Great Lakes Water Quality Agreement
2009–2011 Priority Cycle Report
International Joint Commission

# CHEMICALS OF EMERGING CONCERN

2009–2011 Priority Cycle Report on

# CHEMICALS OF EMERGING CONCERN

Prepared by the
Chemicals of Emerging Concern Work Group
For the

INTERNATIONAL JOINT COMMISSION

Canada and United States


COMMISSION MIXTE INTERNATIONALE

Canada et États-Unis

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# INTRODUCTION

Over the past 10 years, the emphasis on environmental monitoring has shifted from the so-called legacy pollutants, such as PCBs, to a wide array of new chemicals being discovered in the environment. The term "chemicals of emerging concern" has come to characterize the increasing awareness of the presence in the environment of many chemicals used by society, and the risk that they may pose to humans and ecosystems (Daughton, 2001). Chemicals of emerging concern include new compounds that have gained entry into the environment or those that have been recently characterized due to increases in concentrations in the environment or improvements in analytical techniques. In the United States and Canada few of these compounds have regulations governing their release. Of concern is the uncertainty of potential adverse effects on wildlife and humans due to chronic exposure to low concentrations of these compounds. Some of these chemicals are accumulating in sediments, birds, fish, and other aquatic life, as well as in humans.

*Chemicals of emerging concern include new compounds that have gained entry into the environment or those that have been recently characterized due to increases in concentrations in the environment or improvements in analytical techniques.*

In October 2007, the International Joint Commission (Commission) established multi-Board priorities to be undertaken by its Great Lakes advisory groups during the 2007–2009 biennial reporting cycle. Within the context of the Nearshore Framework Priority, the Chemicals of Emerging Concern Work Group was charged with reviewing the scientific and policy aspects related to identification, impact, and management of chemicals of emerging concern in the Great Lakes. The Work Group found that discharges from wastewater treatment plants are a significant source of contaminants to surface waters in the Great Lakes basin (IJC, 2009), as concentrations of many chemicals of emerging concern were generally highest in the discharge vicinity. These results pointed to a need to assess, and improve existing treatment technologies as large wastewater volumes are discharged without receiving adequate treatment to remove chemicals.

Another key finding was the necessity to assess the impacts of chemicals of emerging concern on human and ecological health in the basin. Human health and ecological health are interconnected. The health of ecological communities and populations may act as a sentinel for human health. Research to systematically determine the biological effects that may be occurring as a result of exposure to potentially toxic substances is limited. From an ecological perspective, analytical approaches for monitoring contaminants of possible concern can be supplemented with biological effects-based testing to understand contaminant effects at various levels of biological organization (sub-cellular, cellular, organ system, individual, and population levels). Monitoring the effects of chemicals detected in the environment provides information that can bridge the gap between chemical contamination and altered ecological status.

Under the current 2009–2011 priority cycle, the Commission charged the Chemicals of Emerging Concern Work Group to assess the performance of wastewater treatment plants for removal of chemicals of emerging concern and to assess human and ecological health effects from exposure to these chemicals. In order to address the charge, the Work Group developed a work plan that covered the topics of wastewater treatment, ecological heath impacts, and human health impacts. Human health effects resulting from exposure to chemicals of emerging concern would be most effectively addressed by the Commission's Health Professionals Task Force. The activities for these three topics are described in the following chapters. Based on its investigation and findings, the Work Group prepared recommendations for the Commission's consideration.

*The term "chemicals of emerging concern" has come to characterize the increasing awareness of the presence in the environment of many chemicals used by society, and the risk that they may pose to humans and ecosystems.*

## OBJECTIVES

Under the 2009–2011 priority cycle, the Chemicals of Emerging Concern Work Group was charged to assess the performance of wastewater treatment plants in the Great Lakes basin with respect to the removal of chemicals of emerging concern. The Work Group was further instructed to provide the Commission with a sampling of the information which might be derived if a more extensive evaluation were undertaken, specifically examination of the performance of a subset of wastewater treatment plants in the Great Lakes basin. Further, literature review and analysis of removal technologies was expected to provide insight into an array of potential wastewater treatment plant upgrades.

The Work Group's work plan encompassed four major activities:

- develop an inventory of municipal wastewater treament plants which discharge into the basin;
- conduct a detailed survey of operational data for selected facilities;
- conduct a literature search and analysis of the effectiveness of various treatment technologies to remove chemicals of emerging concern; and,
- develop an inventory of government and scientific society reports of field studies which have assessed the performance of full-scale facilities.

The findings from these activities served as the foundation for an expert consultation held in Romulus, Michigan on January 25–26, 2011. Proceedings of the expert consultation and the list of participants are provided in Appendix A. The Work Group's advice in this report reflects the culmination of these activities.

## INVENTORY OF U.S. AND CANADIAN WASTEWATER TREATMENT FACILITIES

In order to understand and comment on the effectiveness of municipal wastewater treatment systems which discharge into the basin, an inventory of wastewater treatment systems was developed for Canada and the United States. The objectives of the project were to:

- tabulate the total number of facilities which discharge into the basin;
- differentiate the facilities based on type of treatment (primary, lagoon, secondary/activated sludge, tertiary/advanced); and,
- analyze the distribution of facilities with respect to wastewater flow and population served.

To develop the inventory, information was sought from both the U.S. and Canadian governments. The Work Group confirmed that the facilities indeed discharge into the geographic/hydrogeological boundaries of the Great Lakes basin, as defined by the Commission.

Environment Canada and the Ontario Ministry of the Environment had previously created a database and map showing the locations of municipal plants. The database contains key relevant information, such as location, type of facility, wastewater flow, and population served. A total of 470 municipal wastewater treatment plants in Ontario discharge into the basin (Table 1). Of these, 212 and 68 are secondary/activated sludge and tertiary/advanced treatment facilities, respectively. Note that smaller communities are served by 175 lagoon treatment systems, and only 8 facilities consist of primary treatment only.

Analysis of treatment type with respect to total wastewater flow shows that, for Ontario >95% of

the municipal wastewater discharged into the basin receives either secondary (activated sludge) or tertiary (advanced) treatment.

| Facility Type | Number of Facilities | Percentage of Total number of Facilities | Total Average Daily Flow (MLD) | Percentage of Total Average Daily Flow |
|---|---|---|---|---|
| Primary | 8 | 1.7% | 96 | 1.7% |
| Community Septics (all types) | 7 | 1.5% | 1 | 0.0% |
| Lagoons (all types) | 175 | 37.2% | 178.0 | 3.1% |
| Secondary | 212 | 45.2% | 5038.1 | 87.3% |
| Tertiary | 68 | 14.5% | 456.8 | 7.9% |
| **Totals** | **469** | **100.0%** | **5769.1** | **100.0%** |

MLD = million liters per day
***Table 1.*** *Distribution of Ontario Wastewater Treatment Plants in the Great Lakes Basin.*

The U.S. Environmental Protection Agency's Clean Watersheds Needs Survey was the information source for U.S. municipal wastewater treatment plants. This survey is the only nationwide source of comparable municipal wastewater treatment plant information.

Clean Watersheds Needs Survey database is not specific to treatment technology, but rather defines treatment in terms of facility performance. For U.S. facilities, secondary treatment refers to the minimum level of treatment that must be achieved for discharges from all municipal wastewater treatment facilities, and generally requires treatment that will produce an effluent quality of 30 milligrams per liter of both 5-day biochemical oxygen demand (BOD5) and total suspended solids (TSS). Further, secondary treatment must remove 85% of BOD5 and TSS from the influent wastewater, although lower percentage removals are authorized in some circumstances. Advanced treatment is more stringent than secondary, requiring the facility to achieve one or more of the following: BOD5 in the effluent <20 mg/L, nitrogen removal, phosphorus removal, ammonia removal, metal removal, or specific synthetic organic removal.

| Facility Type | Number of Facilities | Percentage of Total number of Facilities | Total Average Daily Flow (MGD) | Percentage of Total Average Daily Flow |
|---|---|---|---|---|
| Secondary Treatment | 311 | 31.8% | 135.9 | 4.2% |
| Advanced Treatment | 563 | 57.6% | 3111.8 | 95.8% |
| Unknown* | 104 | 10.6% | n/a | n/a |
| **Totals** | **978** | **100.0%** | **3247.7** | **100.0%** |

MGD = million gallons per day
*Detailed information is not available
***Table 2.*** *Distribution of U.S. Wastewater Treatment Plants in the Great Lakes Basin.*

Of the 978 U.S. facilities which discharge into the basin, 311 achieve secondary and 563 achieve advanced treatment. Detailed information was not available in the survey database for 104 facilities, but likely the remaining facilities achieve at least secondary treatment performance, which is the minimum standard in the United States.

Analysis of treatment performance with respect to total wastewater flow, show that >95% of the wastewater discharged into the basin meets the performance requirement for advanced treatment. Although 311 facilities meet the secondary treatment performance requirement, these facilities receive only about 4% of the total flow.

Additional work is currently underway to characterize the distribution of treatment operations (primary, lagoon, activated sludge, tertiary) for the U.S. facilities. The objective is to develop a database with information comparable to that available for Canada.

## FINDINGS

A total of 1,448 municipal wastewater treatment plants discharge 18 billion liters (4.8 billion gallons) per day of treated effluent to the Great Lakes basin.

Approximately 1% of the plants in Ontario (primary and community septic tanks) do not practice secondary treatment.[1] Lagoons provide a low rate of secondary treatment and, while they may constitute 37% of the facilities, they process only 3.1% of the total flow. The remaining facilities provide secondary treatment or better for >95% of the wastewater flow.

Based on Clean Watersheds Needs Survey, 4% and 95% of the wastewater flow into the basin meet the performance standards for secondary and advanced treatment, respectively.

Although there are differences in how the two countries define such systems, collectively the combined group of secondary, advanced and tertiary plants treats 98% of the total wastewater flow discharged to the Great Lakes basin.

Many flows into the Great Lakes basin are not accounted for in the above analysis, including wastewater by-pass events, combined sewer overflows, industrial discharges, millions of private septic systems, and agricultural runoff, some of which are not treated. Although, combined sewer overflows may represent a relatively small percentage of annual sewage flow into the basin, they may be responsible for substantial releases of organic contaminants to the environment, especially during high precipitation or severe storm events. Also, biosolids from wastewater treatment plants are often applied to agricultural land in the basin. This practice has the potential to contaminate surface and groundwater with organic, inorganic, and microbiological contaminants.

## SURVEY OF OPERATIONAL DATA FOR SELECTED FACILITIES

In order to provide a more detailed understanding of the performance of municipal wastewater treatment systems, a survey of the operational data from a subset of wastewater treatment plants in the basin was undertaken. Although not intended to be a statistical representation, the facilities selected represent the range of plant sizes, treatment technologies, and geographic location in the basin. Data were also collected on parameters that are used to control and evaluate plant operation, including solids and hydraulic residence times, wastewater flow, organic and nutrient concentrations, and temperature. A report summarizing the study is provided in Appendix B.

Of the 25 facilities responding to the survey, the most common secondary treatment technology is the activated sludge process (17 plants). This group includes various modes of operation, including plants designed for organic (BOD) removal only and facilities designed to remove both organic and inorganic nutrients (*e.g.* ammonia). Chemical precipitation of phosphorus is practiced at the majority of these plants. The second most common secondary treatment technology in use is based on biological fixed film technology; three plants use biological aerated filtration and one deploys the trickling filter/solids contact process. Fixed film processes are more advanced than the historically more common trickling filter process. Of the remaining plants, two are lagoon-based and two employ only primary treatment or activated carbon and chemical oxidation.

[1]Two of the eight municipal primary treatment plants are currently being upgraded to secondary treatment. The six other municipal primary treatment plants have received major capital funding assistance from Ontario and Canada and are in various stages to complete upgrades to secondary.

One critical operating parameter that has been correlated with removal efficiencies for many biodegradable chemicals of emerging concern is the solids (biomass) residence time. Some chemicals are difficult to biodegrade, and the microorganisms that have adapted to degrade them grow slowly. Because the solids residence time is related to the microbial growth rate, it is a useful surrogate of the ability of the activated sludge process to retain the slower growing organisms and therefore to degrade the biodegradable chemicals of emerging concern. Further, activated sludge systems designed for biological nutrient (ammonia) removal are operated at higher solids residence times than those designed to remove organic (BOD) only and, as a result, biological nutrient removal systems remove various chemicals of emerging concern more efficiently than activated sludge systems operated at lower solids residence times. Consequently, the effectiveness of ammonia removal provides a useful surrogate of the removal of biodegradable chemicals of emerging concern.

Three years of performance data from the 25 facilities were reviewed. The activated sludge plants that reported solids residence time data were divided into two groups: residence times of <5 days and >5 days. Some facilities that operated at the lower residence times showed little to no change in ammonia from influent to effluent, indicating low biological nutrient removal (nitrification). These plants are most likely to show poorer removals for chemicals of emerging concern.

*Although combined sewer overflows may represent a relatively small percentage of annual sewage flow into the basin, they may be responsible for substantial releases of organic contaminants to the environment, especially during high precipitation or severe storm events.*

In contrast, many of the activated sludge plants that are operated with higher solids residence times generally showed effluent ammonia concentrations <1.0 mg/L, indicating almost complete nitrification and a high level of performance on a year-round basis. Also common to these plants was a greater hydraulic residence time, indicating that the plants were conservatively designed with a year-round capability of nutrient removal. Given the correlation previously discussed, removal efficiencies for biodegradable chemicals of emerging concern by these facilities are likely to be sustained throughout the year.

One of the plants evaluated operated their activated sludge process in a membrane bioreactor mode. It produces a very high quality effluent with <0.2 mg/L ammonia as well as very low effluent BOD5 and total suspended solids concentrations. The high degree of nitrification is attributed to the higher level of control over solids residence times that can be achieved with a membrane in place of a secondary clarifier. This plant, too, will likely achieve a high level of removal during summer and winter.

However, it is not necessary to invoke membrane bioreactor technology to achieve high quality effluent. For example, one of the lagoon systems evaluated achieved the lowest effluent ammonia concentrations of all 25 plants (<0.1 mg/L). The effluent BOD5 and suspended solids concentrations were similarly very low (2 and 6 mg/L, respectively). This remarkable performance illustrates that the plant has been designed conservatively and is well operated. Of course, lagoon technology cannot be deployed in large population centers due to the large area required, but this plant does illustrate what can be achieved in small to medium-sized communities.

## FINDINGS

Detailed operating conditions were evaluated for a spectrum of facilities which discharge into the Great Lakes basin. Of the 25 plants, 17 use activated sludge or advanced treatment technologies, 4 use fixed film technologies, 2 are lagoon based systems, and 2 are primary treatment plants. Wastewater flow rates for the facilities ranged from <10 to >50 million gallons per day. Because the survey was not a statistical representation of the plants in the basin, extrapolation to other facilities in the basin cannot be made.

Effective removal of the wide variety of chemicals of emerging concern is dependent on both the nature of the substance and the design and operation of the wastewater treatment plant. Examination of the performance data collected suggests that some plants are operated very well while others are not. Facilities designed for primary treatment are unlikely to adequately reduce the concentrations of biodegradable chemicals of emerging concern. Some very large cities are serviced by wastewater treatment plants designed for organic (BOD) removal only.

Many facilities are operated at high solids residence times and are effective in both organic (BOD) and nutrient (ammonia) removal. Such facilities are likely to show effective reductions of biodegradable chemicals of emerging concern.

Conventional parameters (BOD, ammonia) are useful surrogates to assess removal efficiencies for biodegradable chemicals of emerging concern. However, different indicators are required for substances that are poorly or non-biodegradable or that have a propensity to adsorb to biomass.

## REVIEW OF THE EFFECTIVENESS OF WASTEWATER TREATMENT TECHNOLOGIES

In the absence of long-term measurements of the removal efficiencies for chemicals of emerging concern by municipal wastewater treatment plants within the Great Lakes basin, comparisons may be made of currently available data from published studies that have reported influent and effluent concentrations of various contaminants from wastewater treatment systems that practice similar technologies. A comprehensive literature search was performed for the period 2000–2010. Much of the available information describes the removal of pharmaceuticals, personal care products, surfactants, and hormones in the activated sludge process.

A database was created and analyzed from a weight-of-evidence perspective. Because of the lack of sufficient data to permit meaningful statistical analysis, the analysis was limited to the treatment of 42 substances by activated sludge treatment facilities. A report summarizing the study is provided in Appendix C.

Table 3 summarizes the results of analysis of the 42 substances. They were grouped according to the likelihood that they would achieve a given removal efficiency during wastewater treatment as a function of the frequency of their observation in wastewaters. Removal efficiencies may be the result of biodegradation or physical processes such as adsorption.

Some substances such as DEET and testosterone were infrequently detected but demonstrated a high likelihood of removal. Other substances such as carbamazepine and diclofenac were frequently detected but poorly removed. Only acetaminophen, caffeine and estriol occurred frequently and had a high probability of at least 75% removal efficiency. More than half of the 42 substances fell into the middle, that is, they occurred at a medium-to-high frequency and had a medium-to-high probability of attaining 75% or better removal efficiency.

*Only acetaminophen, caffeine and estriol occurred frequently and had a high probability of at least 75% removal efficiency.*

| Confidence level (n = # of records) | Low removal efficiency (<25% probability of 75%+ removal) | Medium removal efficiency (25-75% probability of 75%+ removal) | High removal efficiency (>75% probability of 75%+ removal) |
|---|---|---|---|
| Low (n<9) | Atrazine<br>Pyrene | Benzophenone<br>Indomethacin<br>Sulfamerazine | Musk ketone<br>Di (2-ethylhexyl) adipate (DEHA)<br>N,N-diethyl-toluamide (DEET)<br>Testosterone |
| Medium (9≤n≤15) | Gemfibrozil<br>Perfluorooctanoic acid (PFOA)<br>Perfluorooctyl sulfonate (PFOS) | Di (2-ethylhexyl) phthalate (DEHP)<br>Norfloxacin<br>Ranitidine<br>Roxithromycin<br>Tetracycline | |
| High (n>15) | Carbamazepine<br>Ciprofloxacin<br>Clofibric acid<br>Diclofenac<br>Erythromycin<br>Trimethoprim | Bezafibrate<br>Bisphenol A<br>Estrone (E1)<br>17α-Ethynyl estradiol (EE2)<br>17β-Estradiol (E2)<br>Galaxolide<br>Ibuprofen<br>Ketoprofen<br>Naproxen<br>Nonylphenol<br>Nonylphenol monoethoxylate (NP1EO)<br>Nonylphenol diethoxylate (NP2EO)<br>Octylphenol<br>Sulfamethoxazole<br>Tonalide<br>Triclosan | Acetaminophen<br>Caffeine<br>Estriol (E3) |

***Table 3.*** *Summary of Confidence Level vs. Removal Efficiency for 42 Chemicals of Emerging Concern by Activated Sludge Systems.*

Results of the present study were compared to results of recent investigations published by government agencies or the Water Environment Research Foundation (see Appendix D). For example, Stephenson and Oppenheimer (2007) reported the fate of pharmaceuticals and personal care products in municipal wastewater treatment processes. The fate of 20 compounds was measured at eight municipal plants. The substances were selected based on the frequency of occurrence in municipal wastewaters. All plants used a variation of the activated sludge process, and six operated biological nutrient removal. Results are summarized in Table 4.

Comparison of the results presented in Tables 3 and 4 indicates that removal efficiencies for many of the chemicals common to both studies were similar while others were diametrically opposed. The reason for this discrepancy is unclear but may reflect different operating conditions among facilities.

| Frequency of occurrence in samples | Poor removal (<25%) | Moderate removal (25-75%) | Good removal (>75%) |
|---|---|---|---|
| Infrequent (<25%) | Trichloroethyl phosphate (TCEP)<br>Triphenyl phosphate | Octylphenol | Methyl-3-phenylproprionate |
| Intermediate (25-75%) | Butylated hydroxyanisole (BHA)<br>N,N-diethyl-toluamide (DEET)<br>Musk ketone | Ethyl-3-phenylproprionate | |
| Frequent (>75%) | Galaxolide | Benzophenone<br>Triclosan | Benzyl salicylate<br>Butylbenzyl phthalate<br>Caffeine<br>Chloroxylenol<br>Methylparaben<br>Ibuprofen<br>Octylmethoxycinnamate<br>Oxybenzone<br>3-Phenylproprionate |

***Table 4.*** *Summary of Removal Efficiencies of Pharmaceuticals and Personal Care Products by Activated Sludge Systems (Stephenson and Oppenheimer, 2007)*

Drewes *et al.* (2006) reported on the removal of eight endocrine disruptor compounds by seven municipal treatment plants. All plants used a variant of the activated sludge process and most operated biological nutrient removal. Removal efficiencies for the steroid hormones ranged from 48 to 98%. Concentrations of bisphenol A, nonylphenol, and octylphenol were reduced on average by 93, 61, and 80% respectively. Biodegradation of the compounds was reported as the dominant removal mechanism.

In a follow-up study, Drewes *et al.* (2009) examined the contributions of household chemicals to sewage and their removal in municipal wastewater treatment systems. The fate of 25 substances was measured at seven municipal plants. Most of the facilities used acti-

vated sludge but one employed biological aerated filter technology. All of the plants operated biological nutrient removal. Removal efficiencies were variable for the compounds but generally exceeded 80%. Notably, 2-phenoxyethanol, hydrocortisone, camphor, propylparaben and isobutylparaben achieved ≥98 % removal efficiency. Removal efficiencies for butylated hydroxytoluene, butylated hydroxyanisole, DEET, 3-indolebutyric acid and triclocarban ranged between 60 and 70%.

## FINDINGS

Although municipal wastewater treatment systems were not designed to remove chemicals of emerging concern, results of the present study (Appendix C), as well as government and Water Environment Research Foundation reports (Appendix D) suggest that well operated, conventionally designed plants are capable of achieving effective reductions of a variety of substances.

The weight-of-evidence suggests that at least half of the 42 substances examined in the present study are likely to be removed in municipal wastewater treatment plants. An analysis as described above is limited in terms of reaching definitive conclusions about the extent to which Great Lakes wastewater treatment facilities, as currently operated, are able to remove various contaminants, to what extent and with what reliability.

None of the analyses examined the impact of operating conditions on plant performance. Insufficient granularity and reproducibility in the various datasets preclude discerning the impact of operating conditions such as temperature, loading rate, solids and hydraulic residence times. Likely much of the variability in the reported data can be explained by differences in operating conditions at the various facilities.

Much has been learned about the presence of chemicals of emerging concern in wastewaters during the past few years. However, the inability to answer questions is not surprising given the number of and range in molecular complexity of the various compounds, combined with the spectrum of technologies employed by municipal wastewater treatment plants and the range of operating conditions.

Publicly available environmental fate information for many chemicals of emerging concern is lacking. Approximately 250 of the 300 compounds identified in the literature search lacked information on biodegradability. This is a major impediment to the development of simulation models for predicting the removal efficiency (extent and reliability) of wastewater treatment systems.

*Although municipal wastewater treatment systems were not designed to remove chemicals of emerging concern, results of the present study, as well as government and Water Environment Research Foundation reports suggest that well operated, conventionally designed plants are capable of achieving effective reductions of a variety of substances.*

## RECOMMENDATIONS

Eight recommendations emerged from the expert consultation held in Romulus, Michigan on January 25–26, 2011 and subsequent discussion. The Work Group recommends to the Commission:

1. Investigate the contribution of combined sewer/storm sewer overflows, by-passes, and industrial discharges to loadings of chemicals of emerging concern to the Great Lakes in the next priority cycle. Combined sewer/storm sewer overflows may be substantial contributors.
2. Encourage primary treatment facilities to upgrade to secondary treatment, with consideration also to advanced treatment technologies[2] and secondary plants to consideradding biological nutrient removal processes and optimizing processes to

[2]Two of the eight municipal primary treatment plants are currently being upgraded to secondary treatment. The six other municipal primary treatment plants have received major capital funding assistance from Ontario and Canada and are in various stages to complete upgrades to secondary.

improve removal of biodegradable chemicals of emerging concern. The utility of advanced oxidation as an advanced treatment process should be further explored.

3. Evaluate improvements to wastewater treatment systems in the context of sustainability and the triple bottom line. Benefits of updating treatment technology needs to be balanced with capital and operational costs, as well as with environmental impacts such as increased power requirements to operate equipment and emissions of greenhouse gases: $CO_2$, $NO_x$ and $SO_x$.
4. Conduct sampling and analysis to determine the effectiveness of wastewater treatment to remove chemicals of emerging concern. This can be done in conjunction with ammonia and BOD as surrogate indicators. Methodologies to analyze wastewater contaminants also need to be standardized and protocols validated. Further, the capacity of contract analytical laboratories must be increased.
5. Develop a list of indicator compounds for use by facilities to assess the effectiveness of their treatment process to remove chemicals of emerging concern. A list of criteria may be needed to define "indicator compounds" for use as surrogates, that is, in addition to the conventional parameters of ammonia and BOD removal. The Water Environment Research Foundation is currently addressing this need.
6. Examine the role of biosolids from wastewater treatment facilities as a source of chemicals of emerging concern to the environment. Biosolids are often used as amendments to agricultural soils. Government agencies are currently addressing this issue
7. Prepare a list of chemicals of emerging concern that are difficult to treat using current technologies and determine which require the development of a risk assessment/risk management strategy. Further, risk-based analysis of compounds needs to be conducted especially in regard to human health.
8. Recommend biological effects monitoring of wastewater effluents. For example, bioassays of wastewater effluents could be used in combination with chemical analysis. Compounds must be sorted with consideration to those that are highly consequential in small concentrations, that is, estrogens versus those that are not, that is, caffeine.
9. Increase public education regarding the use of pharmaceuticals and personal care products and their entrance into the environment and the wastewater treatment process. Public education also includes manufacturers in terms of promoting green chemistry.

## OBJECTIVES

The presence of chemicals of emerging concern in the Great Lakes is well documented (Klecka *et al.* 2010). However, current research to determine biological effects of exposure to such chemicals in the near-shore environment is limited. The premise behind the development of an effects-based strategy is that, in order to understand the consequences of exposures to these chemicals, chemical contaminant monitoring must be supplemented with biological effects-based assessments at several levels of biological organization (subcellular, cellular, organ system, individual, and population levels).[3] To establish relative causality of various stressor categories, other stressors must also be examined and evaluated.

From a Commission initiative to assess various environmental stressors and to evaluate impacts of chemicals of emerging concern[4] in the Great Lakes nearshore, a joint Science Advisory Board/Water Quality Board Work Group developed a report during the 2007–2009 priority cycle. As follow up, the Commission directed the Chemicals of Emerging Concern Work Group to further inves tigate impacts of chemicals of emerging concern on human health and ecology of the Great Lakes nearshore environment. The Work Group undertook four activities:

- literature review of the effects of chemicals of emerging concern on aquatic ecosystem biota;
- literature review of available tools and methods to assess the ecological effects of chemicals of emerging concern;
- development of a draft Strategy for Assessing Exposure to and Effects of Toxic Substances in the Great Lakes (Effects Strategy); and,
- review of field studies that investigate the ecological effects of chemicals of emerging concern in the Great Lakes.[5]

## LITERATURE REVIEW

A preliminary bibliographic review of the effects of chemicals of emerging concern in the Great Lakes is provided in Appendix E.[6]

The review included searches of the primary literature, government documents and risk assessments. Studies were evaluated for quality control, including the use of standard methods. Findings and conclusions are presented below.

## FINDINGS

Concerns over the potential impact of chemicals of emerging concern on the Great Lakes ecosystem have grown over the last decade, but the specific magnitude,

[3] Effect-directed analyses utilize laboratory or field bioassays to assess the effect of chemical exposure on organisms through the measurement of endpoints that may relate to behavior, reproduction, survival, protein expression, enzyme activity, or other responses (Ankley *et al.* 2010, Van Aggelen *et al.* 2010).

[4] The term "chemicals of emerging concern," defined in the 2009 Work Group Report on Chemicals of Emerging Concern (IJC 2009), refers to synthetic musks, fluorinated surfactants, brominated diphenyl ethers, other flame retardants, alkylphenol ethoxylates, chlorinated paraffins, phthalates, pharmaceuticals, veterinary drugs and personal care products, and current use pesticides.

[5] Currently, field studies are being undertaken through the Great Lakes Restoration Initiative (GLRI) by the U.S. Environmental Protection Agency, U.S. Fish and Wildlife Service, U.S. Geological Survey, and the National Oceanic and Atmospheric Administration (NOAA). Field studies are incomplete and results are expected in 2012. Environment Canada manages a monitoring program that analyzes biological effects of industrial effluents. The Ontario Ministry of the Environment has developed programs such as Sportfish Monitoring and Niagara River Monitoring. These programs are presented in Appendix I.

[6] The review provides a limited assessment of selected chemicals of emerging concern and has not been peer-reviewed.

nature, and significance of their impacts remain largely unknown. Of particular importance is understanding the nature of ecosystem impacts, regardless of cause, at the population level:

- The available literature includes an abundance of acute mortality information for several model species, and much research focuses on reproductive effects in a subset of species and development effects in an even smaller subset of species.
- Detailed information on mechanisms of action is limited. The most active area of research is the impact of chemicals of emerging concern on the reproductive system and its related mechanisms, but other mechanisms may also be relevant.

Assessment and characterization of impacts to individuals within an ecosystem—except in special cases—is only significant to the extent that the information can be applied to determining impacts of chemicals of emerging concern on populations.

## CONCLUSIONS

A preliminary review of the available literature regarding the potential impacts of chemicals of emerging concern on wildlife and ecosystems suggests that additional data are needed, including:

- understanding the relationships between observed responses and impacts, i.e. when a noted response should be termed an impact;
- understanding how effects at lower levels of biological organization are linked to effects at the population level and higher;
- sublethal chronic impacts of chemicals of emerging concern at low and environmentally realistic exposures;
- impacts of mixtures of chemicals of emerging concern with traditional pollutants and methods of measuring effects in the field;
- impacts of byproducts or metabolites, which may be more toxic than the parent compounds;
- mechanisms of action at low chronic exposure levels;
- non-lethal endpoints such as growth, reproduction, and metabolism;
- methods to monitor effects in the field and methods to tie laboratory studies to field studies;
- impacts of chemicals of emerging concern at the population, community, and ecosystem levels; and,
- relationships between responses or impacts observed for chemicals of emerging concern and additional stressors that influence a particular sampling and assessment site.

*Limited data are available to characterize the ecological effects of chemicals of emerging concern, particularly field studies assessing the risk posed by these chemicals of emerging concern in the Great Lakes.*

Limited data are available to characterize the ecological effects of chemicals of emerging concern, particularly field studies assessing the risk posed by these chemicals of emerging concern in the Great Lakes. A research strategy must be developed to evaluate the risks to the Great Lakes environment posed by chemicals of emerging concern.

## ANALYSIS OF TOOLS AND METHODS FOR ASSESSING ECOLOGICAL EFFECTS

To support the development of the Effects Strategy, a literature review was conducted to identify effects-based monitoring tools and methods for ecological risk assessment, and strategies for ecological risk assessment of chemicals of emerging concern (Appendix F). Two sessions were held at the Society of Environmental Toxicology and Chemistry (SETAC) conference held November 7–11, 2010 to share findings of the literature review, discuss other large aquatic ecosystem efforts, and refine the draft Effects Strategy:

- Special Symposium: Assessing the Impact of Toxic Substances in Large North American Aquatic Ecosystems.
- Technical Session in Aquatic Toxicology and Ecology: Assessing the Impact of Toxic Substances in the Great Lakes and Other Large Aquatic Ecosystems.

Subsequently, a workshop entitled Expert Consultation: Developing a Strategy for Assessing Exposure to and Effects of Toxic Substances in the Great Lakes was held in Chicago in April 2011. The workshop convened approximately 50 experts in academia, government, and industry to consider literature surveys and the Effects Strategy. Proceed ings of the Expert Consultation are presented in Appendix G. Findings, conclusions and recommendations are presented below.

### FINDINGS

A review of the published literature and grey literature identified six major categories of methods and endpoints for ecological risk assessment of chemicals of emerging concern:

- traditional survival, growth, development, reproduction endpoints;
- methods focused on organ-based system responses;
- biochemical markers/enzyme activity/protein based measurements;
- “omic” technologies and global assessment of mRNA, protein and metabolite abundance;
- genotoxicity and mutagenicity; and,
- behavioral endpoints.

The best characterized and most widely applied effects-based methods have been those that primarily rely on apical endpoints, measured at the whole organism level of biological organization. However, a notable trend observed in the literature survey was the increasing use of endpoints reflecting cellular or sub-cellular responses, and the integration of methods from different levels of organization (*e.g.* traditional apical endpoints and sub-cellular biomarkers) was thought to provide a time/cost-effective means of assessing multiple levels of sensitivity and biological organization.

A limited number of studies have investigated effects in the field (*versus* the lab), resulting in a lack of established tools available for a field monitoring program.

Many chemicals of emerging concern are released into the environment through discharges from wastewater treatment plants. While these chemicals are increasingly being quantified in wastewaters, their effects on the aquatic environment are not routinely studied. Ecotoxicological data are available for some but lacking for others.

Few ecological risk assessment studies based on empirical data were found in the peer-reviewed lit-

erature. Many management strategies were found to evaluate available effects information. Collaboration among government and industry scientists is needed to share available information on existing aquatic risk assessments for chemicals of emerging concern.

There is no comprehensive field monitoring strategy to evaluate the ecological risk of chemicals of emerging concern in the Great Lakes. These chemicals are regulated to varying degrees under national programs in the U.S. and Canada. A multitude of approaches are being undertaken at the state, regional, and international levels. Coordinated and standardized approaches are needed to maximize information and minimize resources.

Biological monitoring programs that may be considered model programs or building blocks for monitoring the effects of chemicals of emerging concern on an ecosystem include:

- The Canadian Environmental Effects Monitoring Program, under the authority of the Canadian Fisheries Act, currently implemented for pulp and paper mills and metal mining sites, with future monitoring to occur at municipal wastewater treatment plants.
- The Canadian Area of Concern program is a well established effects-based monitoring program.
- The U.S. Geological Survey Biomonitoring of Environmental Status and Trends (BEST) Program is a river-based fish program focused on chemical contaminant measures, indicators of general fish health, and biomonitoring of environmental status and trends.
- The Toxics-Focused Biological Observing System (TBiOS) is a biologically based framework for toxics monitoring and research in Puget Sound, developed by the Washington Department of Fish and Wildlife and NOAA Fisheries for the Puget Sound Partnership.
- Effects work described at a SETAC special workshop on mixtures held in Brussels in February 2011.
- Ohio EPA Statewide Biological and Water Quality Monitoring and Assessment.
- U.S. and Canadian regulatory records containing exposure and effects information used to support product registrations and approvals.

The 2010 Water Environment Research Foundation report *Diagnostic Tools to Evaluate Impacts of Trace Organic Compounds* can be used as guidance in the consideration of site selection and chemicals of emerging concern prioritization approaches for the proposed Effects Strategy.

## CONCLUSIONS

There are many existing biomonitoring and chemical monitoring programs within the Great Lakes basin. To date, most have not been coordinated across agencies (*e.g.* federal *vs.* state programs) or disciplines (*e.g.* chemistry *vs.* ecology). A comprehensive and pragmatic ecological risk assessment program is needed to coordinate long-term analytical research and effects monitoring, collate the science, and utilize the full range of tools and information to improve understanding of the ecological effects of chemicals of emerging concern in relationship with other ecosystem stressors and to support risk management actions.

A clear objective for the proposed Effects Strategy is essential to guide strategy development efforts. The development of conceptual model(s) tied to the management objective can help to identify pathways, tools, and species to monitor.

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Several biomarker-based assays have been investigated for their potential use to assess the potential impact of chemicals of emerging concern. While there is a large knowledge gap relating lab-based results to field-based population results, future work should be carried out to close the gap.

Many chemicals of emerging concern emanate from municipal wastewater treatment plants as well as confined animal feeding operations. Understanding the potential effects of these chemicals should focus upon scenarios where wastewaters reach ambient receiving waters that have a demonstrated biological impact beyond legacy pollutants and other stressors, *e.g.* in stream habitat alteration.

To monitor for changes, there must be an understanding of the baseline reference condition (normal).

Based upon causal relationships of chemicals of emerging concern with ecological impacts, a "smart surveillance" system should be employed to verify these relationships throughout the Great Lakes basin. Such a system must be cost effective as it will concentrate resources on potentially impacted sites. Further, the types of analyses may be adjusted appropriately to site-specific needs, *e.g.* tiered approach.

Verification of the significance of observed responses and determination of the role of other stressors relative to the cause of the response are needed for causal conclusions to be drawn.

## RECOMMENDATIONS FOR EFFECTS MONITORING AND SURVEILLANCE IN THE GREAT LAKES

1. A coordinated strategy for assessing exposure to and effects of toxic substances in the Great Lakes should be implemented. The draft Effects Strategy (Appendix H) should be finalized and implemented in the Great Lakes basin. The Work Group recommends the following for the Effects Strategy:
   - Develop a conceptual model within an ecological risk assessment framework to guide the design of a biomonitoring program based on clear management goals and objectives:
     - Develop standardized methodology and endpoints for *in-situ* effects-based monitoring to assess the ecological risk of chemicals of emerging concern to Great Lakes populations and communities.
     - Evaluate the status and trends of key indicators of ecosystem function. Conduct additional causal investigations, as required, when adverse effects are observed.
     - Evaluate confounding factors, in addition to chemicals of emerging concern, to determine relative risks and causal factors. Also consider concentration-response and mixture effects.
     - Develop tools currently in the research phase that have potential utility for monitoring in the long term.
     - Utilize traditional apical endpoints and proven indicators of function of major systems and ecosystem stress.
     - Employ site-specific, ecologically relevant, abundant keystone species.
     - Foster collaboration and sharing of data among jurisdictions.

- Design a biomonitoring program using information available from current, well established programs with input from a broad representation of ecologists and the risk assessment community.
- Begin by conducting pilot studies at sites with the highest likelihood of observing a signal, *e.g.* per the WERF 2010 site identification process. Combine with baseline data-gathering using similar metrics at a broad array of locations. Work toward cyclical monitoring that is standardized across the Great Lakes, adapting the program along the way as the science improves – to improve sensitivity and robustness.
- Long-term monitoring is critical for assessing whether conditions are improving or degrading over time. Leverage existing biomonitoring efforts by integrating effects monitoring into current programs in Canada and the U.S.
- Emphasize population- and community-level metrics and do not rely solely on biomarkers. Employ traditional apical endpoints and proven indicators of function of major systems and ecosystem stress.
- Consider top-down and bottom-up approaches; predictive response patterns; toxicology, biology, and ecology endpoints; receptor traits; end use of the data; data quality objectives.
- Require frequent reporting of results, to generate interest and continued support.
- Develop a risk communication framework for communicating results to policy makers, researchers, stakeholders and the general public.

2. Additional tools and methods for assessing ecosystem effects should be developed to support and maintain a robust surveillance system in the Great Lakes. For example, further research is needed before genomic techniques can be used routinely as part of the Effects Strategy. Research is also needed to improve understanding of:
   - relationships among endpoints and different levels of biological organization;
   - effect levels and mechanisms of action; and,
   - impacts of other, non-chemical stressors.

3. A web-accessible database should be developed for uploading and sharing data among jurisdictions. This will facilitate utilization and reporting of monitoring results, interagency collaboration, and continued funding.

## OBJECTIVES

In August 2009, the Chemicals of Emerging Concern Work Group assessed the current status of chemicals of emerging concern within the scope of the Great Lakes Water Quality Agreement (Agreement). The Work Group addressed the issue of inadequate scientific knowledge and proposed priorities for new approaches. The Commission formed the Work Group with a mandate to assess the impacts of chemicals of emerging concern on human health and the ecology of the Great Lakes. The Work Group requested the assistance of Commission's Health Professionals Task Force to benefit from the latter's group expertise in the area of human health impacts. This allowed the Work Group to focus on ecological impacts and prepare a separate summary report, presented in previous section.

The current report is a culmination of the Health Professionals Task Force's work over the past two years with a contractor and other related work within the Task Force. Initially the contractor was retained by the Chemicals of Emerging Concern Work Group to perform both the ecosystem and human health bibliographic review. The contractor was instructed by the Work Group to update the report developed during the 2007–2009 priority cycle, entitled Chemicals of Emerging Concern in the Great Lakes Basin: An Analysis of Environmental Exposures (later published by Klecka *et al.,* 2010), and to use seven similar categories (excluding legacy chemicals), emphasize the point source emerging pollutants, and use peer-reviewed published scientific journals as the determinant of quality assurance. That review resulted in 271 scholarly publications. The Work Group then requested a separation of the effort between ecosystem and human health and requested that the Health Professionals Task Force assume primary responsibility for the status report on human health. The contractor's goals included: characterization of the diversity and complexity of the topic, suggestion of new risk assessment paradigm(s), and recommendations to risk-assessors and policy-makers for future directions for the Commission regarding chemicals of emerging concern and human health. This chapter highlights the contractor's report and provides the Health Professionals Task Force's recommendations for the Commission's next two-year priority cycle.

## DEFINITION AND LIMITATIONS

The term "chemicals of emerging concern", while both appropriate and descriptive for the Commission mandate, was deemed inadequate by the Health Professionals Task Force. The term "chemicals" from the Commission perspective might not include the potential indirect chemical effects on human health (such as promoting antibiotic resistance in microorganisms) or quasi-chemical substances, such as nanoparticles, which are not uniformly regulated as chemicals. Therefore, "contaminants of emerging concern" may be adopted as a more appropriate term in the future. However, since pathogens and nanomaterials were not part of the initial mandate to the Task Force or the contractor, "chemicals of emerging concern" was deemed adequate for the present report since it is more widely recognized.

An additional concern is that the mandate specifically excluded legacy chemicals (*e.g.* PCBs, DDE, mercury). Human health impacts of most legacy chemicals have never been adequately addressed and there are ongoing and "emerging concerns" which need to be considered as a part of the recommendations from the Task Force, although those legacy chemicals are not specifically addressed under the mandate. Also, the primary focus for the scope of work of this paper was an emphasis on point source exposures to better match the other two

reports from the Chemicals of Emerging Concern Work Group (wastewater and ecosystem effects). Therefore, currently used pesticides and agrichemicals (especially agri-pharmaceuticals) will receive a more thorough treatment in the next work cycle.

Finally, there is a prodigious amount of relevant environmental human health data available in the published literature which could not be fully included in the limited time assigned to the contractor nor in the time allotted to the Health Professionals Task Force to prepare this summation for the Commission. Therefore, the contractor and the Task Force used their expertise to provide examples related to aquatic exposure routes that were related to the potential impacts in the Great Lakes. Also, to be more efficient, this report is an update from the literature included in the August 2009 Work Group report, *Chemicals of Emerging Concern in the Great Lakes Basin: An Analysis of Environmental Exposures.*

## RELATIONSHIP BETWEEN HUMAN HEALTH AND ECOSYSTEM IMPACTS

Although the Chemicals of Emerging Concern Work Group focused on the ecosystem and the Health Professionals Task Force on human health, the contractor and the Health Professionals Task Force recognize that human health and contaminant risks to the ecosystem are not independent. Jacques-Yves Cousteau once remarked, “We forget that the water cycle and the life cycle are one.” With Cousteau’s quote in mind, the Task Force believes that treating human health and ecosystem impact as separate issues must be avoided. This position is supported by the Commissioner’s declarations in both the 2006 International Joint Commission Advice to the Governments (IJC, 2006) and more recently in the 15th Biennial Report (IJC, 2011), regarding the importance of including human health in future changes to the Agreement. The Task Force believes that human health should not be restricted to the Agreement Annexes, but the Agreement should be more explicit in concern for human health. Terms like “drinkable, swimmable, or fishable” are appropriate for translating the concerns to the public, but clearer and stronger support is needed in technical documentation.

## STATUS OF HUMAN HEALTH ISSUES AND CHEMICALS OF EMERGING CONCERN

The North American Free Trade Agreement-sponsored Commission for Environmental Cooperation regularly provides a status report entitled, Taking Stock, regarding pollutants from Canada, the United States, and Mexico. Chapter 2 of the most recent Taking Stock report released by the Commission for Environmental Cooperation (2011) reminds people of the magnitude of International Joint Commission’s chemicals of emerging concern charge and the inadequacy of health sciences methods. The time constraints and scope restraints often require limited summations of very broad categories of effects *e.g.* Toxic Equivalency Potentials (TEPs) using cancer, non-cancer, developmental/reproductive toxicant scoring). Similar to past use of persistent organic pollutants (POPs), the Taking Stock report has adopted the term “Persistent, Bioaccumulative and Toxic (PBT)” contaminants to help emphasize the focus on bioaccumulating, bioconcentrating, and biomagnifying toxicants (CEC, 2011). This summary approach by the Health Professionals Task Force on the issue of chemicals of emerging concern in the Great Lakes is by necessity incomplete and will require ongoing updates. However, the Task Force can begin to form conclusions and establish flexible approaches utilizing the Nearshore Priority Work Group’s call for “adaptive management”, also described in the Commission’s *15th Biennial Report.*

The scope of the contractor's report did not include examples of the human health surveillance studies currently underway or "health effects" studies that focused on legacy chemicals. For example, a number of studies were listed in the SOLEC (2009) Indicator #4177 "Biological Markers of Human Exposure to Persistent Chemicals" funded primarily by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR) under the ongoing Great Lakes Human Health Effects program. However, relevant past ATSDR-funded Great Lakes studies such as the African-American fisheaters of metropolitan Chicago (McGraw and Waller, 2008) and Ojibwa Health Study (Dellinger, 2004) do not appear in recent SOLEC assessments. This is because the data collection for those studies ended around 2002. Additionally, many of the earlier ATSDR studies were not included in the present review because they focused on "legacy chemicals" (PCBs and mercury) which were excluded by the mandate. Both of the latter studies provided observational data and conclusions which may link diabetes to PCBs through fish contaminants. In general, epidemiology norms would discount observational, non-randomized studies from proving causality in humans. This severely limits the ability of the Health Professionals Task Force or any other health policy advisory group from making a strong statement regarding "human health effects" evidence.

When discussing legacy chemicals or chemicals of emerging concern (as in the contractor's report, in Appendix J) the SOLEC status is usually rated as "not assessed" and "undetermined" for each of the lake-by-lake assessments (EC and EPA, 2009). The conclusions are that there is a great need for more surveillance and health risk analysis, especially on a Great Lakes basin-wide scope. Ongoing ATSDR and other Great Lakes research initiatives may help address some of the data gaps, but they are designed to provide human contaminant surveillance data, and linkage to human health effects may be very difficult. These exposure studies will be very important components and will rely on TEP or other risk analysis methods that cannot directly assess the actual "human health effects" but which will build databases useful for future risk assessments when combined with ecosystem and laboratory effects studies.

It will also be very important to integrate the U.S. Centers for Disease Control and Prevention's (CDC) National Health and Nutrition Examination Study (NHANES) and National Children's Study data as those studies progress. By design, these last two studies only include relatively small cohorts of Great Lakes participants as well as classifications by demographic ethnicity (*e.g.* Native Americans and other minorities). Data are collapsed across regions inappropriate for Great Lakes health studies. However, those data will be useful for comparisons with subsequent Great Lakes cohort studies.

## ANALYSIS OF THE HUMAN HEALTH EFFECTS REVIEW

### SUMMARY OF THE CONTRACTOR'S REPORT

The contractor reviewed the classes of chemicals similar to those outlined in the 15th Biennial Report (IJC, 2011). These categories were also similar to those used by the Chemicals of Emerging Concern Work Group as published by Klecka *et al.* (2010). The categories are: (1) brominated flame-retardants, (2) alkylphenolic substances, (3) perfluorinated compounds, (4) current-use pesticides, (5) chlorinated paraffins, (6) synthetic musks (included as personal care products), and (7) organic wastewater constituents (including pharmaceuticals). The primary literature search was conducted under a separate work

agreement by the contractor for the Work Group. The contractor's literature search primarily used the ISI Web of Science, cross referenced with PubMed. The review was supplemented by the guidance of the Health Professionals Task Force members to secure adequate examples of "human health effects" publications. Furthermore, the paper was supplemented with explicit reference to the Commission's *15th Biennial Report (IJC, 2011)* and the *2006 International Joint Commission Advice to the Governments (IJC, 2006).*

The contractor identified four priorities: (1) update toxicity testing for better integrated ecosystem and human health risk assessments; (2) develop better risk assessment strategies for mixtures of chemicals of emerging (which may occur at very low concentrations); (3) develop new methods to better manage contaminants with poorly understood or unknown mechanisms leading to human health effects; and (4) move away from the legalistic cause: effect focus to better define concern through a probabilistic approach that evaluates any potentially increased risk.

The contractor concluded that there are inadequate human health effects data to address public health risks for the seven categories of chemicals and not enough data to evaluate the aggregate exposures of multiple chemicals as commonly found in environmental exposures. The current chemical-by-chemical risk assessment for public health concerns is being re-examined by most risk assessing agencies to address the multitude of newly emerging pollutants.

For example, National Research Council (2007) cites substantial progress in the elucidation of cellular-response networks—interconnected pathways composed of complex biochemical interactions of genes, proteins, and small molecules that maintain normal cellular function, control communication between cells, and allow cells to adapt to changes in their environment. These advances could transform toxicity testing from a system based on whole-animal testing to one founded primarily on *in vitro* methods that evaluate changes in biological processes (NRC, 2007).

The opportunities presented by recent advances are important; however, the National Research Council (2007) points out that much refinement, development, funding, and years of research will be required before a new and efficient system of toxicity testing can be established. It is important to understand that shifting the paradigms in which assessors and researchers employ techniques to identify hazards and assess risk may also allow us to enhance these fields using relatively simple models such as zebrafish. Researchers can make these shifts now to form the first steps in establishing this much needed novel and efficient framework. To do this, the support of policy makers and funders will be required. The contractor summarized that, in researching this topic, we find a common theme: novel approaches are needed if we hope to assess the toxicity and manage risk from the enormous and growing list of chemical contaminants in the environment.

The development of techniques such as Effects Directed Analysis (EDA) for use in Human Health Risk Assessment (HHRA) could help these protocols to accommodate for complex mixtures of poorly monitored and poorly understood chemicals (*i.e.* real-life conditions). The next step in this process would be to calibrate promising *in-vitro*, *in-vivo*, and *in-situ* assays to respond to "real-life conditions". In this way, EDA would have the potential to serve the same purposes as "Hazard Identification" if properly applied. Also, EDA measures could serve as risk-reduction goals, benchmarks, or standards for regulatory purposes relating to human health. This is

similar to the concept of "biotic integrity" (Karr 1991, 1986) used for ecological risk assessments and compliance with water quality standards for the U.S. Clean Water Act. In certain cases this would require the acceptance of non-apical measures as valid toxicity endpoints. Depending on the situation, it may not be necessary to run specific chemical analysis for all risk assessments. Well understood EDA responses combined with local knowledge (industry, geography, ecosystem and historical events) might be sufficient to make policy and management decisions and test hypotheses for human health responses.

Well established screening assays exist in the literature and are used for various applications. Some examples include fish teratogenicity (Hollert *et al.*, 2003; Keiter *et al.*, 2009; Keiter *et al.*, 2010) and endocrine disrupting assays from the EPA Tier 1 screening list for the Endocrine Disrupter Screening Program (EPA, 2011). We recommend studies that investigate applicability of certain EDA assays to HHRA in conjunction with studies that investigate the ability of certain assays to respond to specific chemicals of emerging concern in both laboratory and natural settings. The Task Force strongly supports such an approach, as it will form an important framework for meeting the future challenges of both ERA and HHRA.

## CONCLUSIONS

In addition to the literature cited by the contractor, North Americans' exposures to many of the chemicals reviewed in the report are presented in the Fourth National Report on Human Exposure to Environmental Chemicals (CDC, 2009). However, the current exposure information and risk assessment methodologies do not provide a basis, as yet, for rec ɔmmendations with respect to the growing list of chemical contaminants in the Great Lakes basin. The CDC stated that the human health effects of most chemicals of emerging concern at low environmental doses or at biomonitored levels from low environmental exposures are unknown (CDC, 2009). This produces a dilemma in identifying human health effects of chemicals of emerging concern.

In general, the findings from the contractor's report are in agreement with the SOLEC Biological Markers of Human Exposure to Persistent Chemicals Indicator #4177, which concludes that, for the Great Lakes, human health assessment was/is "undetermined" and "not assessed."

The topic of chemicals of emerging concern reemphasizes the Commission's 2006 recommendations to the governments on the Agreement: "It is now time for a new Agreement with the requisite resources to produce significant results more rapidly so that the Great Lakes, as well as their tributaries, bays and connecting channels, are drinkable, swimmable and fishable for this generation and those to come" (IJC, 2006).

The contractor's review paper (Appendix J) outlines the need for action to adapt risk assessment, research, and policy to better inform the public regarding the concern for chemical contaminants in humans and the environment. Without these new directions in risk assessment and the support of policy makers, risks to human health in the Great Lakes can be neither adequately nor precisely determined nor managed.

The contractor's report agrees with the 15th Biennial Report and furthermore concludes that the methodologies, especially those regarding assessment of health effects, are inadequate and must be adapted to more closely match the methods evolving in the ecosystem effects work of the Chemicals of Emerging Concern Work Group.

## FUTURE PRIORITIES AND RECOMMENDATIONS FOR GREAT LAKES MONITORING AND SURVEILLANCE

The Health Professionals Task Force concurs with the *15th Biennial Report* and recommends to the Commission:

1. Continue on the chemicals of emerging concern priorities as defined in the 15th Biennial Report. Those priorities include: revision of the Agreement to prioritize chemicals of emerging concern to address concerns rather than just creating lists, establishment of coordinated monitoring programs including exposures and effects, and creation of an easily accessible repository of chemicals of emerging concern data for the Great Lakes to enable more efficient management of risks. Revisions made to the Agreement need to emphasize human health. The Health Professionals Task Force believes this should include using human health data as an indicator for ecosystem integrity.
2. Prioritize chemicals based on the twin criteria of their hazard characterization and the rate of increase in the chemicals of emerging concern burden within the population. Fish contaminants need to be continually assessed for impacts on human health as the primary exposure route for many chemicals of emerging concern, but consumption of fish must also be weighed for the dietary benefits.
3. Address pharmaceuticals entering the environment via non-point source pollution from agriculture and other runoff sources, in addition to point sources such as wastewater treatment plants. Non-point source pollution including agri-pharmaceuticals and currently used pesticides needs to be a priority in the next cycle, where cur rently used pesticides warrant a separate and more complete review.

## REFERENCES


Ankley GT, Bennett RS, Erickson RJ, Hoff DJ, Hornung MW, Johnson RD, Mount DR, Nichols JW, Russom CL, Schmieder PK, Serrrano JA, Tietge JE, Villeneuve DL (2010) Adverse Outcome Pathways: A Conceptual Framework to Support Ecotoxicology Research and Risk Assessment. Environmental Toxicology and Chemistry 29(3):730–741.

Centers for Disease Control and Prevention. (CDC) (2009). Fourth National Report on Human Exposure to Environmental Chemicals. Atlanta, GA: Department of Health and Human Services, Centers for Disease Control and Prevention.

Commission for Environmental Cooperation. (2011). Taking Stock: North American Pollutant Releases and Transfers. Montreal, Canada: Commission for Environmental Cooperation.

Daughton CG (2001) Pharmaceuticals in the environment: overarching issues and overview. In Pharmaceuticals and Personal Care Products in the Environment: Scientific and Regulatory Issues, Daughton CG and Jones-Lepp T (eds.), Symposium Series 791; American Chemical Society: Washington, D.C., pp. 2–38.

Dellinger JA (2004) Exposure Assessment and Initial Intervention Regarding Fish Consumption of Tribal Members of the Upper Great Lakes Region in the United States. Environ. Res. 95:325–340.

Drewes JE, Hemming JDC, Schauer JJ, Sonzogni WC (2006) Removal of Endocrine Disrupting Compounds in Water Reclamation Processes. WERF Report 01-HHE-20T. Water Environment Research Foundation, Alexandria, VA.

Drewes JE, Dickenson E, Snyder S (2009) Contributions of Household Chemicals to Sewage and their Relevance to Municipal Wastewater Systems and the Environment. WERF Report 03-CTS-21UR. Water Environment Research Foundation, Alexandria, VA.

Environment Canada and Environmental Protection Agency. (2009). State of the Great Lakes 2009. Environment Canada and U.S. Environmental Protection Agency.

Environmental Protection Agency. (2011). Endocrine Disruptor Screening Program (EDSP). Available at http://www.epa.gov/endo/ [accessed March 2, 2011].

Great Lakes Chemicals of Emerging Concern Advisory Work Group to the International Joint Commission (IJC). (2009). Great Lakes Water Quality Agreement Priorities 2007–09 Series. Work Group Report on Great Lakes Chemicals of Emerging Concern, 2009. IJC, Special Publication 2009–01, Windsor, Ontario, Canada. Available at http://www.ijc.org/en/priorities/2009/reports/2009-chemicals.pdf.

Hollert H, Keiter S, Koenig N, Rudolf M, Ulrich M, Braunbeck T (2003) A new sediment contact assay to assess particle-bound pollutants using zebrafish (Danio rerio) embryos. Journal of Soils and Sediments 3(3):197–207.

International Joint Commission. (2006). Advice to the Governments on their Review of the Great Lakes Water Quality Agreement. Windsor, Ontario: International Joint Commission.

International Joint Commission. (2009). Great Lakes Water Quality Agreement 2007–2009 Priority Work Group Final Report on Chemicals of Emerging Concern. Windsor, Ontario: International Joint Commission.

## REFERENCES


International Joint Commission. (2011). The *15th Biennial Report* on Great Lakes Water Quality. Windsor, Ontario: International Joint Commission.

Karr JR (1991) Biological Integrity: A Long-Neglected Aspect of Water Resource Management. Ecological Applications 1(1):66–84.

Karr JR, Fausch KD, Angermeier PL, Yant PR, Schlosser IJ (1986) Assessing Biological Integrity in Running Waters: a Method and its Rationale. (Illinois Natural History Survey Special Publication No 5). Champaign, Illinois: Illinois Natural History Survey.

Keiter S, Boettcher M, Grund S, Seitz N, Braunbeck T, Hollert H (2009) Decrease in fish populations in the upper Danube River. Umweltwissenschaften und Schadstoff-Forschung 21(2):186–196.

Keiter S, Peddinghaus S, Feiler U, von der Goltz B, Hafner C, Ho NY, Rastegar S, Otte JC, Ottermanns R, Reifferscheid G, Strähle U, Braunbeck T, Hammers-Wirtz M, Hollert H (2010) DanTox-a novel joint research project using zebrafish (Danio rerio) to identify specific toxicity and molecular modes of action of sediment-bound pollutants. Journal of Soils and Sediments 10(4):714–717.

Klecka G, Persoon C, Currie R (2010) Chemicals of Emerging Concern in the Great Lakes Basin: An Analysis of Environmental Exposures. Reviews of Environmental Contamination and Toxicology 207.

McGraw JE and Waller DP (2008) Fish Ingestion and Congener Specific Polychlorinated Biphenyl and p,p' -dichlorodiphenyldichloroethylene Serum Concentrations in a Great Lakes Cohort of Pregnant African American Women. Environment International 35(3):557–565.

National Research Council. (2007). Toxicity Testing in the 21st Century: A Vision and a Strategy. Washington, D.C.: National Research Council.

Stephenson R and Oppenheimer J (2007) Fate of Pharmaceuticals and Personal Care Products through Municipal Wastewater Treatment Processes. WERF Report 03-CTS-22UR. Water Environment Research Foundation, Alexandria, VA.

Van Aggelen G, Ankley GT, Baldwin W, Bearden D, Benson WH, Chipmant J, Collette TW, Craft J, Denslow N, Embry M, Falciani F, George S, Helbing C, Hoekstra P, Iguchi T, Kagami Y, Katsiadaki I, Kille P, Lui L, Lord P, McIntyre T, O'Neill A, Osachoff H, Perkins E, Santos E, Skirrow R, Snape J, Tyler C, Versteeg D, Viant M, Voltz D, Williams T, Yu L (2010) Integrating Omic Technologies into Aquatic Ecological Risk Assessment and Environmental Monitoring: Hurdles, Achievements, and Future Outlook 2010. Environmental Health Perspectives 118(1):1–5.

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