor levels of legacy contaminants in snapping turtles for nearly two decades. Data are available from most of the AOCs on the lower lakes, including Lake Ontario; the most frequently sampled sites include Cootes Paradise in Burlington Bay (Hamilton) and Bay of Quinte. That work is continuing with emphasis on trophic position, stable isotopes and fatty acids (Shane DeSolla). Contaminant studies in mink are continuing with analyses for PCB/OCs, heavy metals and PBDEs in samples from the Niagara, Hamilton

and St. Lawrence AOCs (Pam Martin). Beyond that, there are few data available for other mammals; I am not aware of any CWS data on deer, raccoons, skunks, etc.

### **3. Data or information gaps that should be addressed in 2008**

With the exception of data from Toronto Harbour in 2004, there are no contaminants data from any of the other fish-eating bird species within the last decade or longer. It would be good to have an update on current concentrations in Great Black-backed Gulls, Ring-billed Gulls, Black-crowned Night-Herons, Caspian Terns and Double-crested Cormorants from the east end of the lake. Inter-specific differences in contaminant levels among bird species would be evaluated in light of differences in trophic position/diet composition through SI/FA analyses. These data would feed into a food web model for Lake Ontario that, for the first time, includes fish-eating birds. As well, with one or two exceptions, there have not been any samples taken from any but the three regularly monitored Lake Ontario sites for more than a decade. It would be prudent to have current samples from a central Lake Ontario site as well as from the US side in the SE portion of the lake. Also, while Dr. Rob Letcher has a program to look for new compounds in Herring Gull eggs, including many fluorinated and brominated compounds, there could be additional emphasis and resources directed toward current use compounds of several kinds. For example, there has been little work done on searching for pharmaceutical contaminants, a topic of concern, in Herring Gulls to date.

### **4. Plans for 2008.**

Plans for 2008 involve sampling and analyzing Herring Gull eggs from the three routine monitoring sites on the lake: Hamilton Harbour, Toronto Harbour and Snake Island, near Kingston (Dr. Chip Weseloh). Other work is planned that will try to relate environmental PAHs to exposure (in lungs) of cormorants at Hamilton and possibly Toronto. Monitoring work with Tree Swallows, snapping turtles, and mink in/near Lake Ontario will continue. Rob Letcher's program of tracking newly identified and current use contaminants will also carry on.

### **5. Other factors to be considered for the 2008 Cooperative Monitoring Plan....???**

Submitted by Chip Weseloh (416-739-5846; [chip.weseloh@ec.gc.ca](mailto:chip.weseloh@ec.gc.ca))

Canadian Wildlife Service-Ontario Region, Environment Canada

4905 Dufferin St., Toronto M3H 5T4

Fig. 1. PCB 1:1 (ug/g, wet weight) in Herring Gull eggs at Toronto Harbour, 1974-2005: change-point analysis.

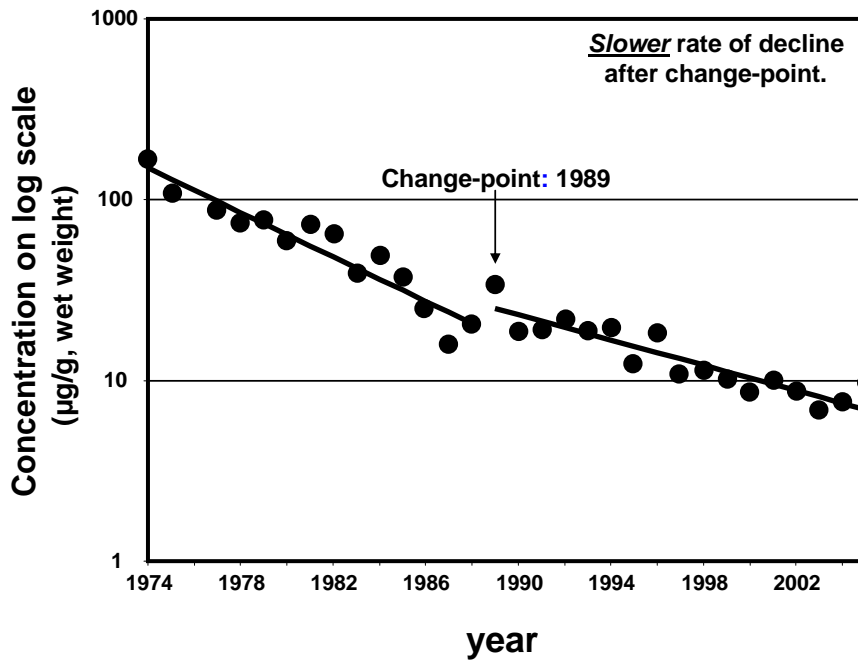
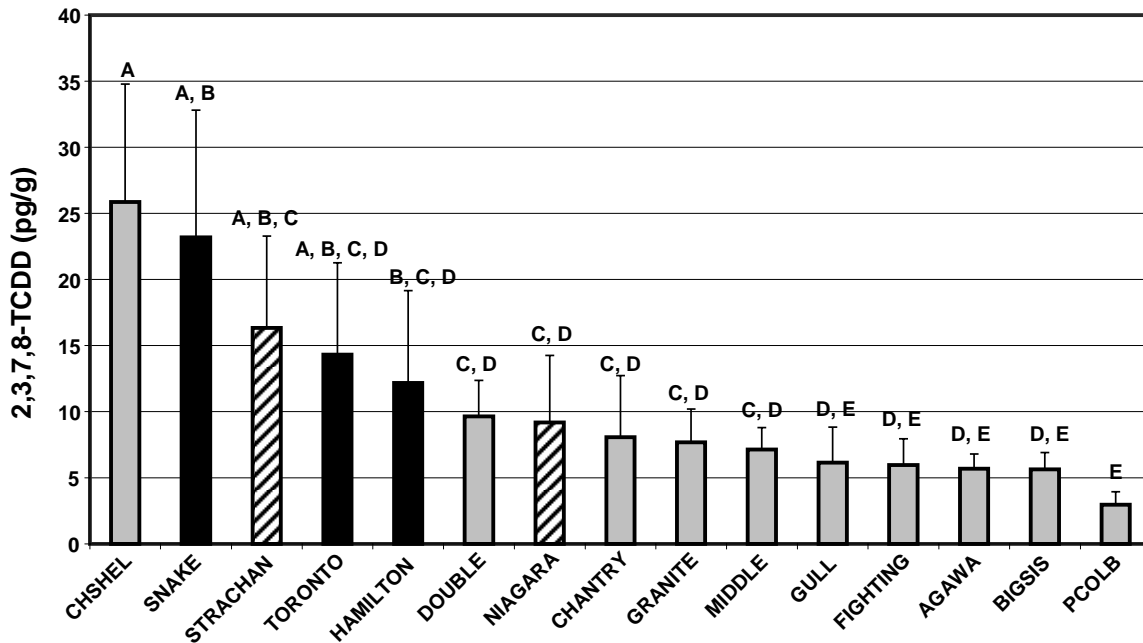
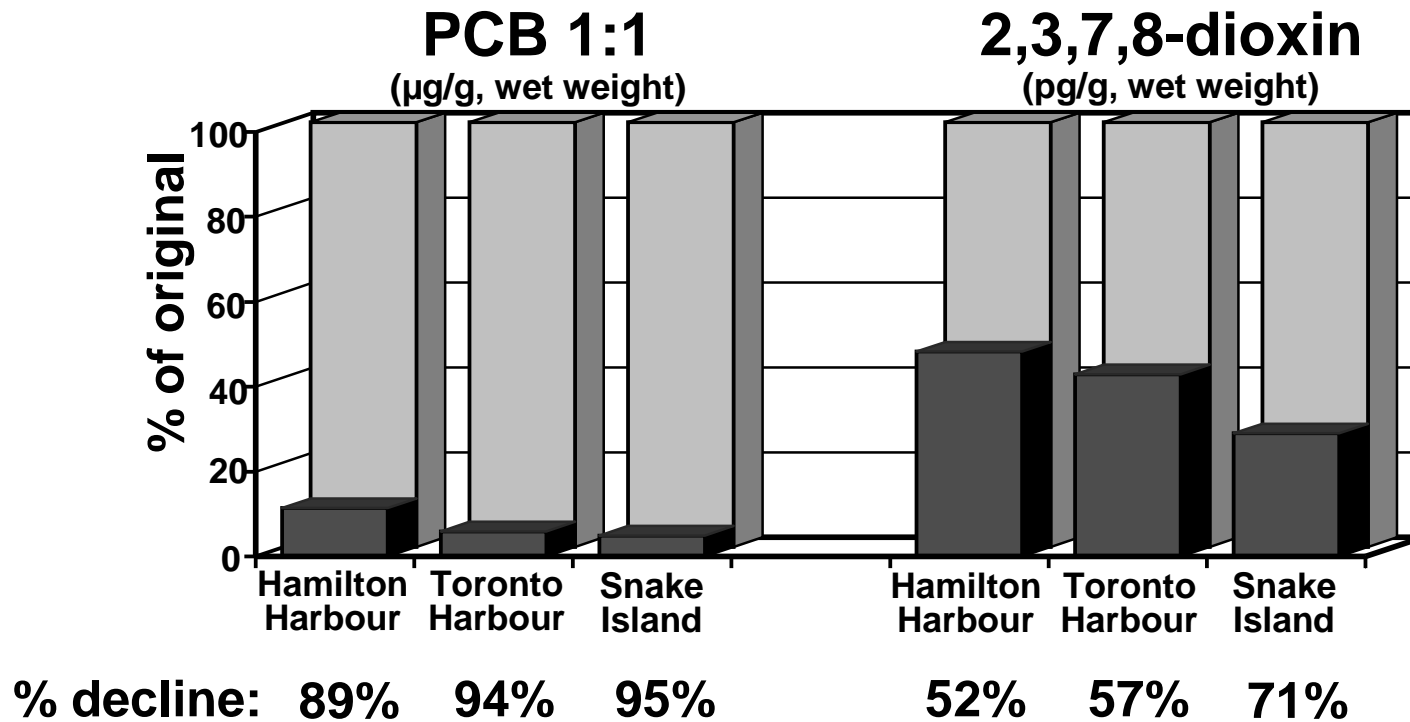


Fig. 2. Spatial Trends for 2,3,7,8-TCDD (1998-2002) at 15 Great Lakes monitoring colonies (Lake Ontario sites shown as black bars; adjoining river sites as diagonal hatched bars). Means ( $\pm 1$  SD) with the same letter are not significantly different (SNK test).



**Fig. 3. % decline (1974-2005\*) at three Lake Ontario monitoring colonies.**

- Concentration measured in 1<sup>st</sup> year of monitoring\*, set to 100%
- % of original concentration\*, measured in 2003 (dioxin) & 2005 (PCB 1:1)



\*PCB 1:1 first measured in 1974 (1981 for Hamilton Harbour); dioxin first measured in 1984

