# Emerging Contaminant Threats and the Great Lakes:

## Existing science, estimating relative risk and determining policies


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# I. Executive Summary

The last two decades have seen growing concern about human health risks from chemical contaminants in the environment. Exposure to some of these manmade and naturally occurring chemicals — known as "emerging contaminants of concern" — is unavoidable, as they end up in wastewater, air and land. Many come from everyday products such as shampoos, plastics, pharmaceuticals and flame retardants. The current U.S. regulatory approach cannot keep pace with the deluge of chemicals entering the marketplace. The Great Lakes have long served as both case study and leader in research on environmental contaminants, and recent findings of emerging contaminants in Lake Michigan drinking water raise public health concerns for millions living in the basin. The impacts of emerging contaminants on the health of organisms in the Great Lakes and human populations around them are largely unknown; the data that do exist suggest they are a health concern, but point to a need for more data and further study.

Addressing the problem of emerging contaminants requires focus on four main areas: new research; new technologies aimed at removing more contaminants during wastewater treatment; behavioral changes in the marketplace; and policy reforms. A formal national, multi-agency research program on emerging contaminants should be established to coordinate studies on exposures to these contaminants and the impacts on people and the ecosystem. Few regulations exist regarding emerging contaminant control. Today's requirement that a chemical cannot be removed from the marketplace without data showing a negative impact on people and the environment underscores the need for a more effective and realistic risk assessment program. Changing federal policies governing the production and use of new chemicals and existing emerging contaminants in the marketplace may well have the biggest impact.


# II. Introduction

The discovery of pharmaceutical byproducts in Lake Michigan and more recently, Lake Erie, has raised concerns about the potential health risk to the more than 40 million people who rely on the Great Lakes for drinking water — as well as questions about what else might be circulating in the waters. In reality, pharmaceuticals represent but a fraction of the chemical contaminants that make up what some researchers look upon as a vast chemical soup stretching from eastern Minnesota to western New York. Exposure to some of these chemicals, known as "emerging contaminants of concern" because so little is known about them, is cause for consternation for people and concern over fish and wildlife impacts. Several studies document declines in fertility rates in people, a rise in certain cancers, and the presence of intersex fish in some watersheds. The causes are uncertain, but scientists have documented many emerging contaminants in areas where intersex fish occur, and correlated higher body burdens of these contaminants with select cancers and fertility problems — leading them to suspect the contaminants' role.

The Great Lakes have long served as both a case study and leader in research on environmental contaminants. Considered a natural holding pen for persistent contaminants because it can take 100 years or more for some of the lakes to "flush" a given pollutant, the lakes were among the first to yield evidence of "endocrine disruption" in wildlife (Colborn et al. 1993). This phenomenon was identified by scientists in the 1990s to describe the effects of exposure to persistent synthetic chemicals in the environment that mimic the body's hormones and affect the development of babies in the womb. Yet the impacts of emerging environmental contaminants on the health of organisms in the Great Lakes and human populations around them are largely unknown, as few studies have measured the presence and distribution of these contaminants in the lakes and associated tributaries. There is a paucity of Great Lakes research on their potential impact on fish and other organisms and little data exist to determine any relationship between contaminants and various human health issues. The data that do exist suggest these contaminants are a health concern, but point to a need for more data and further study.

The last two decades have seen a growing unease about environmental contaminants that previously had not raised concerns about their potential to harm human or environmental health. Some of these contaminants are relatively new to the marketplace; others are just now detectable thanks to technological advances. Among them:

- Polybrominated diphenylethers (PBDEs), commonly found in flame retardants, have been shown to affect endocrine systems — which regulate the body's hormones. Levels of the chemical in breast milk are associated with lower birth weights and body mass.

- Triclosan and triclocarban, antibacterial chemicals commonly found in personal care products ranging from liquid hand soaps to toothpastes to cleaning products, are suspected endocrine disruptors and are toxic to fish crustaceans, algae and fish embryos. Triclosan can also break down into a number of dioxins when exposed to sunlight in the environment.
- Phthalates and bisphenol A, commonly found in plastics ranging from food storage containers and metal can liners to baby bottles and sippy cups, have been found to be endocrine-disrupting and thus can affect the sexual development of children born to exposed mothers.

Other emerging contaminants — such as the chlorinated paraffins found in flame retardants, paints and adhesives — are linked to cancer in laboratory animals. The effects of some newer chemicals, such as manufactured nanomaterials and compounds developed as substitutes for flame retardants, are still unknown.

Emerging contaminants come from a vast variety of products and sources and therefore strategies to address them in the Great Lakes are best coordinated at the binational and national levels. A comprehensive plan should be developed to address research gaps that limit our understanding of the risks emerging contaminants pose to people and natural systems. This plan should include a Great Lakes research agenda, prioritize emerging contaminants of the greatest concern, and evaluate the viability and economics of developing new treatment tools for removing emerging contaminants from the environment. Policy reform is also needed to change behaviors, both on the production side and in consumers' use of these chemicals.

The review that follows is an overview of the research field, a summary of the policy implications, and recommendations for moving forward. Note that this review provides representative references but not an all-inclusive bibliography of studies.

# A. What is an "Emerging Contaminant of Concern"

One of the first challenges in developing a strategy for addressing emerging environmental contaminants will be to create a common definition for this form of pollution. Already, several federal agencies and state governments have developed their own definitions of what constitutes an emerging contaminant. Industry and wastewater treatment groups often refer to emerging contaminants within the category of "trace organic compounds," as current environmental regulations aim to control organic components being emitted as waste and do not address emerging contaminants as a pollutant category. In this document these "trace organics" will be referred to as emerging contaminants.

The U.S. Environmental Protection Agency (EPA) and the U.S. Department of Defense (DoD), in various publications, have defined an emerging contaminant as "a chemical or material that is characterized by a perceived, potential or real threat to human health or the environment or lack of published health standards. A contaminant may also be 'emerging' because of the discovery of a new source or a new pathway to humans, or a new detection method or treatment technology has been developed." (DoD 2006). The U.S. Geological Survey (USGS) defines emerging contaminants as "any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects."

The Environmental Council of the States recently completed a survey of how state agencies currently define and address emerging contaminants (Jones and Graves 2010). Definitions varied by state but, by and large, states — including most Great Lakes States — do not have a clear definition of emerging contaminants and most lack defined programs to deal with them. Most related state or regional efforts involve USGS or EPA-led collaborations to monitor emerging contaminants in waterways. Minnesota appears to be one state that has both a clear definition and state research program. Minnesota's Clean Water Contaminants of Emerging Concern program defines emerging contaminants as "chemicals that have been released to or detected in Minnesota waters (surface water and groundwater) or have the potential to migrate to Minnesota waters, and for which health-based standards either do not exist or need to be updated to reflect new toxicity or occurrence information." Other states have state or local efforts regarding education or waste collection (particularly regarding pharmaceuticals), but appear to rely on federal programs for support and guidance.

Creating a consistent definition of "emerging contaminants" or a consistent name for these compounds will be important in defining a research or policy agenda to address environmental issues surrounding these chemicals. In addition, a definition of emerging contaminants will provide a mechanism to identify which compounds will be addressed through regulatory efforts, and how they will or won't be regulated. A common definition of emerging contaminants shared by federal and state governments will also help align research and regulatory efforts.


# B. Classes of compounds identified as "emerging contaminants"

Because of the varying definitions for "emerging contaminants," there is broad variation in the types of categories of contaminants that may be considered "emerging contaminants." These include:

- Pharmaceuticals: medications including hormones, pain relievers, psychopharmaceuticals, lipid regulators, antibiotics, etc.
- Personal care products: antiseptics (triclosan/triclocarban), sunscreen components, cosmetics, etc.
- Phytoestrogens: plant products that are similar to vertebrate hormones
- Brominated compounds: include PBDE flame retardants, plastic and insulation compounds
- Fluorinated compounds: perfluorinated compounds (found in surfactants, stain-resistant fabric protectors and non-stick cookware), flame retardants, etc.
- Synthetic musks: fragrances in perfumes, personal care products, home products, etc.
- Chlorinated paraffins: flame retardants, sealants, plastic additives, etc.
- Nonhalogenated compounds: formaldehyde, carboxylic acid, etc.
- Phthalates: plasticizers
- Bisphenol A: additive to plastics
- Nanomaterials: manufactured particulates less than 100 nanometers (nm) in size
- Pesticides and herbicides


# C. Sources of emerging contaminants

There are literally hundreds of sources of emerging contaminants stemming from consumer products that end up in our wastewater, air and land. Many of these sources include everyday products such as shampoos, sunscreens, plastics, pesticides, flame retardants and pharmaceuticals. Though state and federal governments have made great strides in controlling point-source pollution from industrial sources, the diffuse pollutant stream of emerging contaminants could complicate control efforts regarding this class of chemicals.

Emerging contaminants are consumed purposefully, as with pharmaceuticals, or accidentally, via chemically tainted food and water and exposure to household chemicals. The contaminants are eventually excreted and make their way into sewage treatment plants and septic systems. Solids from waste treatment and livestock facilities also contain various contaminants and are used to fertilize agricultural land, parks and residential yards. Chemicals such as pesticides are purposefully introduced into the environment. Compounds are also emitted directly from production facilities into streams and lakes; other chemicals are carried through the atmosphere or ride ocean currents to remote locations.

The relative contribution of each of these sources is debatable. For example, when looking at the presence of byproducts from pharmaceutical and personal care products in urban settings, wastewater treatment facilities can emit from 1,000-2,000 nanograms/liter (ng/L) of a single compound — and are often blamed for the majority of the pharmaceutical load. This may not be the only source within a watershed, however. Shala and Foster (2010) recently estimated the loads of pharmaceuticals and personal care products in Washington, D.C.'s Anacostia River. They estimated that only as much as 1.5% of these products in the river came from the sewage treatment facility upstream, begging the question: Where did the rest of the material originate? The researchers suggest that, in this case, more of these chemicals may be emitted from septic fields, leaky infrastructure and landfills than from the sewage treatment facility. Although their results may not apply to all watersheds, the study emphasizes that there are multiple and possibly diffuse sources of these contaminants, even in a case where a single major culprit seems at fault.

Point discharges from hospitals and pharmaceutical manufacturing plants have also been fingered as a major source of contamination. Recent research in other countries does not show hospitals to be a major source of pharmaceutical contamination (Langford and Thomas 2009, Ort et al. 2010), but pharmaceutical plants — despite being regulated by the U.S. FDA and EPA — do appear to have a significant impact on these compounds in the environment. Phillips et al. (2010) found pharmaceutical concentrations from 10 to 1,000 times higher in effluent from manufacturing facilities than those found in typical wastewater treatment effluents.

Land application of biosolids from wastewater treatment onto agricultural fields may also be a significant source of emerging contaminants, as manure can contain any of the antibiotics and hormones that are used on the farm (Kjaer et al. 2007). In addition, sewage treatment facilities often offer sludge from their bioreactors to farms as fertilizers. Organic wastewater contaminants, particularly the water-insoluble components, often bioaccumulate to a greater degree in sludge and can have a significantly larger concentration per volume of these compounds than the treated water from the sewage plant (Kinney et al. 2006). The application of these solids on the land can therefore be a significant source of emerging contaminants and can reintroduce these compounds into the environment.

Other emerging contaminants, such as flame retardants, plasticizers and coatings, are also present in wastewater effluent and sludge and are clearly tied to the quantities of the products used by the general population (e.g. Rickland et al. 2009, La Guardia et al. 2007). Brominated flame retardants, for example, are found in sludge from U.S. treatment plants at a level 10 times higher than those in Europe (Hale et al. 2003). This can partly be explained by the fact that North America consumes 98% of these chemicals, and that some of these compounds are banned in Europe in light of their persistence and toxicity. These compounds have also been found in remote locations, such as the Arctic, indicating their movement through air transport or ocean currents (de Wit et al. 2010).

# D. Presence in the environment

### 1. Presence measured in the Great Lakes and watersheds

Emerging contaminants of all types have been found in the Great Lakes, which act as a natural holding pen — and case study — for pollutants because of century-long retention times in some of the lakes. Emerging contaminants commonly found in the Great Lakes include flame retardants, modern pesticides, pharmaceuticals, the antibacterial and antifungal agent Triclosan, and the insect-repellent DEET. The now-notorious bisphenol A, commonly used in a wide variety of plastics such as baby bottles and food packaging, was found in more than half the water samples analyzed in all the studies to date (Klecka et al. 2010).

Klecka et al. (2010) recently reviewed and summarized the studies of emerging contaminants in the Great Lakes basin from 1997-2008 for an evaluation by the International Joint Commission (IJC) and their Nearshore Framework Policy. The IJC is a board nominated by the U.S. and Canadian governments to help manage the waters along the border of the two countries. A committee of this organization deals specifically with the issues surrounding emerging contaminants. A summary of the review by Klecka et al. for each compound class of emerging contaminant is below. In some cases this has been supplemented with additional information (e.g. nanomaterials, phytoestrogens). It is important to note that presence alone does not dictate that these compounds are harmful at these concentrations.

*Pharmaceuticals:* Pharmaceuticals are commonly found in the watersheds surrounding the Great Lakes. Where the compounds are present, they measure anywhere from 0.001 micrograms per liter (ug/L) to 0.26 ug/L closer to wastewater facilities. Metcalfe et al. (2003) is the only study to examine the open waters of the Great Lakes, sampling western Lake Erie and a few sites on Lake Ontario taken from multiple areas in Ontario, Canada — including points near sewage treatment plants in Windsor and Petersborough and from the embayment of Hamilton Harbor. In this study, the highest concentrations measured were in Lake Ontario: 0.02 ug/L to 0.06 ug/L for the medications clofibric acid (a herbicide), ketoprofen (an anti-inflamatory drug), fenoprofen (an anti-inflamatory drug), and carbamazepine (a mood stabilizing drug). In sediments, pharmaceuticals ranged from 3.3 nanograms per gram (ng/g) to 75 ng/g in samples taken downstream from storm sewer outfalls. No information was provided for sediments in open lake waters.

*Personal care products:* The antibacterial and antifungal agent Triclosan, and insect-repellent DEET, are the most common compounds measured. The highest concentrations were 1.1 ug/L for DEET, and 34 ng/L for triclosan.

*Phytoestrogens (plant materials):* Cholesterol was the most commonly detected plant compound in waters, and sistosterol and stigmastanol were the most commonly detected such compounds in sediment. Data for these compounds is relatively limited compared to others, although they have been added to EPA monitoring protocols so more data should be available soon. Kang and Price (2009) found that most plant sterols are removed by wastewater treatments, with the dietary supplement daidzein coming through effluent at levels from 2-33 ng/L.

*Fluorinated compounds:* Lake Erie open water samples contained from 11-121 ng/L concentrations of perfluorinated surfactants PFOS (at one time the key ingredient in Scotchgard fabric protector) and PFOAs (used in non-stick coatings for cookware and stain- and water-repellants for fabrics) — as well as their precursors. In Lakes Superior, Ontario and Huron concentrations ranged from 112-162 ng/L. PFOS and its precursor were also found in freshwater organisms in the lakes at much higher concentrations (50-460 ng/g), indicating significant accumulation in certain segments of the food web. Concentrations in biota can be more than 1,000 times greater than surface water concentrations.

*Synthetic musks:* Several studies involving musks have been carried out in the Great Lakes Basin. Water samples indicate certain musk compounds — found in perfumes, shampoos and lotions — to be present at low concentrations of 0-4.7 ng/L in open Lake Michigan waters and up to 41 ng/g in tributaries. Sediments from Lake Ontario had levels measuring up to 16 ng/g. These compounds have also been shown to accumulate in fish up to over 1 ug/g dry weight indicating bioaccumulation.

*Chlorinated paraffins:* Used in flame retardants, plasticizers, rubber, paints, adhesives and caulks, sediment concentrations measured in harbors of the Great Lakes range from 7.3-410 ng/g. Sediments from lake cores were much lower. Concentrations in biota can be as high as 5,000 ng/g, indicating that these compounds bioaccumulate.

*Phthalates:* DEHP (bis(2-ethylhexyl) phthalate — the most commonly used plasticizer, often used in PVC building materials as well as in shower curtains, food containers and diapers — has been detected at 20 ug/L in a single study sample, which exceeds water quality guidelines. DEHP has also been detected at 4,030-29,700 ng/g in sediment, which also exceeds international standards.

*Bisphenol A (BPA):* Commonly used to make plastics, including baby bottles, BPA was present in 57.1% of all the water samples analyzed in all the studies to date in concentrations up to 0.8 ug/L. BPA has also been measured in 65% of the sediment samples of Lake Erie. Concentrations in sediments in the Great Lakes Basin in general ranged from 6.1 ng/g in Lake Erie and 20-60 ng/g in tributaries.

*Nanomaterials:* There is little known about how nanomaterials will be processed through wastewater facilities or if they will end up in the environment through biosolids, industrial waste, aerosols, etc. The first study regarding the potential presence of nanomaterials in waste streams indicates nanomaterials may aggregate to larger sizes and end up in biosolids. Titanium dioxide particles were detected at 5 to 15 ug/L in effluents (Kiser et al. 2009), but at sizes of 0.7 microns and lower.

*Current Use Pesticides and Herbicides:* Compounds detected in various studies include Atrazine, metolachlor, cyanazine, alachlor, acetochlor, prometon, tebuthiuron, diuron, simazine, 2,4 D, glyphosate and methoprene. Glyphosate has been measured at levels from 0.08 ug/L to 40 ug/L. Concentrations reflect seasonal use patterns. The authors point out that very few of these levels exceed water standards in each of the countries for open lake waters, however in urban, suburban and agricultural systems pesticides exceeded aquatic life standards at least once during the year for at least one pesticide. The herbicides atrazine, diallate, metolachlor and simazine were present in 50-100% of the samples, and glyphosate was present in 46.3%. Insecticides were detected less frequently. Atrazine, azinophos-methyl, chlorpyrifos, diazinon and parathion exceeded regulations in up to 32% of samples.

### 2. Presence in drinking water

Emerging contaminants are present in our treated drinking water, whether it comes from the treatment plant or the ground — though most are found at low levels. Current water treatment methods are not designed to remove all contaminants, and the effectiveness of removal varies depends on the compound in question and the treatment method used at each wastewater treatment plant. Benottie et al. (2009) measured for the presence of 51 chemicals in finished drinking water from 19 facilities across the United States. These chemicals included pharmaceuticals, musks, pesticides, bisphenyl A and flame retardants. The presence of emerging contaminants in finished drinking water overall was low, with a majority measuring less than 10 ng/L. Chemicals found at higher concentrations included: the herbicide atrazine (median concentration 49 ng/L); bisphenol A, found in plastics (25 ng/L); galaxolide, a musk (31 ng/L); nonylphenol, a breakdown product from detergents (93 ng/L); BHT, a food additive (26 ng/L); metolachlor, an herbicide, (16 ng/L); DEET, an insect repellent (63 ng/L); tris(2-carboxyethyl) phosphine (TCEP), a reducing agent, (120 ng/L); and tris(1,3-dichloro-2-propyl) phosphate (TCPP), a flame retardant (210 ng/L). Some of these compounds had maximum concentrations that were much higher, including atrazine, for which the highest concentration detected was 900 ng/L. Yet some samples had no detection. The authors reviewed the literature for removal efficiencies estimated by this and other studies, and found it varied from 20-90% removal depending on the compound in question. Ozone has been found to be a good oxidizer for most compounds, though even this treatment provides only partial removal of some pesticides (Broseus 2009).

Emerging contaminants are also found in groundwater sources. A national survey conducted by the USGS that collected water from 47 groundwater sites across 18 states found a variety of emerging contaminants were present across sites. Most common were DEET, bisphenol A (30%), Sulfamethoxazole (antibiotic) and Carbamazepine (antiepileptic) (Barnes et al. 2008, Focazio et al. 2008). Similar results have been found across Europe (Loos et al. 2010). This indicates that groundwater may be equivalent as a water source for emerging contaminants for those who do not directly consume Great Lakes water but are still within the basin. Groundwater also feeds into the Great Lakes and may be a source of contamination.

### 3. Other potential human exposures

The most significant exposure route for some compounds in humans may not be through drinking water or surface water, but through inhalation or skin exposures, our everyday use of consumer products, and food contamination — either via the food web or from food containers leaching contaminants. For example, Johnson-Restrep and Kannan (2009) found that ingestion and skin absorption of house dust are the major pathways of exposure to the flame-retardant PBDE, comprising up to 77% of the intake of this compound. Lorber (2008) estimates house dust alone accounts for 82% of PBDE intake. Direct use of these products can also contribute to exposures. For example, levels of PBDE's in human tissues are 1-2 orders of magnitude higher in the U.S. than in Europe and Japan where PBDE's are now in limited use (Costa et al. 2008).

Food contamination can be a major route of exposure that overwhelms exposure from drinking water sources. For example, exposure to phthalates — added to plastics to increase flexibility — is predominantly via food and is highest in children (Lyche et al. 2009). The highest potential exposure to bisphenol A (BPA) is through contamination of food by containers that transport or hold food (European Union 2003). These containers often have linings made of epoxy resins or plastics containing BPA. Nanomaterials may show up in large concentrations in the environment, but for now the major exposure is most likely food products, personal care products and certain cosmetics (Dekkers et al. 2010).

As many of the chemicals documented above have accumulated in freshwater organisms, including those inhabiting the Great Lakes, there is also a potential for human exposure through ingestion of Great Lakes fish — exposures that have been documented in studies of polychlorinated biphenyls (PCBs) and other known persistent contaminants. As contaminant concentrations in fish are often greater than those of the surrounding waters, each fish consumed contains a greater amount of emerging contaminants than an equivalent amount of water.

## 4. Potential risks to ecology and human health

The effects of exposure to some emerging contaminants include endocrine disruption and cancers, and are thus a serious concern for people and wildlife. Others have been shown to have little impact in the short-term when considered alone at the exposures that occur in the environment. However, there are few studies documenting long-term impacts. The greatest threat may be that certain chemicals, when combined with others in the environment, may produce a greater effect than that of a single chemical. Humans and other organisms are exposed to a multitude of chemicals simultaneously, some of which may have similar mechanisms of action. When considered in combination, the concentration may be at a level that does cause an effect. Some data suggest that the combined — or synergistic — effects of these chemicals can cause a greater impact than would be anticipated from each chemical's individual effects.

The effects of exposure to some emerging contaminants have caused concern for both people and wildlife. These include chemicals such as the personal care products triclosan and triclocarban (Murray 2010), both of which are suspected to be compounds that can disrupt the body's endocrine — or hormonal— system (Witorsch and Thomas 2010) and are toxic to fish crustaceans, algae (Tatarazako et al. 2004) and fish embryos (Oliveira et al. 2009). Other endocrine disruptors include phytoestrogens — such as genistein from soybeans, which has been shown to be estrogenic, teratogenic and to cause other physiological problems in the embryos of fish and mammals. (Eustache et al. 2009, Chan 2009, Jefferson et al. 2009). PBDEs, commonly found in flame retardants, have also been shown to affect endocrine systems (see Costa et al. 2008 and Talsness 2008 for reviews). PBDE levels in breast milk are associated with lower birth weights and decreased body mass, as well as cryptorchidism (undescended testicles) in newborn boys (Chau et al. 2007, Main et al. 2007). Extrapolating from animal studies and body burdens in humans, Cost and Giordano (2007) have estimated that the levels of PBDE's that cause developmental neurotoxicity in animal model experiments is similar to the higher levels seen in humans, indicating it is possible these compounds may be causing the same phenomenon in people. A recent publication has even hypothesized that there may be link between autism and PBDE exposures due to their impacts on thyroid function and development, however this hypothesis remains to be tested (Messer 2010). Phthalates and bisphenol A have also been found to be endocrine-disrupting and thus can affect the sexual development of offspring when mothers are exposed (Lyche et al. 2009, Swan 2008, Wolstenholme et al. 2010).

Other emerging contaminants appear to cause inflamation or cancers, such as chlorinated paraffins and PFOAs (National Toxicology Program 1985, 1986; Bucher et al. 1987). The effects of some newer chemicals, such as manufactured nanomaterials or compounds that have been developed as substitutes for flame retardants, are uncertain. Such chemicals are new, exposure levels have yet to be determined and there is minimal laboratory information on their potential toxicities.

Much of the research on the impacts of emerging contaminants on wildlife and humans has been in the form of laboratory toxicity studies on single chemicals. Studies that do find effects are often done at concentrations that are above those found in the environment. Studies conducted at levels similar to those found in the environment suggest that acute exposures do not pose a risk (Fent et al. 2006). When compounds are tested individually in these studies, their effects vary by class of compound. Some are not believed to cause harm in individual exposures because of their low concentrations in the environment. For example, it is generally believed that the low concentrations of various pharmaceuticals in the environment compared with therapeutic doses should have few adverse health effects in people (e.g. Bruce et al. 2010, Cunningham et al. 2008, Schwab et al. 2005). In reality, however, the low-dose impacts of these chemicals — and particularly mixtures of them – are largely unknown for humans and other species. Where aquatic species are concerned, several authors have attempted to model the potential compounds that may be of highest interest. Most recently, Fick et al. (2010) found that most pharmaceuticals are not considered harmful when the average environmental concentration is considered. At the highest levels of environmental contamination, however, many pharmaceuticals are found at a concentration that is 1,000 times greater than the concentration deemed harmful for either direct effects or potential accumulation. Realistically, however, most exposures are chronic and there are few studies documenting effects from long-term exposures. There are also large gaps in understanding bioaccumulation, specific exposures in the Great Lakes, sub-lethal effects and outcomes, and information regarding impacts on a variety of organisms.

There is now evidence that combinations of emerging contaminants similar to those present in the environment may have an even greater impact than simply adding up the effects of each individual chemical (Schell et al. 2009). This may apply particularly to chemicals that act on similar biochemical pathways in an organism because multiple low-dose exposures may collectively cause an alteration, even while individual exposures do not (e.g. Petersen and Tollefsen 2010; Rider et al. 2010). This has been found to extend to chemicals with different mechanisms of action but the same target (Rider et al. 2010). Overall, this underscores a concern that even if a single chemical has not been shown to cause a significant human or environmental health impact, its effect as part of a mixture may indeed be significant.

### 5. Missing information on fate, presence, accumulation and effects in the Great Lakes

These studies have, by and large, centered on chemical compounds in their primary, or original, state. But there are a multitude of breakdown products associated with these compounds that have not been measured in the Great Lakes and, in some cases, not even identified. Beyond this, there are thousands of chemicals in production that have not been monitored. Howard and Muir (2010) recently completed a survey of chemicals in commerce and identified 610 out of 23,000 that are potential new targets for monitoring efforts in light of their high-volume production and use in the Great Lakes, and their potential to persist in the environment.

The Great Lakes are a dynamic system and dilution from the source of origination into this large system leads to small concentrations of certain compounds in the water column. However, research has shown that certain classes of compounds (non-polar organics, flame retardants) can be transported great distances and accumulate in organisms at a factor of up to 1,000 times greater than the concentrations found in water.

Effects research as a whole has largely focused on acute exposures to single chemicals in a small number of model organisms in the laboratory, with few comparable epidemiological studies or studies of natural populations of organisms. Studies are often based on mortality in acute exposures to a single compound. The lack of information on chronic exposures and sub-lethal impacts is evident. In addition, multiple compounds that act on the same pathway in a particular organism may have a cumulative impact. Some have proposed examining the impacts of emerging contaminants by looking at their effects on reproduction, metabolism or behavior, among others, to try to account for this possibility (Daughton 2004). Analyzing potential links to endpoints such as survival, cancer, reproduction, immune function and stress, and the impact of multiple chemicals on these pathways, may provide more information than a chemical-by-chemical approach.

# E. Policy Implications

The current regulatory approach and focus on individual chemical assessments cannot adequately handle the vast number of chemicals now in use, the thousands of new chemicals introduced each year, and the difficulty of measuring every contaminant in the environment.

An estimated 23 million chemicals were indexed by the American Chemical Society's Chemical Abstracts Service in 2004 (Daughton 2004). More than 7 million of these chemicals were commercially available, with only 230,000 inventoried or regulated by governments worldwide at that time.

## 1. Federal regulations

The Great Lakes and their tributaries and groundwater are the source of drinking water for more than 40 million people living within the basin. Most emerging contaminants here go unregulated, despite the fact they have been detected at drinking water facilities. Efforts are now under way by public health, environmental and trade groups to require that the government regulate or even ban certain chemical compounds that are present in drinking water — among them endocrine disrupters, the antibacterial Triclosan and pharmaceuticals. Efforts to regulate or ban targeted compounds in drinking water include the Canadian Medical Association's call for a ban on antibacterial household products, Beyond Pesticides' call for a ban on Triclosan, and Maine and Michigan's successful banning of certain brominated flame retardants.

The federal Safe Drinking Water Act is intended to protect drinking water and the sources of drinking water. Current EPA regulations for primary drinking water limit microorganisms, disinfectants such as chlorine used in processing, byproducts of this disinfection called trihalomethanes, inorganic chemicals like arsenic and lead, select organic compounds including pesticides, herbicides, gasoline additives and volatile organics and radionuclides like radium. An "unregulated contaminant list" has been created to prompt drinking water supply monitoring for new contaminants. The current list was approved in 2008. There are a select number of facilities that have included these contaminants in their drinking water monitoring efforts, some Great Lakes facilities — such as in Milwaukee — among them. New chemicals are added through a public process and included on the "Contaminant Candidate List" (CCL) based on frequency of occurrence in public water supplies, potential health impacts and the potential for regulation of those compounds having an impact on public health. Lists of potential contaminants are reviewed every five years and new additions are considered. The previous CCLs did not lead to the proposal of any additional regulations. Part of the reason is the heavy burden of proof needed to demonstrate the impact of the chemical on populations at the concentrations found in wastewater or drinking water. Without proof of effects at the concentrations listed, chemicals will not be regulated. The latest list (CCL3) includes several hormone pharmaceuticals, antibiotics, pesticides, PFOA, compounds used in plastics, solvents and others.

Emerging contaminants could also potentially be regulated under several sections of the federal Clean Water Act (Lape 2010). These include sections governing the federal water quality criteria used to set water quality standards for the states (Section 304a) and the disposal of sewage sludge from wastewater facilities (Section 405d).

The EPA is also amending the federal Resource Conservation and Recovery Act (RCRA) universal waste provision to include pharmaceuticals, and they are adding pharmaceutical wastes to the federal universal waste program. These changes, if adopted, would make it easier for generators to collect and properly dispose of pharmaceutical wastes as hazardous wastes, resulting in a simpler and more streamlined waste management system.

The U.S. Food and Drug Administration's (FDA) *Environmental Assessment Technical Assistance Handbook* states that "The assessment of risk to the environment caused by the manufacture, use and disposal of human and animal health drugs is required by the FDA." From 1985-95 the FDA required data on the potential environmental impact of a drug in each New Drug Application. The data from these applications was then evaluated by the FDA, which used this information to create the document *Guidance for Industry — Environmental Assessments for Human Drugs and Biologics Applications*. In this guidance drug manufacturers must provide an environmental assessment when the anticipated concentration of a drug in the aquatic environment will be greater than 1 part per billion. Exclusions are made when this level is not met and the toxicity information provided by the company shows minimal toxicity. There are several issues with this rule. The first is that some medications have been shown to impact aquatic species at levels below parts per billion exposures. Secondly, these rules only include information on terrestrial sediments and the water column and do not account for biomagnification through the food chain. Thirdly, the types of environmental effects documented are usually based on acute assays of lethality and a minimum measure of effects (Boxall 2004). More detailed measures of effects on growth and reproduction are not considered and may be the important endpoints. The Great Lakes Environmental Law Center and the Natural Resources Defense Council (NRDC) in July 2010 petitioned for this exception to be revoked and require full environmental assessment for all new drugs that will enter the environment, regardless of concentration.

The FDA also regulates unused, expired or returned drug products. These medications are to be disposed of through incineration or in landfills. Consumers have been expected to get rid of empty or partially empty containers through domestic solid waste disposal, however, more recently FDA is encouraging take-back programs that incinerate unused medications for consumers.

### 2. Litigation

On January 10, 2010, the Center for Biological Diversity filed a petition asking that EPA publish new national water quality criteria taking into account the effects of endocrine-disrupting chemical ("EDC") pollution. The petition called on EPA to set water quality criteria covering several EDCs. EPA has not responded to this petition.[1]

Other groups have filed citizen petitions with EPA that have prompted formal agency action. For example, several citizen groups led by Beyond Pesticides and Food & Water Watch petitioned EPA for a ban on Triclosan in January 2010. In response to this petition, EPA announced a 60-day public comment period ending February 11, 2011.[2]

1 Per email from Jacki Lopez, Center for Biological Diversity, January 25, 2011.

2 75 Fed. Reg. 76461 (December 8, 2010), online at: *http://edocket.access.gpo.gov/2010/pdf/2010-30850.pdf*

In July 2010, the Natural Resources Defense Council (NRDC) and the Great Lakes Environmental Law Center filed a petition that challenges the 1 part-per-billion exclusion from FDA's environmental review.[3] FDA continues to review this issue, but no date has been provided for FDA's response.[4]

### 3. Other Regulatory Pathways

Some compounds are currently being phased out because of international restrictions, encouragement from the federal government or public scrutiny of the product. Decabromodiphenyl ether (decaBDE), found in flame retardants, is one such compound that is currently being phased out in cooperation with EPA. Howard and Muir (2010), however, have identified replacement flame-retardant products in Great Lakes sediments and waters that may be of equal concern, yet are not currently monitored.

Some states have also attempted to limit the use of emerging contaminants. Prior to the federal action, Michigan passed legislation that restricted flame retardants Penta-BDE and Octa-BDE. This legislation prohibited the manufacture, processing and distribution of products containing more than one-tenth of 1 percent of Penta-BDE or Octa-BDE beginning in June 2006.

3 Noah Hall, "Great Lakes Environmental Law Center and NRDC file petition to close loophole on pharmaceutical drugs in drinking water," Great Lakes Law Blog, http://www.greatlakeslaw.org/blog/2010/07/great-lakes-environmental-law-center-and-nrdc-file-petition-to-close-loophole-on-pharmaceutical-drug.html, (July 13, 2010).

4 Per email from Thom Cmar, NRDC, January 25, 2011.


# F. Current techniques for control

### 1. Take-back programs and hazardous waste collections

Considerable resources have been directed to community hazardous waste collections and pharmaceutical take-back programs that aim to keep these contaminants out of the environment. The basis for much of this activity dates to Feb. 20, 2007 when the White House — through the Office of National Drug Control Policy, the Department of Health and Human Services, and the EPA — released guidelines to address concerns about pharmaceutical disposals in wastewater and the abuse of unused prescription drugs.

At the same time, the federal government opened the door to communities starting take-back initiatives and began to provide funding for communities to help organize and pay for such programs and disposal. Several organizations around the Great Lakes offer these take-back programs, among them sewerage and hazardous waste facilities, police departments, pharmacies and regional federal offices.

Although there are hundreds of tons of medications collected through these events, it is questionable how effective these programs are at restricting the flow of pharmaceutical pollution in the environment. Most pharmaceuticals and their byproducts enter the environment through agricultural practices and human waste, as much of the pharmaceuticals consumed pass through people and livestock either unaltered or slightly altered (Lubick 2010). Take-back programs may help prevent the abuse of medications and prevent the potential release of a small portion of medications into the environment. Focusing on these efforts as a sole or primary solution to environmental exposures will, however, detract from implementation of more targeted and effective solutions.

### 2. Sewage/water/solids treatment

Improving treatment systems may be another way to keep some emerging contaminants out of the environment. However, the removal efficiencies of emerging contaminants vary greatly not only among treatment processes, but also among the various contaminants.

The EPA recently created a database on removing contaminants of emerging concern using current wastewater treatment technologies. This review includes evaluation of data from 88 articles or reports and provides an overview of how effective various treatment technologies are at removing these contaminants (U.S. EPA 2010). The database provides information on 246 contaminants. The authors chose a subset of 16 contaminants from the EPA literature review database that were largely represented across all datasets in order to show and summarize removal efficiencies for these contaminants. Table 1 below is representative of their findings of removal efficiencies across different wastewater treatment systems.

**Table 1.** Average Percent Removal of Selected Emerging Contaminants from Full Wastewater Treatment Systems with Differing Treatment Technologies (modified from U.S. EPA 2010)

| Contaminant | Type of compound | *Activated Sludge | *Chlorine Disinfection | *UV Disinfection | Ozone | Reverse Osmosis |
|---|---|---|---|---|---|---|
| Bisphenol A | plasticizer | 78 | 72 | 85 | 96 | NR |
| Caffeine | food product | 94 | 98 | 97 | NR | 96 |
| Carbamazepine | pharmaceutical | 22 | NR | NR | 60 | NR |
| DEET | pesticide | 54 | 23 | 64 | 74 | NR |
| Diclofenac | pharmaceutical | 44 | 66 | 89 | NR | 90 |
| Estradiol | hormone | 88 | 78 | 76 | 100 | NR |
| Estrone | hormone | 77 | 37 | 74 | 94 | 84 |
| Galaxolide | pharmaceutical | 56 | 57 | 55 | NR | 32 |
| Gemfibrozil | pharmaceutical | 77 | 83 | 90 | 90 | 90 |
| Ibuprofen | pharmaceutical | 90 | 78 | 90 | 95 | 72 |
| Iopromide | medical | 69 | NR | NR | NR | NR |
| Naproxen | pharmaceutical | 85 | 93 | 97 | 84 | 90 |
| Nonylphenol | alkylphenol | 90 | NR | NR | 85 | NR |
| Sulfamethoxazole | pharmaceutical | 58 | 73 | 33 | 96 | NR |
| TCE | solvent | 27 | 4.5 | 50 | NR | NR |
| Triclosan | antibacterial | 89 | 83 | 90 | 99 | 67 |

NR= not reported

* Activated sludge systems involve using a microbial reactor and then solid removal to an anaerobic system for further processing. This is the most common type of treatment system used in the U.S.

* Chlorine disinfection is a process whereby chlorine is added to some stage of the treatment process as a disinfectant to kill pathogens that may be harmful.

* Ultraviolet treatments in wastewater treatment kill pathogens, cleave organic molecules and create hydroxyl radicals that break down organics.

The main finding in examining this data is that one removal process is not the best at removing all contaminants. There may be a potential for greater removal efficiencies with new technologies, but the above technologies are already in use and it would be expensive to retrofit a treatment process.

# G. Future tools for control

## 1. New wastewater technologies

Various wastewater treatment processes that amend current techniques have been proposed to improve the removal of emerging contaminants. These include adding steps in the treatment process such as activated carbon, UV in combination with an oxidizing agent and others. Activated carbon appears to show a significant removal capacity (e.g. Ross et al. 2009), and UV and photocatalytic reactions (Méndez-Arriaga et al. 2010, 2008) may also assist in degrading these contaminants. Nanomaterials, paradoxically themselves a potential emerging contaminant of concern, have also been proposed as an addition to the treatment system. Membranes, oxidants and adsorbents made from nanomaterials have been proposed as a lower-cost treatment option (Bottero et al. 2006). These materials also bear a potential cost, as their production can produce significant waste and the impact of their release into the environment is, for the most part, unknown.

It is important to note that these solutions may solve the problem of the release of only certain contaminants into the environment. There are many others that are airborne or enter our environment through means other than wastewater treatment facilities, such as through agriculture, septic systems and factory pollution.

## 2. Changes in industrial behavior

Changes in treatment technologies are not the only answer. In fact "end of pipe" solutions tend to be the most expensive and fail to target the primary sources of contamination. Reducing chemical production and incorporating planning for a chemical's life cycle may do more to reduce the environmental load of emerging contaminants — with less expense and less regulation. Shirmer and Shirmer (2008) have called for a broader consideration of these issues when conducting risk assessments.

One way to prevent the impacts of emerging contaminants is to address the issue at the beginning of the design process, and to continue examining chemical production and use through the manufacturing, distribution and use of products. Green Chemistry involves using a design approach that considers each of these factors in creating a product. The philosophy of this science dictates that when a chemical is first designed, consideration should be given to: how much hazardous waste the production process will generate; the potential dangers of transportation and disposal; potential byproducts or pollutants generated when the chemical enters the environment; and the product's ultimate health and environmental safety (Anastas 1998).

The key to these concepts is that considerations of human health and the environment are incorporated into a chemical's design before its production and introduction into the marketplace. This is contrary to our current process in which chemicals are designed or created, tested minimally for toxicity, and are not tested for their potential persistence in either the environment or an organism. Rather than relying on ex post facto actions and regulations that occur after chemicals have become a persistent part of the ecosystem, employing such a design philosophy could have dramatic effects on environmental actions needed to mitigate effects and could actually decrease regulatory concerns. Enforcing such a design standard may be difficult, however.

# H. An Action Plan for Emerging Contaminant Control

Emerging contaminants come from a variety of products and sources and therefore strategies to address these pollutants in the Great Lakes may be best coordinated at the binational and national levels. In the United States, the Environmental Protection Agency has a large research program addressing environmental issues associated with the Great Lakes and is charged with protecting the waters of the Great Lakes as part of its mission. That agency, therefore, may be the best suited to take action regarding the threats from emerging contaminants. Related research and regulatory programs in other federal agencies — such as the Food and Drug Administration, U.S. Geological Survey, and U.S. Fish and Wildlife Service — should be coordinated.

Addressing the problem of emerging contaminants requires focus on four main areas: (1) new research, (2) new treatment technologies, (3) behavioral changes in the marketplace, and (4) policy reforms.

A comprehensive research plan should be created and implemented that will address: 1) gaps in research that limit our understanding of the harm these chemicals may be causing people and natural systems, and which chemicals may be most important; and 2) how to evaluate the effectiveness, viability and economics of developing new treatment tools for removing emerging contaminants from the environment. This research will ultimately assist in development of water quality criteria for these chemicals.

The production of chemicals for the marketplace and the way in which we use these chemicals should also be evaluated, as well as how these chemicals fit into existing policies and regulations for chemicals. Each of these four major areas is outlined below.

### 1. A Great Lakes research agenda for emerging contaminants

Despite the fact that the last two decades produced a number of emerging contaminant studies, overall these studies are disconnected and have left many gaps that must be filled before we can determine the potential impacts of unleashing countless emerging contaminants into the environment. A formal national, multi-agency research program on emerging contaminants should be established to coordinate studies on fate, exposures and the impacts on people and various parts of the ecosystem. The program should help prioritize the compounds that are of greatest importance, identify how chemicals are distributed, and understand how long-term, low-dose exposures impact people, wildlife and other organisms. A formal national agenda has been suggested by others (Novak et al. 2011) and should be placed in a Great Lakes context.

### 2. Evaluation of the effectiveness, viability and economics of developing new treatment technologies

New methods for the treatment and removal of existing compounds should be evaluated. Current treatment methods are not designed to remove all contaminants, and the effectiveness of removal varies depending on the treatment used at each wastewater plant. There are also many infrastructure failures that may contribute to additional environmental contamination, as these chemicals may bypass treatment facilities completely. Updating wastewater infrastructure, improving treatment technologies and standardizing them across the Great Lakes should all be assessed as potential methods for control. Finally, investing in research into new treatment technologies could provide solutions for those compounds that do enter wastewater facilities.

### 3. Change behaviors on the production and consumption sides of the marketplace

The greatest mechanism for curbing the release of emerging contaminants into the environment may be decreasing the use of some of these chemicals. As discussed above, considerable pharmaceutical byproduct entering the Great Lakes comes from excretion of metabolic byproducts by humans, not through direct disposal. In addition, not all emerging contaminants enter the environment through wastewater systems, and the main routes for human exposure are through the use of everyday products. We need new ideas about methods of manufacturing and ways to change our chemical consumption behaviors to decrease our exposures to emerging contaminants. Safer alternatives should be investigated. Better labeling and public knowledge of the effects of these chemicals could help individuals choose to use or not use a product based on its chemical content.

### 4. Policy reform and regulation of chemicals

There are few regulations regarding emerging contaminant control in the Great Lakes or, for that matter, elsewhere. Pharmaceutical take-back programs and wastewater and drinking water monitoring efforts do signal a change in attitude toward these contaminants. However, take-back programs ultimately provide little in the way of removing emerging contaminants from the environment and monitoring alone does not provide protection. Today's high burden of proof — the requirement that a chemical cannot be removed from the marketplace without data showing it has a negative impact on people and the environment — underscores the need for a more effective and realistic risk assessment program to evaluate whether these chemicals should be regulated. Changing federal policies governing the production and use of new chemicals and existing emerging contaminants in the marketplace may well have the biggest impact.

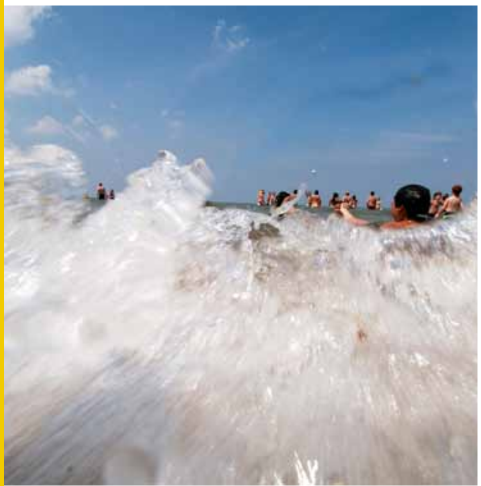
# III. Conclusion

The last two decades have seen growing concern about risks from chemical contaminants in the environment that failed to previously raise red flags from scientists and regulators. Exposure to some of these manmade and naturally occurring chemicals — known as “emerging contaminants of concern” — is cause for concern for people, fish and wildlife. Recent findings of emerging contaminants — specifically, low levels of the nicotine byproduct cotinine and the cholesterol-modifying drug gemfibrozil — in Great Lakes drinking water raise concerns for millions of people in the basin.

There are literally hundreds of sources of emerging contaminants today stemming from consumer products that end up in our wastewater, air and land. Many of these sources include everyday products such as shampoos and sunscreens, plastics and pesticides, flame retardants and pharmaceuticals. An estimated 23 million chemicals have been indexed, with more than 7 million commercially available but only 230,000 inventoried or regulated by governments worldwide. The current U.S. regulatory approach and individual chemical assessments cannot adequately handle the vast number of chemicals now in use; the thousands of new chemicals introduced each year; and the difficulty of measuring the impact of every contaminant in the environment. Further complicating the picture: evidence shows us that combinations of emerging contaminants similar to those found in the environment may have an even greater impact than individual chemicals, and that most exposures to these chemicals are long-term and chronic.

Despite this, most current studies focus on the effects of a single chemical in the lab, and few studies document the effects of long-term exposures. Worse, the number of sources and types of emerging contaminants makes it even more challenging to control this potential threat. Indeed, few states — the majority of the Great Lakes states among them — have even a clear definition of emerging contaminants and most lack defined programs to deal with them.

The unknown level of threat from emerging contaminants demands a multi-pronged and precautionary approach. As emerging contaminants originate from a variety of products and sources, strategies to address these pollutants in the Great Lakes may be best coordinated at the binational and national levels. A comprehensive plan should be developed to address research gaps, prioritizing the most damaging emerging contaminants, and setting out a Great Lakes research agenda. Reducing chemical production and incorporating planning for a chemical’s life cycle may do more to reduce the environmental load of emerging contaminants, however, with less expense and less regulation. Efforts to change behaviors of both producers and consumers of these chemicals may be most effective as they will lead to fewer inputs into ecosystems like the Great Lakes.



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Dr. Rebecca Klaper is a Shaw Associate Scientist at the Great Lakes WATER Institute, School of Freshwater Sciences at the University of Wisconsin-Milwaukee. Her research examines the impact of various emerging contaminants (e.g. nanomaterials, pharmaceuticals) as well as natural stressors on freshwater organisms. She has authored numerous publications, including “Emerging Contaminant Threats and the Great Lakes: Existing Science, Estimating Relative Risk, and Determining Policies” in collaboration with the Alliance for the Great Lakes. Dr. Klaper obtained her Ph.D. in Ecology and M.S. in Entomology from the University of Georgia, and a B.S. in Honors Biology from the University of Illinois.

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Lyman C. Welch is the program manager of the Alliance for the Great Lakes’ Water Quality Department, with a focus on enhancing recreational waterways, addressing pharmaceutical pollution, reducing airborne mercury, and other clean water projects. Lyman is an attorney formerly with the Chicago law firm of Mayer, Brown & Platt. Prior to joining the Alliance, he served as associate director and general counsel of the Mid-Atlantic Environmental Law Center at Widener University Law School in Wilmington, Del. He received his J.D. degree in 1993 from the Northwestern University School of Law in Chicago. In 1990, Lyman graduated cum laude from Colgate University in Hamilton, N.Y.

ALLIANCE FOR THE GREAT LAKES

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## About Alliance for the Great Lakes

Alliance for the Great Lakes serves as the voice of the 40 million people who rely on Great Lakes water for drinking, recreation and commerce. Formed in 1970, it is the oldest independent Great Lakes protection organization in North America. Its mission is to conserve and restore the world's largest freshwater resource using policy, education and local efforts, ensuring a healthy Great Lakes and clean water for generations of people and wildlife. Its headquarters are in Chicago, with offices in Buffalo, Cleveland, Detroit, Grand Haven and Milwaukee.


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