Keeping Great Lakes Water Safe:
Priorities for Protecting against Emerging Chemical Pollutants

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Priorities for Protecting against Emerging Chemical Pollutants

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Executive Summary

More than 85,000 chemicals are in production and use in the United States today and the number is growing. Of those, more than 2,200 are produced at a rate of 1 million-plus pounds a year, and nearly 20,000 registered pesticide products have entered the market since registration began in 1947. Still more are on the way. Advances in chemistry and biotechnology mean new compounds are being synthesized at an unprecedented rate. These chemicals don’t simply disappear after fulfilling their intended uses, but find their way into the environment and the water. As the number of chemicals around us continues to grow, the potential for these chemicals to end up in the Great Lakes — with retention times of up to nearly 200 years — also grows.

While prevention is ultimately the key to avert pollution, many potential contaminants have already made their way into the environment and the Great Lakes. Public water utilities are in a position to take the first steps in reducing exposure by collecting data and possibly implementing controls, but managing the sheer number of substances is a challenge. With hundreds of different compounds detected in surface waters today, most of them unregulated, it is critical to identify priority chemicals that pose the greatest threat to the health of the Great Lakes and the 40 million people who depend on them as a source of drinking water. A growing number of studies are raising concern about the toxicological effects of these chemicals on the body’s endocrine system — which controls key functions such as growth and development, metabolism and reproduction. Once priority substances are identified, it will be equally critical to put control strategies in place along various points in the Great Lakes water cycle in order to lessen chemical loading and exposure to these so-called “contaminants of emerging concern.”

This report implements a practical framework to rank chemicals previously detected in national waters that are representative of their occurrence in the Great Lakes. The methodology was developed by environmental engineers from Michigan State University and examines surface as well as treated drinking water. The ranking identifies the top 20 emerging contaminants for surface water and top 20 chemicals for purified drinking water based on occurrence, ecological and human health impacts, and the treatment capabilities of water utilities. These compounds include a variety of everyday chemicals such as hormones, synthetic musks, antibiotics, pharmaceuticals, antimicrobials and preservatives, UV blockers, flame retardants, pesticides and chemicals related to plastic production. The report also highlights current voluntary efforts undertaken by municipalities to monitor for unregulated emerging
contaminants on the shores of southern Lake Michigan. Based on data collected by local water utilities in southern Lake Michigan, the surface water there contains six of the top 20 priority chemicals, among them flame retardants and a popular cholesterol-lowering drug. Among the top 20 priority chemicals analyzed in finished drinking water, water suppliers detected a single flame retardant.

Municipalities that conduct water monitoring or studies of emerging contaminants include Milwaukee and Chicago, as well as the Central Lake County Joint Action Water Agency, which supplies drinking water from Lake Michigan to communities in northern Illinois. Smaller communities such as Gary, Ind. and Racine, Wis. are currently not voluntarily monitoring for emerging contaminants because of the absence of clear guidance for how to do so. The case studies highlight the need for comprehensive and collaborative initiatives to understand the fate of emerging contaminants in the Great Lakes water cycle that can serve as a model for municipalities, and to prioritize interim controls to protect Great Lakes water. Establishing clear prioritization rankings for emerging contaminants can serve as a basis for utilities to implement focused and lower-cost monitoring programs. In addition, rapid prioritization of the thousands of known compounds could hasten the work of regulatory agencies to develop analytical methods and conduct critical risk assessments. Finally, with a charge to develop lists of “chemicals of mutual concern” under the newly renegotiated Great Lakes Water Quality Agreement, the governments of the U.S. and Canada should draw on prioritization methods to set binational objectives for controlling those contaminants deemed highest priority.
Introduction

Contamination of water resources and the drinking water that flows from our taps has long topped the list of environmental concerns for the American public (Pacific Institute, 2012). Indeed, more than 75 percent of Americans surveyed in Gallup’s 2011 Environment poll stated they are concerned a great deal or a fair amount about the health of our water — a broad category that includes contamination from toxic waste, pollution of rivers, lakes and reservoirs, and pollution of drinking water (Gallup Poll, 2012). Communities across the Great Lakes region have been especially concerned about protecting the water resources that shape and enrich their lives. Home to vibrant ecosystems and unrivaled natural beauty, the Great Lakes provide endless recreational opportunities and supply drinking water to more than 40 million people in the region. The sensitivity of current analytical methods has allowed for the detection of chemicals in the water at extremely low concentrations — measured at parts per trillion (Kolpin et al., 2002; Focazio et al., 2008). Simply detecting chemicals in water does not equate to negative health effects. Yet, as scientists conduct more and more studies about the chemicals found in the water and the media continues to report on these findings, the public struggles to understand the implications of this new information and how it affects them. There is ample reason to be concerned: many questions remain unanswered and a lack of knowledge is no assurance that our water is safe. So we are left to wonder which chemicals do we really need to be concerned about? What exactly is being found in our drinking water? How did it get there and what should we be doing about it?

Addressing these questions requires a significant outlay of time, effort and money from researchers, regulatory agencies, water utilities and the public. The sheer number of chemicals in use today and their interactions with the environment and each other paint a complex and challenging picture. The effects of climate change also must be investigated and considered. But this is no excuse for inaction. By prioritizing which chemicals potentially pose the biggest threat to our natural resources and the people who rely on them, we can begin to address concerns about emerging contaminants already in the water and put in place appropriate controls to reduce the exposure to these chemicals and their ability to cycle through the environment. Prioritization represents just one element of a framework that promotes prevention. The approach should be more comprehensive, and include the ability to prevent the use and production of chemicals not yet brought to market before we are certain that they will not harm the environment or people’s health. In the interim, focusing on top-priority chemicals rather than attempting to monitor for hundreds — if not thousands — of compounds will allow utilities to use their resources
more effectively, and to develop consistent sampling protocols, rely on similar standards and methods, and work collaboratively. This in turn will advance the understanding about the occurrence and fate of contaminants as they move through the water cycle.

Concern about emerging contaminants in the water is valid and a precautionary approach is warranted. We note that some exposure to these chemicals is unavoidable, and many of them — caffeine, the bug spray DEET — are now ubiquitous in the environment. It is unrealistic to propose to regulate all of them as water contaminants. This underscores the need to prevent hazards, rather than react to them by installing expensive end-of-pipe controls. The fact that caffeine is detected in the water doesn’t mean we must adopt new water standards regulating caffeine. It is absolutely critical, however, to identify those emerging contaminants present in the environment that are most likely to pose a threat to people and wildlife — given the uncertainty in the data — and then work to understand the impacts and gather information for a more thorough risk assessment and possible regulation. Traditionally, depending on the chemical’s usage, the burden of proving a chemical is harmful lies with either the U.S. Environmental Protection Agency or the U.S. Food and Drug Administration — not the manufacturer. The burden is also on the public that may be exposed to these chemicals unintentionally. In some situations, the government has trained its focus on specific chemicals in response to the public and public interest groups that have voiced concern. For any chemical, though, the process of evaluating toxicity, risk and impacts, and making and vetting regulatory decisions, requires time, resources and political will. Further, the process assesses a single chemical and therefore does not take into account real-world hazard and exposure scenarios. These scenarios include a combination of exposure to low-level chemical mixtures, duration of exposure, chemical concentration or dose, route, and relevant human and ecological processes that may be affected at multiple levels of biological organization.

Unfortunately, the chemical manufacturer is not required to test these various aspects. Nor does the current framework incorporate evaluation of effects relating to exposure to mixtures or transformation products — compounds that form as a result of chemical reactions during the treatment process — whose toxicity and interactions with each other and biological systems are largely unknown. Fortunately, the U.S. EPA Great Lakes National Program Office, working in collaboration with National Oceanic and Atmospheric Administration, U.S. Fish and Wildlife Service, U.S. Geological Survey and Environment Canada, launched a comprehensive emerging contaminant surveillance and monitoring program to document the presence of these chemicals in water, air, sediments, fish and birds, and identify effects these chemicals might have. The outcome of this work, and how the data it generates will be used, will be of significant importance in the context of implementing the new Great Lakes Water Quality Agreement and ideally lead to binational coordination to address chemicals — rather than leave it to the respective countries to address chemicals detected in the Great Lakes. Implementation of Annex 3 of the agreement, titled “Chemicals of Mutual Concern,” will advance comprehension of the issues, and develop and implement prevention strategies through scientific and public engagement. EPA is also currently developing a strategy to assess exposure to and effects of toxic substances in the Great Lakes based on their mode of action and chemical type, rather than dealing with each individual chemical — a daunting task. This work sets the stage for a national conversation about chemicals of emerging concern detected in waters across the country.

This report does not attempt to put forth a complete risk assessment, nor develop toxicological profiles for potential chemicals of emerging concern in the Great Lakes region. It does not provide specific recommendations on national toxics policy reform. Instead, it proposes ways in which utilities and regulatory agencies can take steps now to address issues that will inevitably face them in the near future.
Ongoing discussions about changes to the federal Toxic Substances Control Act and the potential for listing contaminants in wastewater discharge permits will affect how utilities come into compliance with new rules. Attention to prioritizing potential contaminants will help prepare them to implement appropriate changes. Steps that utilities can take now include monitoring for a critical subset of chemicals that pass through water treatment facilities, and developing an understanding of the trends in the transport and fate of these potential contaminants. This can be accomplished by establishing common sampling protocols to study occurrence and fate of contaminants such that the data can be used more effectively, and shared with scientists, regulatory agency staff and other stakeholders. Assessing the problem through monitoring is the first step to identifying appropriate control strategies.

The first step is to identify priority emerging contaminants, which will be done in this report using a prioritization method developed by scientists working in the Department of Civil and Environmental Engineering at Michigan State University. The prioritization framework addresses source water and finished drinking water separately based on a combination of criteria, among them human health, ecological health impacts, occurrence of the chemical in the water, and water treatment capabilities (Kumar and Xagoraraki, 2010). The prioritization framework is comprehensive, allowing users to customize for different geographic locations, or give more weight to ecological impacts for waterways heavily impacted by stormwater runoff or wastewater effluent discharges. It compiles existing data on all chemicals included in the evaluation and also identifies data gaps for future research. Previously published in a peer-reviewed scientific journal, this would be the first time this ranking method would be utilized by real-world public water utilities. The prioritization method is described in detail in the following sections of this report.

The list of chemicals evaluated and prioritized originated from a literature review of studies conducted between 2001 and 2009 in a variety of sites in the United States, with a subsequent compilation of all the toxicological data available at the time. The chemicals listed are found in a wide geographic range, but this report focuses on Lake Michigan waters and also presents water quality data collected by water utilities in the most densely populated and impacted areas around southern Lake Michigan, including the Chicago and Milwaukee metropolitan areas. Some of the water utilities in this region are already involved in voluntary monitoring efforts and studies, and their findings further highlight the need to establish common guidelines and priorities. The data they collect could be useful to researchers in academia and regulatory agencies and, of course, of interest to the general public. Future coordination among these groups will be critical to addressing the issue of emerging contaminants, and such a prioritization approach could be expanded to include other parts of the Great Lakes region.
Water Use Cycle in the Great Lakes

The Great Lakes contain 20 percent of the world’s surface freshwater supply and support complex ecosystems within and near their shores. The water budget in the Great Lakes incorporates many factors: the inflows — precipitation, tributary flows, runoff and groundwater infiltration; and outflows, such as evaporation, diversions, consumptive uses, and flow to the Atlantic Ocean through the St. Lawrence Seaway. The connecting channels serve as both inflows and outflows as they facilitate the flow of water from one lake to the next. In addition to this hydrological water cycle is another water cycle that involves the use of the Great Lakes’ natural surface waters as both a source of potable drinking water and recipient of treated sewage discharges from residential and commercial users. This water use cycle is shown in Figure 1. Each of the circles represents a stage in the water cycle where we can make a choice about implementing strategies to prevent contamination. The Great Lakes’ long retention times mean these discharges slowly circulate around the lakes — for up to a century in Lake Michigan — making pollution control in the Great Lakes Basin especially critical.

Emerging contaminants in the Great Lakes affect ecosystems and threaten a major drinking water source for 40 million Great Lakes residents in the U.S. and Canada

Natural surface waters — or source waters — provide habitat for aquatic life and a place for people to enjoy and recreate. The chemicals of most concern are those having the potential to cause ecological impacts, such as bioactivity, persistence and bioaccumulation in the environment. Although pharmaceutical and hormone compounds tend to have a much shorter half-life in the environment than some chemicals, these compounds are continuously entering the water — potentially leading to chronic exposure for aquatic species. Furthermore, because chemicals such as pharmaceuticals and pesticides are designed to target specific receptors and biological pathways, they act as potent agents that can affect fish and other aquatic and terrestrial organisms even at very low concentrations (Parrott and Blunt, 2005; Kidd et al., 2007). Persistent compounds can be transported long distances, affecting ecosystems far beyond the immediate release zones; bioaccumulative chemicals can pose a health risk to humans through fish consumption.
Sources of contaminants

These chemicals enter the water via a variety of point sources — or regulated pipe discharges, and non-point sources — which are diffuse and hard to quantify. Discharges from wastewater facilities carry many pharmaceuticals and personal care product residues. Drugs that are partially metabolized by people are excreted into the municipal waste stream. A portion of the medicines that are sold go unused and may end up down the drain, as do cosmetic products, soaps and other household cleaning products. As conventional treatment is not designed to remove these types of compounds, some remain in treated wastewater at trace concentrations and enter the surface waters when the effluent is discharged into the lakes. Similar to wastewater effluent, combined sewer overflows (CSOs) can also ferry drugs and personal care products. Although the volume of CSOs flowing into waterways is much lower than treated effluent, their contaminant concentration is much higher because this overflow stream does not receive any treatment. Agricultural and urban runoff is another contaminant source to waterways, as it can carry insecticide and herbicide residues as well as veterinary drugs. Other potential pathways for emerging chemicals of concern include: atmospheric deposition, in which pollutants are transferred from air to water; and direct release from sunscreens, lotions and other cosmetics that people apply before swimming. Plastic litter, which can transport and leach chemicals into surface waters, is yet another source. Because of the lack of coordinated efforts to track this information and monitor the loading of these chemicals into the water, the relative contributions from these sources are difficult to quantify.
Drinking water treatment: Can we make it cleaner?

The next stage of the water use cycle is the withdrawal and treatment of source water for human consumption and use. This is the stage where elimination or control of emerging contaminants might occur because water is filtered, disinfected and tested at the water treatment facility. Although conventional treatment was not necessarily designed to remove organics, some of the compounds are removed with varying degrees of success by chlorine disinfection, UV or ozone treatment. Treatment processes may result in simply converting one chemical to another, however, rendering it either more or less toxic. One of the questions water suppliers can address, starting with priority compounds, is to look at how well the current treatment system removes the chemical of concern from the water, identify and measure subsequent transformation products, and look for potential indicator compounds that might be representative of a group of chemicals. Characterization and optimization of the treatment process can be done within the existing infrastructure. Also, by monitoring for these compounds, water supply utilities can assist in gathering occurrence data to quantify exposure for risk assessment. It should be stressed, however, that relying on such end-of-pipe controls is inadequate and must be accompanied by a strong regulatory framework focused on prevention at the source. The prevention framework would create efficiencies in the system that would also aim to reduce the demands placed on treatment plants.

Two sides of residential water use: Potential for exposure and ways to reduce contaminants in the future

Human exposure to chemicals in drinking water occurs through consumption and adsorption through skin. Here, chemical contaminants of potential concern should be prioritized based on their intrinsic hazard as well as physical and chemical properties discussed above. This is currently done on a chemical-by-chemical basis, but chemical mixtures must be considered as well in order to provide a more realistic representation of exposure. Deleterious health outcomes associated with these contaminants could include carcinogenicity, mutagenicity, developmental effects, immunotoxic effects, endocrine-disrupting effects, and effects on the unborn fetus. Toxicity data are limited for many of these chemicals, which makes hazard and risk assessments challenging. Developing a priority short list, and a robust monitoring program to characterize the occurrence and fate of these chemicals, will allow for a more rapid risk assessment.

Preliminary assessments indicate that many pharmaceuticals found in the environment and in treated drinking water may not pose a serious risk for healthy human adults (Snyder et al., 2009; Bruce et al., 2010; Schriks et al., 2010). One study of pharmaceuticals in the drinking water supply shows that, to get an equivalent of the minimum daily therapeutic dose of the active pharmaceutical ingredient based on predicted environmental concentrations, one would have to consume a massive volume of water. For example, a single dose of atorvastatin — the cholesterol-lowering medication, Lipitor, the best-selling drug in the history of pharmaceuticals (Associated Press, 2011), one would have to drink an average of 2 liters of water per day for 1,721 days (Kostich and Lazorchak, 2008). For the reproductive hormone estradiol, similar analysis showed it would take 406 days to ingest a single dose (Kostich and Lazorchak, 2008). An analogous calculation for caffeine, ubiquitous at trace levels in the water, showed that to consume a dose equivalent to a 5-ounce cup, one would have to drink 2 liters per day for 45 years (Toot-Levy et al., 2010). This perspective may help calm the public’s fears about pharmaceuticals found at trace levels in their drinking water. Yet it still raises concern about the robustness of the regulatory process to address serious problems when they arise and, more importantly, to prevent serious threats. The fact that some compounds found in the environment and in drinking water today are innocuous does not mean
that other chemicals out there do not pose a significant potential risk. There is still much that is not fully understood about long-term exposure to complex mixtures of emerging contaminants, including their synergistic effects, as well as formation of, fate, and exposure to transformation and degradation products (de Jongh et al., 2012). Furthermore, various subgroups of the population — young children or people with a compromised immune system — may be more sensitive to the hazard of contaminants.

Caffeine is hardly a chemical we should be worried about, yet it is often measured as a marker of human sewage contamination and serves as an indicator of other contaminants (Handwerk, 2012) that may be found in water. Epidemiological studies for some endocrine-disrupting chemicals, such as atrazine, point to links between exposure through drinking water and human health (Swan et al., 2003; Chevrier et al., 2011; Cragin et al., 2011). It should be noted that the widely used herbicide atrazine — primarily used on row crops and applied most heavily in the Midwest — is a regulated drinking water contaminant in the United States. Notwithstanding the presence of a drinking water standard, atrazine continues to contaminate the waterways while evidence mounts that atrazine levels measured below the maximum allowable contaminant level can have endocrine-disrupting effects. EPA plans to review the registration of atrazine starting in 2013, but the European Union has taken more aggressive action to ban its use and reduce water contamination. This further suggests that the current regulatory framework may not be protective enough of drinking water, highlighting that end-of-pipe controls are insufficient and that source control — such as elimination of the chemical in the marketplace — is necessary. Furthermore, concerns exist about the potential development of superbugs from antibiotic and antimicrobial disinfectant compounds present in the water (Kostich and Lazorchak, 2008). Compounds such as triclosan are coming under increasing scrutiny as studies point to potential toxicity and effects on the functions of skeletal and cardiac muscle tissue (Veldhoen et al., 2006; Zorrilla et al., 2008; Cherednichenko et al., 2012). Used municipal water and sewage waste carries these compounds down the drain from kitchen sinks and bathrooms to wastewater treatment facilities, with little thought given to their fate or their effect on human health and the environment.

Improving infrastructure to reduce emerging contaminant releases into the Great Lakes

The wastewater infrastructure in the Great Lakes region is in dire need of improvement and updates. As municipalities work to update their pipes and eliminate combined sewer overflows that carry pathogens, they will also reduce the amount of chemicals in stormwater runoff that currently enters the waterways. By reducing inflow and infiltration, the facilities will reduce the volume of water they must treat as well as the amount of contaminants that can trickle in with that water through leaky pipes. Developing ways to address nutrient pollution can also potentially increase removal efficiencies for other contaminants, such as pharmaceuticals. At the national level, the U.S. Environmental Protection Agency has developed an Integrated Municipal Stormwater and Wastewater Planning Approach Framework, which was released in June 2012 (U.S. EPA, 2012). The framework will guide municipalities in developing plans to achieve the human health and water quality objectives of the federal Clean Water Act, and facilitate the use of sustainable and comprehensive solutions. An ability to focus on a short list of priority compounds and to incorporate this into the overall facility’s planning process would allow municipal wastewater treatment plants to begin addressing this problem right now and, at the same time, take steps toward protecting Great Lakes water. The renegotiated Great Lakes Water Quality Agreement of 2012, a binational agreement between the U.S. and Canada, further addresses protecting the Great Lakes from chemical pollution. Annex 3, “Chemicals of Mutual Concern,” outlines the steps through which human health and the environment will be protected by cooperative and coordinated measures to reduce the anthropogenic release of chemicals of mutual concern to the waters of the Great Lakes (Canada and United States, 2012).
Opportunities to reduce sources of contaminants in the water

Ranking methodologies to prioritize potential chemical contaminants in drinking water must consider detection of their frequency in the finished water, how effectively they are removed from source water, and their potential to affect human health. A variety of chemicals are introduced into the water cycle via domestic and commercial water use. These include unused or partially metabolized medicines that are flushed down the drain, personal care products such as cosmetics and cleansers that rinse off in the shower, and detergents and other cleaning products. Additionally, chemicals found in everyday products in people’s homes, in dust and in fabrics, also end up in wastewater. Reducing the entry of waste into the waste stream is another potential control strategy at this point in the water cycle, and can be achieved through proper waste disposal policies and further educational outreach to the public. Water utilities are in a unique position to provide information to their customers about the water cycle, how contaminants may be introduced and what can be done to protect precious Great Lakes water resources. Consumer demands can often drive companies to develop alternatives that are environmentally friendly and avoid the use of potentially harmful chemicals in their products.

As the ultimate pollution control strategy is one that focuses on prevention, extended producer responsibility statutes can help shift the burden to the manufacturer rather than the taxpayers to assess a chemical’s potential hazard and fund monitoring and remediation if necessary. This will give manufacturers an incentive to come up with safer chemical products, and represents yet another option in the spectrum of potential controls for contaminants entering the Great Lakes.

Wastewater treatment: Returning water to the Great Lakes

Finally, the water flows to municipal wastewater facilities for treatment before it is discharged back into the Great Lakes — sometimes via outfalls discharging directly to the lakes, sometimes via outfalls discharging to streams and rivers that feed the Great Lakes. Similar to drinking water treatment, the wastewater treatment processes were not originally engineered to remove trace organic contaminants. Advances in treatment technology today allow at least partial removal, however. Wastewater treatment plants are logical points for implementation of control strategies because they discharge treated effluent into the Great Lakes and produce biosolids that can also hold contaminants. As chemicals move through the treatment process, some of them partition into sludge that is applied to agricultural fields as biosolids, or fertilizer, thereby potentially reintroducing contaminants into the environment. In addition, wastewater effluent is a major contributor to emerging contaminant releases into Great Lakes surface waters, and a heavily monitored point source. Control strategies may include: developing coordinated monitoring programs; gathering data to assess and optimize removal efficiencies and characterize transformation products; and partnering with local organizations to provide opportunities to collect items, such as unused medication, to eliminate them from the waste stream altogether.

The lists of priority contaminants for source water might differ from those for finished drinking water because of the differences in prevalence patterns, and relative differences in the evaluation of human health and ecological effects. Still, many similar steps can be taken by wastewater utilities to address these issues. By focusing on a short list of chemicals, the facilities can more efficiently evaluate treatment alternatives under different flow conditions and establish seasonal trends, if they exist. A priority list is critical to manage the current chemical soup and is an essential part of any preventive chemical regulatory framework to assess new chemicals, or even new categories of substances — such as nanomaterials — bound for the market. Regulatory agencies will still need to define priorities and incentives for manufacturers to develop safer alternatives.
Prioritization Process

The ability to detect compounds at trace levels (parts per trillion or ng/L) relies on relatively recent technologies and analytical methods. Similarly, technological advances in chemistry and biotechnology result in new compounds being synthesized at an unprecedented rate, most of which end up in the environment and in waterways. There are more than 85,000 chemicals in the federal Toxic Substance Control Act inventory (U.S. EPA, 2011) and more than 2,200 of those are high-production volume chemicals, with 1 million-plus pounds produced annually (U.S. EPA, 2012a). These chemicals range from precursors used in industrial manufacturing to preservatives used in consumer products. Since the registering of pesticide products began in 1947, there are now nearly 20,000 registered pesticide products, including combinations of 1,221 active ingredients (U.S. EPA, 2012b). The EPA regulates these under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Additionally, the U.S. Food and Drug Administration has approved more than 56,000 pharmaceuticals for human use (U.S. FDA Center for Drug Evaluation and Research, 2012) and more than 1,000 products for veterinary use (U.S. FDA Center for Veterinary Medicine, 2012) that are eventually released into the environment as excreted waste, either unprocessed or as metabolites. When new pharmaceuticals are developed, the FDA is responsible for the registration and approval of their production and use. This process requires assessment of human and environmental health risks associated with exposure to newly developed agents. The Canadian Environmental Law Association recently released a comprehensive report reviewing chemical management policies for the Great Lakes region on both sides of the border that can provide more information on the existing regulatory framework (Wordsworth et al., 2009).

A layer of complexity is added with chemicals used in a variety of consumer products. For example, triclosan has traditionally been regulated as a pesticide by EPA under FIFRA, but there are now more than 140 kinds of consumer products that include triclosan as a component. FDA regulates triclosan differently depending on its use: when incorporated for health purposes in products such as toothpaste, it is designated a pharmaceutical; when intended for cosmetic purposes — deodorant, for example, it is regulated as a cosmetic; when intended for use in a household cleaner, it is regulated by EPA as a pesticide (Wordsworth et al., 2009). The ubiquitous nature of triclosan and some other compounds creates a challenge in regard to source identification and control. And, as the number of chemicals around us continues to grow, the potential for these chemicals to end up in the Great Lakes increases. The current risk assessment framework does not adequately capture some of the factors
associated with toxicity testing — such as length and mode of exposure, dose response, and a variety of endpoints. Meanwhile, a growing number of studies are raising concern about the toxicological effects of chemicals on the body’s endocrine system which, among other things, controls growth and development, metabolism and reproduction. Exposure to transformation products, metabolites and mixtures also is not addressed. The greatest challenge, perhaps, is the uncertainty and gaps in knowledge about exposure and hazard and, therefore, in the interpretation of data.

In contrast to the thousands of chemicals in use today, water suppliers are currently required to monitor for just 87 substances that fall within National Primary Drinking Water regulation under the federal Safe Drinking Water Act. There is also limited monitoring of compounds: a total of just 30 compounds for the 2013-15 monitoring program listed under the Unregulated Contaminant Monitoring Rule (UCMR). The UCMR includes chemicals that are under consideration for potential regulatory action. The current Candidate Contaminant List includes 104 chemicals and 12 microbial contaminants (Richardson and Ternes, 2011). Under the Clean Water Act, in addition to the conventional pollutants that require monitoring (e.g. total suspended solids, biochemical oxygen demand, pH, etc.) there are 65 chemicals or groups of chemicals listed as toxic pollutants and an additional 126 compounds listed as priority pollutants (U.S. EPA, 1979). Although these lists would seem to include a large number of chemicals, they represent only a fraction of chemicals in commerce that may pose a risk to the water supply. Furthermore, there seems to be little overlap between the regulatory frameworks for drinking water and wastewater utilities because different sets of contaminants are targeted. For the Great Lakes, this connection is critical. The Great Lakes and their tributaries serve as receiving waters for 1,448 municipal facilities discharging 4.8 billion gallons of effluent daily (Chemicals of Emerging Concern Workgroup, 2011), and 2,393 industrial facilities (U.S. EPA, 2010), reporting to the EPA’s Toxic Release Inventory, as well as a drinking water supply for more than 40 million people. There is an urgent need for a more comprehensive and integrated regulatory framework that can protect the nation’s water resources for both aquatic life and human consumption.

It is impractical and cost-prohibitive for water utilities to monitor thousands of chemicals, and standard analytical methods exist for only a handful of these compounds. This suggests that the burden related to chemical use should be shifted to the users and manufacturers so we have in place necessary toxicity information to show that substances are safe before entering the market. Prioritization is critical to guide long-term prevention, as is immediate action — such as monitoring, research and interim control mechanisms to reduce exposure. A number of approaches dealing with chemical waste and pollution and corresponding prioritization methodologies have been explored at state and national levels, as well as proposed by research groups. These include the Critical Materials Register developed by the Michigan Department of Natural Resources in 1987 (Michigan Environmental Protection Bureau, Environmental Services Division, 1987). The register is intended to identify chemicals that require reporting on production, use and release. The EPA developed a Waste Minimization Prioritization Tool (WMPT) in 1997 to assist in making decisions about waste management and waste minimization (U.S. EPA, 1997). Neither of these programs directly addresses water contamination, however. The Scoring and Ranking Assessment Model (SCRAM) for the Great Lakes looked at identifying priority pollutants. SCRAM is used to rank persistent, bioaccumulative and toxic organic compounds, but does not address pharmaceuticals and personal care products (Mitchell et al., 2002). Some prioritization methods have focused only on pharmaceuticals (Cooper et al., 2008; Kostich and Lazorchak, 2008; Roos et al., 2012), while others looked at one part of the water cycle — either at wastewater (Muñoz et al., 2008) or surface water (Arnot and Mackay, 2008; Schriks et al., 2010). Each of the proposed ranking systems
Water Quality Standards for Surface Waters and Drinking Water

The Safe Drinking Water Act (SDWA), originally enacted in 1974, requires the U.S. Environmental Protection Agency to produce National Drinking Water Regulations (U.S. EPA, 1974). Individual states can choose to adopt these or develop their own individual standards, provided they are at least as stringent as the recommendations. These standards must be met by all public water systems. The 1996 amendment of the SDWA created a process for evaluating new or emerging pollutants for inclusion in the regulations. The process for evaluating a contaminant begins with its inclusion on the Contaminant Candidate List (CCL) (U.S. EPA, 1997). The EPA develops this list and is required to make regulatory determinations on at least five CCL contaminants every five years. Regulatory determinations include an analysis of each contaminant’s potential for adverse effects, how widely it occurs, and if it presents a meaningful opportunity for health risk reduction. This results in a determination of whether the chemical should be regulated.

In the event there is insufficient data on the prevalence of a candidate contaminant on the current third iteration of CCL, the EPA may elect to include it on the Unregulated Contaminant Monitoring Rule (UCMR) list. The UCMR is updated every five years and provides a means to conduct sampling for up to 30 contaminants at a representative sample of public water systems. Data from the UCMR is used to inform regulatory determinations of CCL contaminants (U.S. EPA, 1997). Since 1996, EPA has evaluated 60 contaminants included in the first and second CCL and issued 20 regulatory determinations. Only perchlorate has been adopted into the national drinking water regulations. For the current CCL, the EPA reevaluated its process, employing a much broader evaluation of potential contaminants. This involved a preliminary screening of thousands of potential contaminants. EPA included 116 contaminants on the final CCL list; regulatory determinations are expected in 2013.

On the other end of regulatory efforts to protect water resources is the federal Clean Water Act (CWA) which, among other things, provides the framework for regulating the surface water quality of waters of the United States and celebrates its 40th anniversary this year. The CWA required the EPA to develop water quality standards; these are released as the national recommended water quality criteria. The authority to develop water quality standards in most cases lies with individual states or tribes. The process begins with a state or tribe assigning use designations — such as drinking water source, wildlife habitat or recreation — to each water body or segment. Designated uses may be uses that are already possible or goals for uses desired in the future. The CWA requires that, at a minimum, such use designations be inclusive of the “fishable/swimmable” interim goal stated in section 101 of the CWA. Once selected, these use designations are the ultimate guide for the development of water quality standards and subsequent regulation of discharges. In support of these use designations, each state or tribe may elect to adopt the national recommended water quality criteria or develop their own. At a minimum the water quality standards must support the use designations and be at least as stringent as the recommendations, or be scientifically defensible. Prior to submission to the EPA for final approval, the draft standards must be subject to public review and a comment period. Once submitted, the EPA can choose to approve the water quality standards. The standards would become enforceable pending state or tribal legislative approval and inclusion in an enforcement tool, such as a national pollution discharge elimination system (NPDES) permit. In the event that EPA denies the proposed water quality standards, the state or tribe will have an opportunity to adopt the required changes provided by EPA, or EPA will proceed with promulgating standards on their own. Regardless of how the standards are promulgated, they serve as the regulatory tool ensuring that all authorized discharges are conducive to meeting the use designations for the water body.

Unlike the SDWA, the CWA does not as explicitly indicate how new or emerging pollutants are evaluated and included in individual state or tribal standards. There are several mechanisms in place, however, to ensure due consideration is given to new or emerging pollutants. Section 303(c)(1) requires each state or tribe to review its standards at least every three years. It is during these triennial reviews that states or tribes are required to evaluate their standards based on monitoring data, new research, or requests from the public, environmental groups or industry in each state (U.S. EPA, 1994). In addition to these state or regional considerations of new and emerging pollutants, new potential pollutants can also be added at the national level through the priority pollutant list. If a new contaminant is added to the priority pollutant list, a state or tribe would have to evaluate that pollutant for inclusion in its water quality standards during the triennial review. Pollutants on the priority pollutant list were evaluated for inclusion based on the following criteria: 1) Was included on the list of toxic pollutants, 2) Has methods developed to quantify its presence, 3) Has been found in water with a frequency of at least 2.5 percent of the time, 4) Was produced domestically in substantial quantities. During reevaluation, if a priority pollutant no longer meets these criteria it can be removed. Three have been removed since its inception. Once a state or tribe has completed a triennial review and incorporated appropriate revisions, the updated standards are subject to the same EPA review and public comment processes as the initial water quality standards.
addresses a particular aspect of prioritization, answering specific questions regarding toxicity, the need for more research, or addressing a particular class of chemical species.

The main objectives for establishing a priority ranking system for the Great Lakes is to (1) protect Great Lakes surface water and ecosystem health, (2) protect drinking water and human health, and (3) identify appropriate control strategies for regulatory agencies, water utilities, producers and end users. For the analysis in this report, we utilized a multi-attribute ranking system based on utility theory developed by Irene Xagoraraki and Arun Kumar (Kumar and Xagoraraki, 2010) at Michigan State University. This particular method was chosen because it addresses concerns relevant to both surface and drinking water, and evaluates broad categories of chemicals. The proposed framework prioritizes chemicals for surface water and drinking water separately — in recognition of different exposure pathways, and addresses ecological and human health impacts.

The ranking system addresses a variety of chemical classes such as pharmaceuticals (including hormones and antibiotics), personal care products, pesticides, and other industrial chemicals known to cause endocrine disruption. This work was sponsored by the Emerging Opportunities Program at the Water Research Foundation, which is devoted to drinking water research that can provide practical solutions to current and future challenges facing the drinking water community. The next phases of this program will focus on fine-tuning the prioritization framework through stakeholder engagement nationwide. With a prioritization framework already in place, however, water utilities in the Great Lakes region have an opportunity to follow it as a guide for piloting water monitoring for emerging contaminants now, rather than wait three- to four more years before the next phases of the research project are completed. This provides an opportunity to test proposed prioritization methods and identify which factors might be necessary to accommodate site-specific conditions.

The proposed ranking system calculates scores based on the available data for each of the chemicals of concern based on four main criteria: occurrence, treatment, ecological effects and human health effects. Criteria include categories and sub-categories depicted in Figure 2. Occurrence comprises two categories: prevalence, or how frequently a compound is detected; and magnitude, the concentration of the chemical in the water. Treatment criterion considers only one category: how efficiently the compound is removed by conventional treatment or, more specifically, what percentage of the parent compound is absent from the effluent compared to the influent. Accounting for transformation products produced during treatment would, of course, improve our understanding of treatment effectiveness. Ecological effect criteria include: bioaccumulation and ecotoxicology (based on acute toxicity to aquatic indicator species — fish, daphnids and algae). The human health component includes: teratogenicity (effects on the fetus through mother’s exposure), and all other effects (sub-categories include carcinogenicity, mutagenicity, fertility impairments, central nervous system effects, developmental effects, immunotoxicity and endocrine disruption). The ranking is conducted separately for surface water and finished drinking water and based on published data available to date. Surface water rankings consider occurrence, and ecological and human health impacts. Drinking water rankings evaluate occurrence, treatment and human health criteria. All criteria and categories are weighted equally, in order to avoid bias in the overall ranking.
The resulting prioritization and identification of the top-ranked compounds can guide the action of utilities or regulatory agencies — either through the monitoring and removal of the compounds, or a proper risk assessment of the chemicals based on the monitoring data that is collected. Also, the framework provides an uncertainty score where data is missing, which helps to identify compounds requiring further investigation. Rankings were calculated for 100 compounds, based on those that were reported as detected in 23 studies conducted across the United States from a range of sources. The top 20 chemicals for surface water and drinking water are listed in Table 1. Categories of contaminants include: Hormones, Synthetic Musks, Antibiotics, Pharmaceuticals, Antimicrobial Disinfectants & Preservatives, UV blockers, Flame Retardants, Pesticides, and Plastic Production-related (BPA &
phthalate). Two chemicals, Lindane and Bis(2-ethylhexyl)phthalate, appear on both lists. Both are, in fact, regulated drinking water contaminants and listed on the priority pollutant list. Yet, the existence of water quality standards by itself does not preclude the discharge and occurrence of these contaminants in the water and the risks they pose to ecosystem and human health.

<table>
<thead>
<tr>
<th>Overall rank for stream water/source water occurrence, ecological effects, human health</th>
<th>Overall rank for finished drinking water occurrence, treatment, human health</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mestranol – hormone</td>
<td>Mestranol – hormone</td>
</tr>
<tr>
<td>Bisphenol A (BPA)** – plastic production chemical</td>
<td>19-norethisterone – hormone</td>
</tr>
<tr>
<td>AHTN (trade name: Tonalide)** – synthetic fragrance</td>
<td>Demeclocycline – antibiotic</td>
</tr>
<tr>
<td>Tris (dichloroisopropyl) phosphate** – flame retardant</td>
<td>Flumequine – antibiotic</td>
</tr>
<tr>
<td>Estrone* – hormone</td>
<td>Tri(2-butoxyethyl) phosphate** – flame retardant</td>
</tr>
<tr>
<td>Tri(2-butoxyethyl) phosphate** – flame retardant</td>
<td>Methylbenzylidene camphor – UV blocker</td>
</tr>
<tr>
<td>ADI (trade name: Celestolide) – synthetic fragrance</td>
<td>Estriol – hormone</td>
</tr>
<tr>
<td>Ethylhexyl methoxycinnamate – UV blocker</td>
<td>Bis(2-ethylhexyl)phthalate† – plasticizer</td>
</tr>
<tr>
<td>Musk xylene – synthetic fragrance</td>
<td>17α-estradiol – hormone</td>
</tr>
<tr>
<td>Musk ambrette – synthetic fragrance</td>
<td>Cis-androsterone – hormone</td>
</tr>
<tr>
<td>Bezafibrate – cholesterol drug</td>
<td>Equilenin – hormone</td>
</tr>
<tr>
<td>Propylparaben – cosmetics preservative</td>
<td>Equilin* – hormone</td>
</tr>
<tr>
<td>Linuron – herbicide</td>
<td>Methyl parathion – insecticide</td>
</tr>
<tr>
<td>HHCB (trade name: Galaxolide)** – synthetic fragrance</td>
<td>Triclosan – antibacterial</td>
</tr>
<tr>
<td>Atorvastatin – cholesterol drug</td>
<td>Ciprofloxacin – antibiotic</td>
</tr>
<tr>
<td>Lindane† – insecticide, pharmaceutical</td>
<td>Norfloxacin – antibiotic</td>
</tr>
<tr>
<td>17β-Estradiol* – hormone</td>
<td>Oxytetracycline – antibiotic</td>
</tr>
<tr>
<td>Benzophenone-3 – UV blocker</td>
<td>Sulfathiazole – antimicrobial</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl)phthalate† – plasticizer</td>
<td>Warfarin – anticoagulant drug</td>
</tr>
<tr>
<td>Gemfibrozil** – cholesterol drug</td>
<td>Lindane† – insecticide, pharmaceutical</td>
</tr>
</tbody>
</table>

Table 1. Top 20 chemicals considered contaminants of emerging concern in source and drinking water.
* Compounds listed in the UCMR 3 for monitoring in 2013 by water suppliers
† Compounds in the National Primary Drinking Water Regulations and listed on the Priority Contaminant List
** Compounds detected in southern Lake Michigan and finished drinking water from Lake Michigan.

**Understanding human and ecological toxicity**

Risk assessment involves understanding exposure to, and the hazard of, a given chemical. Consideration of a chemical’s hazard or toxicity to human health encompasses evaluations of effects on a host of endpoints within the human body. These include the functioning of the nervous system, endocrine system and immune system. The chemical can also affect fertility or cause developmental problems, be carcinogenic or mutagenic. Another endpoint that must be evaluated is the impact the chemical might have on the developing fetus of a woman exposed to the chemical, called the teratogenic effect.

Because of the complexity of ecological systems, ecotoxicity is typically evaluated in a subset of indicator organisms by looking at acute and chronic toxicity. Acute toxicity identifies a lethal dose for 50 percent of the sample, while chronic toxicity examines adverse effects associated with exposure for 50 percent of the sample. These include effects on development, reproduction and survival. Bioaccumulation is yet another factor used in assessing ecological health, and occurs when an organism removes the toxin from its body slower than it is absorbed. In aquatic food webs, bioaccumulation often leads to biomagnifications and can result in an additional source of exposure to the chemical among people via fish consumption.
Lake Michigan has a retention time of 99 years, the second longest after Lake Superior. Since the production of synthetic chemicals took off following World War II, we have yet to see a complete turnover of Lake Michigan’s waters. Halfway through the cycle, however, we are beginning to see alarming trends in regard to the multitude of chemicals found in our waterways and to realize the complexity of the problem facing Lake Michigan and communities living along its shorelines. Southern Lake Michigan, in particular, is one of the most urbanized and industrialized areas in the entire Great Lakes Basin, home to approximately a third of the Great Lakes population (U.S. EPA Region 5, 2012). The emerging contaminant loading that comes from municipal and industrial wastewater, stormwater runoff and other sources affects water quality, contributes to continuous contaminant exposure for aquatic species, and risks contaminating the drinking water supply. Without clear guidance and priorities, or adequate resources, few communities in the Great Lakes Basin are in a position to develop extensive water monitoring programs, however.

Risk assessment is necessarily a function of exposure to, and hazard of, the chemical in question. Before risk assessment can be conducted by any organization, it is necessary to establish the exposure by documenting occurrence of the chemicals in the water and other pathways in conjunction with toxicity studies. Water utilities process billions of gallons of water and wastewater daily and are thereby in a unique position to develop monitoring programs to document occurrence and exposure. While it is not feasible to survey for all the chemicals that could be present, those ranked high on the priority list should be the focus of monitoring programs to assist in the data collection required to conduct a proper risk assessment. This information can advance the understanding of the fate of the contaminants as they move through the treatment facility, and facilitate the development of control removal strategies that will protect regional water resources and ensure the highest water quality. The information can also be used to develop educational tools for the community they service.

This section of the report highlights some of the voluntary monitoring and research activities municipalities in southern Lake Michigan have undertaken to address this issue (Figure 3). These include the cities of Chicago and Milwaukee and their respective metropolitan areas, as well as several of the smaller municipalities in those areas. Although the facilities serving the major metro areas have been able to develop and implement monitoring programs and collaborate with academic groups, smaller municipalities are challenged by a lack of resources and guidance about how to address the situation.
Chicago, Ill.

Metropolitan Water Reclamation District of Greater Chicago (MWRD) – The district owns and operates the world’s largest water reclamation plant — the Stickney Water Reclamation Plant in Cicero, Ill. — in addition to six other plants and 23 pumping stations, treating an average of 1.4 billion gallons of wastewater each day overall. The effluent from the three largest plants is discharged into the Chicago Area Waterway System (CAWS), a network of streams and canals that includes the Chicago River and the Calumet River system and connects Lake Michigan to the Mississippi River watershed. After an audacious engineering project more than a century ago to reverse the flow of the Chicago River in order to protect the Lake Michigan drinking water supply from sewage, effluent now flows down the Mississippi River to the Gulf of Mexico. Given current proposals to restore the hydrological separation between Lake Michigan and the Mississippi River basins to prevent the flow of invasive species between the two basins, Chicago’s treated wastewater may flow into Lake Michigan again in the future. This would raise the specter of trace organic contaminants, such as pharmaceuticals and personal care products that may not have been removed by conventional treatment, appearing in the drinking water supply. The district has a Monitoring and Research Department that conducted voluntary semiannual monitoring in 2010 and 2011 of about a...
dozen emerging compounds — ciprofloxacin, codeine, diazinon, diphenhydramine, fluoxetine, gemfibrozil, ibuprofen, naproxen, thiabendazole, triclocarban and triclosan — in their influent, effluent, sludge and waterway samples. They also conduct bimonthly monitoring of nonylphenols and bisphenol A in the network of canals and streams where the effluent is discharged. Their sampling sites included stations on the: North Branch Chicago River, Chicago Sanitary and Ship Canal, North Shore Channel, Des Plaines River, Higgins Creek, Salt Creek, West Branch DuPage River, Little Calumet River, and the Calumet-Sag Channel. The district also collaborates with academic institutions to study the impacts of bioactive chemicals on aquatic species in effluent-affected streams (Barber et al., 2011), as well as to understand the fate of contaminants such as triclosan, triclocarban and perfluorinated chemicals in biosolids (Xia et al., 2010; Sepulvado et al., 2011). In addition, from 2003 to 2006, the district collaborated with the U.S. EPA Region 5 to conduct semiannual monitoring of alkylphenols and alkylphenol ethoxylates in influent, effluent and sludge samples from seven plants. The district has also actively participated in unused medicine collections sponsored by the U.S. Drug Enforcement Administration to prevent or reduce accidental drug contamination of streams, rivers and lakes.

City of Chicago, Department of Water Management – The city of Chicago services residents of Chicago and 125 suburban communities who consume close to 1 billion gallons of water from Lake Michigan daily. The city embarked on a two-year study in 2009 to examine the occurrence of emerging contaminants (City of Chicago, 2012). The sampling program entails collecting Lake Michigan source water and finished drinking water samples six times over two years to capture both temporal and laboratory variability. Sampling sites included the offshore crib intakes, shore intakes, and finished water outlets at the two treatment facilities the city operates. The study screened for endocrine-disrupting chemicals, pharmaceuticals and personal care products — 138 compounds total, ranging from artificial sweeteners and hormones to plasticizers and herbicides. Thirty of those chemicals were detected at least once in the source water, and 28 were detected at least once in the finished drinking water. The most prevalent compounds detected in source and finished water included caffeine and nicotine (and metabolites), atrazine (and metabolites), DEET, fluorsurfactant perfluorooctane sulfonate (PFOS), and the antibiotic sulfamethoxazole. Since the study’s conclusion in 2011, the city has posted this data on its website, but the report is pending. The city does not plan to continue a sustained monitoring of source and drinking water beyond the chemicals included in the UCMR 3, which include some of the chemicals identified as emerging contaminants.

Central Lake County Joint Action Water Agency (CLCJAWA) – The agency represents 12 communities in Lake County, Ill. and provides potable water to a population estimated at 207,000. The agency’s Lake Michigan water supply system became operational in 1992. The agency has conducted voluntary monitoring of a suite of unregulated contaminants in source and finished drinking water since 2004, including pharmaceuticals and personal care products. Five such compounds were detected in 2011 in source water at trace concentrations: atenolol, cotinine, diltiazem, meprobamate and sulfamethoxazole.
Milwaukee, Wis.

**Milwaukee Metropolitan Sewage District (MMSD)** – The district owns and operates two water reclamation facilities on the shores of Lake Michigan, which receives the treated wastewater. The district’s service area is the subject of an ongoing four-phase MMSD Corridor Study contracted with the U.S. Geographical Survey (USGS) in 2001 in an effort to improve the understanding of water resources in the MMSD planning area and assist managers and policy makers with their planning. Part II of the study involved identifying sampling locations and collecting water quality data. Although the focus was not on emerging contaminants, the analysis of the samples indicated the presence of pesticides and other industrial and municipal wastewater contaminants in the streams feeding Lake Michigan and the Milwaukee Harbor. Overall, testing was done for nearly 100 compounds. In streams, the most frequently detected class of compounds were herbicides, followed by nonprescription human drugs — with detection frequencies measured at greater than 90 percent and 80 percent, respectively. In harbor samples, the most frequently detected class of constituents was flavors and fragrances (greater than 60 percent detection frequency), closely followed by insecticides and solvents (Thomas et al., 2007). The district is also collaborating with faculty at the University of Wisconsin-Milwaukee’s School of Freshwater Sciences (formerly the Great Lakes WATER Institute), and Veolia Water Milwaukee on characterizing the fate of emerging contaminants in the treatment process, the removal efficiencies of 48 different pharmaceutical and personal care products at the district’s facilities, and further study of 10 of those pollutants to assess their efficacy as indicator compounds (Klaper, 2012; Treguer and Royer, 2012). The district has an ongoing research partnership with the School of Freshwater Sciences to analyze how effectively chemicals are removed from liquid into sludge during treatment. Furthermore, in an effort to remove some of the pharmaceutical compounds from the waste stream, the district is working with more than a dozen police departments in Milwaukee County to provide year-round medicine collections (MMSD, 2012). Since traditional wastewater treatment is not designed to remove trace organics — such as pharmaceuticals — from the water, the district works to provide opportunities for the public to dispose of unused medicines properly rather than flush them down the drain.

**Milwaukee Water Works (MWW)** – Home to a Cryptosporidium outbreak in 1993 — the largest waterborne disease outbreak in documented U.S. history, the city takes its water supply seriously. In addition to required water monitoring, Milwaukee Water Works staff collect water samples annually and analyze them for about 500 unregulated compounds in raw Lake Michigan water, finished water and in the distribution system. The Milwaukee Water Works was one of the first utilities in the U.S. to test for endocrine-disrupting compounds, beginning in 2004, and for pharmaceuticals and personal care products, beginning in 2005. The voluntary monitoring is conducted to collect baseline data, learn more about water quality, and to prepare to take further action on the issue. The data is available to the public on its website, along with information about MWW’s water treatment process and other educational materials. In 2011, the most recent year for which information was available, only a handful of compounds were detected: DEET, PFOS, sulfamethoxazole, atenolol and cotinine in finished water; the hormones
progesterone and testosterone, in addition to the above-mentioned compounds, in source water (City of Milwaukee, 2012). The water intake is located in Lake Michigan — 1.24 miles from shore, five miles north of the Milwaukee Harbor, and in water measuring 62 feet deep. This location is much cleaner than in the Milwaukee Harbor or in the Milwaukee-area tributaries that are heavily affected by urbanization — sites where the USGS and MMSD conducted water quality tests for the aforementioned Corridor Study. This appears to indicate that nearshore areas of the lake and urban streams are much more affected. Still, despite significant dilution, several compounds are prevalent in the surface waters of Lake Michigan. The effort put forth by MWW is commendable as it is leading the way among public water utilities. More frequent monitoring for priority chemicals could help to establish temporal trends — if any exist — in the occurrence of emerging contaminants.

**Racine, Wis.**

**City of Racine** — The city of Racine provides drinking water and wastewater treatment to its residents and takes great pride in its water resources. Racine’s Lake Michigan drinking water was the winner of the 2011 National City Water Taste Test Competition. Held at the U.S. Conference of Mayors, 73 cities across the U.S. competed and nearly 100 mayors participated in blind taste tests to choose the winner. Racine currently complies with all federally mandated testing and is in compliance with all analytical data. The city, however, currently does not have any programs that monitor for emerging contaminants in wastewater or in source water used for drinking as the EPA does not mandate it. Racine is not alone; most water utilities test only for that which the EPA requires of them. In 2006, Racine participated in an EPA wastewater study. The survey measured concentrations for a target list of chemicals found in sewage sludge, as well as in influent and effluent, in publicly-owned treatment plants using secondary treatment or better. The survey included metals, inorganic ions, and certain organics — such as polycyclic aromatic hydrocarbons, semivolatiles, polybrominated diphenyl ethers, pharmaceuticals, steroids and hormones. Voluntary participation in the 2006 study by Racine generated an initial set of data that begins to examine the prevalence and distribution of emerging contaminants entering the waste stream and, potentially, the environment. The city also has permanent year-round medicine collection as well as biannual collection events in cooperation with surrounding communities. The Racine Wastewater Utility administers a permanent Household Hazardous Waste Program to eliminate hazardous household chemicals from being dumped into the local landfill or flushed to the wastewater treatment plant.
Gary, Ind.

**Gary Sanitary District** – The district services residents of Gary and five local communities, and treats wastewater from a large number of industrial facilities in Northwest Indiana. The city of Gary’s Department of Green Urbanism and Environmental Affairs is working on water quality protection and monitoring efforts. The aim is to collect data to inform scientific and policy efforts to protect water quality and the drinking water supply. Additionally, Gary’s stormwater program is working on a green infrastructure strategy that will improve water quality and minimize the runoff entering waterways. The city, however, currently does not have any programs that monitor for emerging contaminants in wastewater. Indiana American Waters is the national company that provides drinking water to many communities, including Northwest Indiana. Emerging contaminants are not being monitored at any of Indiana American Waters’ facilities.

City of Wyoming, Mich. – Providing High-Quality Drinking Water and Looking Ahead

The city of Wyoming, Mich. and its leaders are motivated by the desire to ensure safe and reliable drinking water to more than 250,000 customers. The city also wants to be prepared when water quality monitoring for emerging contaminants will be required by the Michigan Department of Environmental Quality. Wyoming has been proactive on the emerging contaminants issue and has conducted voluntary monitoring for a suite of chemicals of concern in the city’s influent, effluent and landfill leachate it receives for treatment, as well as in Lake Michigan source waters and finished drinking water for the past four years. The city has also organized drug collection centers to help residents curb the release of unused medication into the environment. In 2011, water tests conducted by the MWH Laboratories in California indicated that the following compounds were detected in the Lake Michigan source water: 2,4-D, 4-nonylphenol, Acesulfame-K, Atrazine (and atrazine degradates DACT, DEA, and DIA), BPA, DEET, Estrone, Gemfibrozil, Ibuprofen, Iohexal, Naproxen, Sucralose, TCEP, and Triclosan. Finished tap water contained: 1,7-Dimethylxanthine, Acesulfame-K, Atrazine (and atrazine degradates DACT, DEA, and DIA), DEET, and Quinoline.
Impacts on Lake Michigan Waters

Based on the rankings from the prioritization method described above, and the monitoring efforts undertaken by municipalities in the southern Lake Michigan area, we can examine how Lake Michigan has been affected by emerging contaminants. This section of the report examines the priority compounds detected in southern Lake Michigan and the drinking water that comes from it. Compounds detected in the source water by local water utilities (MWW, CLCJAWA) in 2011 are: progesterone, cis-testosterone, atenolol, perfluorooctane sulfonate (PFOS), cotinine, DEET, diltiazem, meprobamate, and sulfamethoxazole. In finished water, DEET, PFOS, atenolol, cotinine and sulfamethoxazole were detected. All except PFOS were evaluated by the ranking system and scored below chemicals ranked in the top 20. PFOS, along with several other perfluorinated surfactants, is listed in the UCMR 3 for monitoring by water utilities for potential regulatory action.

Chicago’s Department of Water Management does not analyze for emerging contaminants routinely, but conducted a two-year study of emerging contaminants in Lake Michigan source water and finished water at the city’s treatment plants. Most of the compounds detected in source water were also detected in finished water, evidence that removal of these chemicals through conventional treatment is not sufficient. The data from water analysis showed that the following compounds were detected in both: 2,4-D, atenolol, atrazine and atrazine transformation products, BPA, caffeine, cotinine, cyanazine, dehydronifedipine, furosemide, gemfibrozil, iopromide, meprobamate, DEET, nicotine, PFOS, phenytoin, progesterone, simazine, theobromine, and Tri(2-butoxyethyl) phosphate (TBEP). Of the compounds on the priority lists, BPA, gemfibrozil and TBEP were detected in Chicago’s source water, and TBEP was detected in finished drinking water.

A study by the MMSD and the USGS in the Milwaukee Metropolitan Sewerage District service area analyzed water in the Milwaukee River watershed and Milwaukee Harbor and reported the occurrence of 80 different compounds in the streams and harbor. Of those on the stream-source water priority list, Tris (dichloroisopropyl) phosphate (Fyrol FR 2), TBEP, HHCB and AHTN were detected. The fact that many more compounds were detected in the Chicago Department of Water Management study and the MMSD/USGS Milwaukee study could be attributed to the fact that many more samples were collected and analyzed than in the annual monitoring done by Milwaukee Water Works (MWWW) and Central Lake County Joint Action Water Agency (CLCJAWA). Many of the priority-ranked compounds weren’t even tested for in the Chicago Department of Water Management study, the MMSD/USGS Milwaukee study, or by the CLCJAWA.
The data from municipalities is difficult to compare because each utility follows its own protocol for water sampling, screens for different compounds, and uses different analytical labs which, in turn, have different detection limits. This further supports the need to develop a priority list of emerging contaminants for utilities so they can coordinate their monitoring efforts, or use it as a starting point for facilities seeking to develop a monitoring program. Existing data indicates that processed drinking water drawn from Lake Michigan is not significantly burdened with contaminants — only one chemical of the top 20 has been detected. Lake Michigan’s surface waters are affected more, however, with six of the top 20 chemicals detected in them. Yet, the data collected so far provides just a snapshot of what might be in the water, making it difficult to draw any broad conclusions. Further, because different sampling protocols and analytical laboratories were used, data reported also had varying detection limits and sensitivities. Some of the chemicals detected in lake water weren’t included in the ranking, and the studies did not test for all of the chemicals ranked in the top 20.

Drinking water utilities are required to monitor for chemicals listed under the federal UCMR. Yet drinking water as well as wastewater utilities voluntarily develop monitoring programs for emerging contaminants in order to provide the highest quality drinking water to the communities they serve, and to protect the ecological health of the waterways. The lack of uniform standards for data collection, analysis and reporting is just one of the technical challenges these facilities face, as such consistent and reproducible protocols are needed for monitoring data to be credible and appropriate for analysis. Some facilities send water samples to contracted laboratories, while others conduct in-house analysis or collaborate with university labs that specialize in a particular technique. Reporting limits vary among all of these, making it difficult to conclude with certainty whether a chemical is not detected because it isn’t there, or because the limit of detection is not sufficiently low. Some facilities conduct annual testing, while others conduct studies to address a particular research question. Coordination among water utilities that are involved in, or interested in, developing monitoring programs will strengthen the quality of the data. Likewise, focusing on monitoring for a list of priority contaminants — a single test can cost between $250 and $450 — would reduce the expenses needed to finance a monitoring program (State Hygienic Labs, University of Iowa).

### Fluorinated Surfactants in Humans and Animals Globally Distributed

Perfluorooctane sulfonate (PFOS) is a man-made chemical that was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in May 2009. It was used as a main ingredient in Scotchgard, a consumer product manufactured to prevent stains on fabrics, furniture and carpeting. It is also used in a variety of other applications, such as the production of fire-fighting foams and anti-reflective coatings for semiconductors.

Production of fluorinated surfactants began in 1949. Less than two decades later, in 1968, organofluorine content was detected in human blood serum. Subsequent studies characterized its chemical nature and linked the source to compounds such as PFOS (Giesy and Kannan, 2002). By the late 1990s, PFOS was detected in blood from global blood banks. PFOS was also detected in polar bears and other wildlife. In 1999, the U.S. Environmental Protection Agency began investigating perfluorinated compounds after receiving data on the global distribution and toxicity of PFOS. The primary American producer of PFOS, 3M, announced in May 2000 the phaseout of the production of PFOS, PFOA and PFOS-related products. More than 50 years have passed since this chemical went into production; however, water utilities will only begin monitoring for PFOS in their water supply in 2013 as PFOS is included in the federal Unregulated Contaminant Monitoring Rule 3.
It should be noted that drinking water is not the only pathway of exposure to many of the emerging chemicals of concern discussed above. People may be exposed to them through the inhalation of dust inside their home, consumption of contaminated foods, or skin contact. For this reason, it is important to understand that water and wastewater utilities are not exclusively responsible for the prevention and control of contaminants in Great Lakes water. Preventing contamination and protecting the source water in the Great Lakes should be the overarching goal and will also alleviate the burden on water utilities. To this end, a comprehensive approach is needed that involves not only technological solutions, but invites collaboration among utilities, regulatory agencies, public health officials and environmentalists. Together these entities must work with stakeholders — including the public — to encourage policy, social and behavioral changes that propel chemical producers to evaluate chemicals before they enter the marketplace, and encourage individuals to reduce their use of chemicals and thus lessen the risks associated with their eventual release into the environment.
Conclusion

The Great Lakes are a repository for 20 percent of the world’s surface freshwater, but also increasingly for a class of chemical compounds known as emerging contaminants of concern. These contaminants often originate from everyday products such as shampoos, pharmaceuticals, textiles and home furnishings, but researchers are finding effects that are far from benign. Indeed, a growing number of studies are raising concern about these chemicals’ effects on people and wildlife, specifically their toxicological effects on the body’s endocrine system — driver of such key functions as growth and development, metabolism and reproduction. Existing data shows that processed drinking water drawn from Lake Michigan is not significantly burdened with contaminants, with only one chemical detected of the top 20 identified in the report. Lake Michigan’s surface waters are affected more, with six of the top 20 chemicals detected. The data collected thus far provides just a snapshot of what might be in the open water, however, and does not address emerging contaminants in rivers, groundwater and inland lakes. Nor does it take into account the health risks that bioaccumulating chemicals in the water pose to people who eat Great Lakes fish.

Conventional sewage treatment is not designed to remove these types of compounds, so some remain in treated wastewater at trace concentrations and are discharged directly into the Great Lakes. Other emerging contaminants take a more indirect course, making their way into the Great Lakes via atmospheric deposition, stormwater runoff and combined sewer overflows — intentional releases of untreated or partially treated sewage that occur when wastewater treatment plants are overwhelmed by heavy rains. Persistent compounds can also be transported long distances to and from the Great Lakes, affecting distant ecosystems.

There appears to be little overlap between the regulatory frameworks for drinking water and wastewater utilities, as both target different contaminants. For the Great Lakes and their tributaries — receiving waters for 1,448 municipal facilities discharging 4.8 billion gallons of effluent daily, and 2,393 industrial facilities reporting to the EPA’s Toxic Release Inventory — this connection is critical and underscores the urgent need for a more comprehensive and integrated regulatory framework. Blurring the picture for facilities undertaking voluntary action to address emerging contaminants is the absence of uniform guidelines, protocols and standards for data collection, analysis and reporting — necessary protocols for monitoring data to be credible and appropriate for analysis. Funding the development
of consistent, uniform regional monitoring standards is an important step toward gaining a clearer understanding of emerging contaminant levels in Great Lakes surface water and drinking water.

With hundreds of mostly unregulated compounds detected in Great Lakes surface waters today, it is equally critical to identify those chemicals that pose the greatest threat to the health of the lakes and the people and wildlife that depend upon them. Establishing clear prioritization rankings for emerging contaminants can serve as a basis for utilities to implement focused and lower-cost monitoring programs. Additionally, rapid prioritization of the thousands of known compounds could hasten the work of regulatory agencies to develop analytical methods and conduct critical risk assessments.

Water treatment plays a key role in helping to remove contaminants, but it is important to emphasize that water and wastewater utilities are not exclusively responsible for preventing and controlling contaminants in Great Lakes water. To that end, a comprehensive approach is needed that involves not only technological solutions, but invites collaboration among utilities, regulatory agencies, public health officials, manufacturers and environmentalists. Together these entities must work to encourage policy, social and behavioral changes that propel businesses to evaluate chemicals before they enter the marketplace, and individuals to reduce their use of chemicals — thereby lessening the risks associated with the chemicals’ eventual release into the environment.

The EPA’s Great Lakes National Program Office, working in collaboration with the National Oceanic and Atmospheric Administration, U.S. Fish and Wildlife Service, U.S. Geological Survey and Environment Canada, has launched a comprehensive emerging contaminant surveillance and monitoring program to document the presence of these chemicals in water, air, sediments, fish and birds, and to identify any effects these chemicals might have. The outcome of this welcome collaborative effort will be important as the U.S. and Canada work to meet their charge to develop lists of “chemicals of mutual concern” under the newly renegotiated Great Lakes Water Quality Agreement. The two governments should draw on prioritization methods to set binational objectives for controlling those Great Lakes contaminants deemed highest priority, and seek to achieve these objectives through domestic policy reforms. The public, as well as most other stakeholder groups, agree the time is ripe to reform the federal Toxic Substances Control Act, passed in 1976, and in so doing potentially re-craft it to feature a framework that places pollution prevention at the forefront of new chemical design and production. In the meantime, it is imperative we use the tools already at our disposal and collaborate to put in place critically needed controls to curb contaminants entering the Great Lakes.
About the Author

Olga Lyandres
Olga Lyandres is research manager at the Alliance for the Great Lakes, working to enhance the scientific basis for the policy work at the Alliance and address emerging threats to the Great Lakes ecosystems. She has a Ph.D. in Biomedical Engineering from Northwestern University, where she has worked on developing optical biosensors with a focus on in vivo spectroscopic glucose detection. She subsequently worked as a postdoctoral researcher, also at Northwestern University, in the Department of Environmental Engineering, studying titanium dioxide nanocomposites and their application to photocatalysis and removal of organic pollutants.
Acknowledgments

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### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>USGS</td>
<td>United States Geological Survey</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and Drug Administration</td>
</tr>
<tr>
<td>SDWA</td>
<td>Safe Drinking Water Act</td>
</tr>
<tr>
<td>CWA</td>
<td>Clean Water Act</td>
</tr>
<tr>
<td>TSCA</td>
<td>Toxic Substances Control Act</td>
</tr>
<tr>
<td>FIFRA</td>
<td>Federal Insecticide, Fungicide, and Rodenticide Act</td>
</tr>
<tr>
<td>CSO</td>
<td>Combined Sewer Overflow</td>
</tr>
<tr>
<td>UCMR</td>
<td>Unregulated Contaminant Monitoring Rule</td>
</tr>
<tr>
<td>CCL</td>
<td>Candidate Contaminant List</td>
</tr>
<tr>
<td>WMPT</td>
<td>Waste Management Prioritization Tool</td>
</tr>
<tr>
<td>SCRAM</td>
<td>Scoring and Ranking Assessment Model</td>
</tr>
<tr>
<td>MMSD</td>
<td>Metropolitan Milwaukee Sewerage District</td>
</tr>
<tr>
<td>MWWW</td>
<td>Milwaukee Water Works</td>
</tr>
<tr>
<td>MWRD</td>
<td>Metropolitan Water Reclamation District</td>
</tr>
<tr>
<td>CLCIWA</td>
<td>Central Lake County Joint Action Water Agency</td>
</tr>
<tr>
<td>CAWS</td>
<td>Chicago Area Waterway System</td>
</tr>
<tr>
<td>LC-MS/MS</td>
<td>Liquid Chromatography Tandem Mass Spectrometry</td>
</tr>
</tbody>
</table>

### List of Chemicals and their Uses

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
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<tbody>
<tr>
<td>TBEP</td>
<td>Tri(2-butoxyethyl) phosphate – flame retardant chemical</td>
</tr>
<tr>
<td>TCEP</td>
<td>Tris(2-chloroethyl) phosphate – flame retardant chemical</td>
</tr>
<tr>
<td>Tris</td>
<td>Tris (dichloroisopropyl) phosphate (Fyrol FR 2) – flame retardant chemical</td>
</tr>
<tr>
<td>HHCB</td>
<td>Galaxolide – synthetic musk</td>
</tr>
<tr>
<td>AHTN</td>
<td>Tonalide – synthetic musk</td>
</tr>
<tr>
<td>ADBI</td>
<td>Celestolide – synthetic musk</td>
</tr>
<tr>
<td>PFOS</td>
<td>Perfluorooctane sulfonate – surfactant chemical</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphenol A – precursor chemical for plastic manufacturing</td>
</tr>
<tr>
<td>Quinoline</td>
<td>– precursor for specialty chemicals</td>
</tr>
<tr>
<td>4-nonylphenol</td>
<td>– industrial surfactant and precursor for detergents</td>
</tr>
<tr>
<td>DEET</td>
<td>N,N-Diethyl-meta-toluamide – insect repellant</td>
</tr>
<tr>
<td>2,4-D</td>
<td>2,4-Dichlorophenoxyacetic acid – herbicide</td>
</tr>
<tr>
<td>Diazinon</td>
<td>– insecticide</td>
</tr>
<tr>
<td>Thiabendazole</td>
<td>– fungicide and parasiticide</td>
</tr>
<tr>
<td>Simazine</td>
<td>– herbicide</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>– pesticide</td>
</tr>
<tr>
<td>Atrazine</td>
<td>– herbicide</td>
</tr>
<tr>
<td>DACT</td>
<td>(didealkyl atrazine) – Atrazine degradation product</td>
</tr>
<tr>
<td>DEA</td>
<td>(desethyl atrazine) – Atrazine degradation product</td>
</tr>
<tr>
<td>DIA</td>
<td>(deisopropyl atrazine) – Atrazine degradation product</td>
</tr>
<tr>
<td>Acesulfame-K</td>
<td>– artificial sweetener</td>
</tr>
<tr>
<td>Sucralose</td>
<td>– artificial sweetener</td>
</tr>
<tr>
<td>Estrone</td>
<td>– estrogenic steroid hormone</td>
</tr>
<tr>
<td>Progesterone</td>
<td>– reproductive steroid hormone</td>
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</table>

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Testosterone</td>
<td>– androgenic steroid hormone</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>– cholesterol-lowering drug</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>– nonsteroidal anti-inflammatory drug</td>
</tr>
<tr>
<td>Naproxen</td>
<td>– nonsteroidal anti-inflammatory drug</td>
</tr>
<tr>
<td>Codeine</td>
<td>– opiate pain reliever</td>
</tr>
<tr>
<td>Iohexol</td>
<td>– contrast agent for intravascular use</td>
</tr>
<tr>
<td>Iopromide</td>
<td>– contrast agent for intravascular use</td>
</tr>
<tr>
<td>1,7-Dimethylxanthine</td>
<td>– caffeine metabolite</td>
</tr>
<tr>
<td>Cotinine</td>
<td>– nicotine metabolite</td>
</tr>
<tr>
<td>Triclosan</td>
<td>– antimicrobial disinfectant</td>
</tr>
<tr>
<td>Triclocarban</td>
<td>– antimicrobial disinfectant</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>– antibiotic</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>– antibiotic</td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>– pharmaceutical used to treat allergies</td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>– antidepressant pharmaceutical</td>
</tr>
<tr>
<td>Meprobamate</td>
<td>– antianxiety pharmaceutical</td>
</tr>
<tr>
<td>Atenolol</td>
<td>– pharmaceutical used to treat hypertension</td>
</tr>
<tr>
<td>Diltiazem</td>
<td>– pharmaceutical used to treat hypertension</td>
</tr>
<tr>
<td>Theobromine</td>
<td>– pharmaceutical used to treat hypertension</td>
</tr>
<tr>
<td>Dehydrofenedipine</td>
<td>– metabolite of the pharmaceutical Nifedipine, hypertension drug</td>
</tr>
<tr>
<td>Furosemide</td>
<td>– pharmaceutical used to treat congestive heart failure and edema</td>
</tr>
<tr>
<td>Phenytoin</td>
<td>– antiepileptic pharmaceutical</td>
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</tbody>
</table>
References


Parrott, J.L., Blunt, B.R., 2005. Life-cycle exposure of fathead minnows (Pimephales promelas) to an ethinylestradiol concentration below 1 ng/L reduces egg fertilization success and demasculinizes males. Environmental Toxicology 20, 131–141.


Suggested Reading


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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