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CHEMICAL INTEGRITY IN THE GREAT LAKES
November 29-30, 2005

CONFERENCE PROCEEDINGS

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Table of Contents

INTRODUCTION **5**
What is SOLEC? 5
What is Chemical Integrity? 5
Chemical Integrity Monograph 5
SUMMARY OF CHEMICAL INTEGRITY PLENARY PRESENTATIONS **5**
What is chemical integrity? (Brian Eadie, National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory) 5
Naturally-occurring chemicals in the Great Lakes basin – Part 1 (Peter Richards, Heidelberg College) 6
Naturally-occurring chemicals in the Great Lakes basin – Part 2 (Joseph DePinto, LimnoTech Inc.) 6
Anthropogenic chemicals in the Great Lakes basin – Part 1 (Daniel Hryhorczuk, University of Illinois at Chicago) 6
Anthropogenic chemicals in the Great Lakes basin – Part 2 (Scott Brown, Environment Canada – National Water Research Institute) 6
Assessing chemical integrity in the Great Lakes basin (Keith Solomon, University of Guelph) 6
CHEMICAL INTEGRITY BREAKOUT SESSIONS – DAY 1 ..... **7**
Naturally-Occurring Chemicals – Sessions 1 & 2 7
Anthropogenic Chemicals – Session 1: What Do We Know? 10
Anthropogenic Chemicals – Session 2: What Do We Need to Learn? 11
CHEMICAL INTEGRITY BREAKOUT SESSIONS – DAY 2 ..... **13**
Naturally-Occurring Chemicals – Session 3: Key Issues and the Path Forward 13
Anthropogenic Chemicals – Session 3: Key Issues and the Path Forward 15
Summary Thoughts (Murray Charlton) 19
Anthropogenic Chemicals 19
APPENDIX A – WORKSHOP AGENDA **21**
APPENDIX B – SOLEC 2006 DRAFT AGENDA **25**
APPENDIX C – WORKSHOP ATTENDEES **29**
APPENDIX D – PLENARY PRESENTATIONS **33**

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Please note: Many of the statements included in this summary are the opinions of the individual participants and are not necessarily those of the federal governments of Canada and/or the United States of America.

INTRODUCTION

What is SOLEC?
The State of the Lakes Ecosystem Conferences (SOLEC) are hosted by the U.S. Environmental Protection Agency and Environment Canada on behalf of the two countries. These conferences are held every two years in response to a reporting requirement of the binational Great Lakes Water Quality Agreement (GLWQA). The conferences are intended to report on the state of the Great Lakes ecosystem and the major factors impacting it, and to provide a forum for exchange of this information amongst Great Lakes decision-makers. These conferences are not intended to discuss the status of programs needed for protection and restoration of the Great Lakes basin, but to evaluate the effectiveness of these programs through analysis of the state of the ecosystem. The goal of the conference is to provide information to people in all levels of government, corporate, and not-for-profit sectors that make decisions that affect the Great Lakes and through this to achieve the overall purpose of the GLWQA, "*to restore and maintain the physical, chemical and biological integrity of the Great Lakes Basin.*"

These conferences are a culmination of information gathered from a wide variety of sources and engage a variety of organizations. In the year following each conference, the Governments prepare a report on the state of the Great Lakes based in large part upon the conference process.

What is Chemical Integrity?
The following definition was proposed in the Chemical Integrity Workshop during SOLEC 2004:

> *"Chemical Integrity is Integrity is the capacity to support and maintain a balanced, integrated and adaptive biological system having the full range of elements and processes expected in a region's natural habitat."*

The purpose of this session was to facilitate planning for SOLEC 2006. This session considered the state of science on chemical integrity, the relationship between chemical, physical and biological integrity, and the research that is currently being performed or planned for the future.

Chemical Integrity Monograph
SOLEC organizers are in the initial stages of developing a monograph on the subject of Chemical Integrity. This book will be comprised of a series of contributed papers. If possible, papers for each of the topic areas that were explored at the Chemical Integrity Workshop will be included, as well as some topics for which there was not enough time for discussion. Each paper would review the published literature and summarize our current state of knowledge, i.e. What do we know about a specific chemical? What don't we know but would like to know? What are known or potential impacts from this chemical on the environment in the Great Lakes basin? What known or potential impact does the chemical have on human health in the basin? Each paper should also explore research and monitoring needs and management implications, i.e. What are the messages to managers? What are the recommended actions? What should we do about the situation, if anything? Draft papers may serve as reference information for SOLEC 2006, and they would be formally submitted for publication following the conference.

Co-authors are desired for each paper, particularly from 2 or more sectors, e.g., industry, government, environmental organizations, and academia, to help ensure a balanced presentation of status and issues. Consensus is not expected on all topics, but all pertinent issues should be raised. Disagreement on a subject may be the message itself.

SUMMARY OF CHEMICAL INTEGRITY PLENARY PRESENTATIONS

Presentations are posted online at: http://www.epa.gov/glnpo/solec/solec_2006/presentations/index.html

What is chemical integrity? (Brian Eadie, National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory)

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Brian Eadie discussed issues related to chemical integrity, including: persistent bioaccumulative toxic chemicals (PBTs) are declining but their presence still results in fish consumption restrictions/advisories; phosphorus is increasing in the central basin of Lake Erie and nitrogen is increasing everywhere; and chemical contaminant concerns in Areas of Concern (AOCs). Dr. Eadie provided suggestions for topics to cover regarding chemical integrity including, but not limited to: impacts of pharmaceuticals and climate change, aging infrastructure of sewage and water treatment facilities, recruitment and retention of younger Great Lakes scientists, constituent loads (including tributaries and global loads), and modeling. He also suggested improving risk assessment tools and using satellite imagery to assist with better defining at chemical integrity.

Naturally-occurring chemicals in the Great Lakes basin – Part 1 (Peter Richards, Heidelberg College)
Peter Richards discussed trends in water quality in Lake Erie's U.S. tributaries, e.g., general improvements for most parameters in most rivers during 1975-1995; worsening conditions in total phosphorus, dissolved reactive phosphorus, and total kjeldahl nitrogen since 1995 with an inflection point between 1993 and 2000; and mixed results for nitrate. He also discussed the recent increases in the percentage of phosphorus that is dissolved, and the fact that total nitrogen, total phosphorus, nitrate, and dissolved reactive phosphorus are decreasing or are at stable levels. He stated that the causes for some of these trends could be changes in weather, population growth and exurbanization, concentrated animal agriculture, and global climate.

Naturally-occurring chemicals in the Great Lakes basin – Part 2 (Joseph DePinto, LimnoTech Inc.)
Joseph DePinto discussed the chemical integrity of naturally-occurring substances in the Great Lakes. He explained that ecological integrity cannot be achieved simply by managing chemical integrity, but that physical and biological integrity have to be incorporated. He indicated that we cannot understand chemical integrity in an ecological vacuum, but instead must understand the ecosystems' feedback mechanisms to define the boundaries of chemical integrity. Ecosystem integrity cannot be achieved by managing single issues independently of understanding interactions with other management issues, but instead requires coordinated modeling, monitoring, and research programs. He concluded with saying that if we have learned anything over the last 30 years, it is that we need a Great Lakes Basin *Ecosystem* Agreement.

Anthropogenic chemicals in the Great Lakes basin – Part 1 (Daniel Hryhorczuk, University of Illinois at Chicago)
Daniel Hryhorczuk discussed persistent toxic substances in the Great Lakes basin, including heavy metals and polycyclic aromatic hydrocarbons, and chemicals of emerging concern, such as PBDEs. Key findings included elevated body burdens of contaminants in persons who consume large quantities of Great Lakes fish; developmental deficits and neurological problems in children of some fish-consuming parents, endocrine dysfunction among fish eaters; and disturbances in reproductive parameters. Dr. Hryhorczuk summarized some recent human health studies regarding fish consumption versus contaminant levels, children's growth and development, endocrine disruption, and reproductive health. In one study, Windsor, Ontario, ranked the highest of 17 Canadian AOCs for selected health points. He ended his talk with an overview of some of the known effects of emerging chemicals of concern, such as PBDEs.

Anthropogenic chemicals in the Great Lakes basin – Part 2 (Scott Brown, Environment Canada – National Water Research Institute)
Scott Brown provided an overview of anthropogenic chemicals including a review of the history of beneficial use impairments in AOCs. The good news is that many deleterious effects on wildlife and fish have been recognized in recent decades and some have been mitigated, e.g. the return of fish-eating birds populations to the Lake Ontario basin. Dr. Brown reviewed the most recent data on wildlife and fish health effects in the AOCs, e.g., benthic and pelagic fish, snapping turtles, herring gulls and mink, and found that health changes are detectable, with effects mostly found at sites near AOCs. Early Mortality Syndrome (EMS) has been observed between hatch and first feeding in Great Lakes salmonids. EMS is a symptom of degraded ecosystem and its presence emphasizes the need to maintain biodiversity. Other effects include sporadic blue-green algae blooms and botulism outbreaks.

Assessing chemical integrity in the Great Lakes basin (Keith Solomon, University of Guelph)
The closing plenary presentation, given by Keith Solomon, explained how to assess chemical integrity in the Great Lakes basin. He stated that in order to make this assessment, we must identify chemicals of concern as well as sources. We also need to assess the effects above the level of the organism and assess the risks of chemicals of concern; we cannot simply rely on traditional tests with traditional endpoints. He concluded by stating that dealing with mixtures is complex and whole effluent testing offers advantages.

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CHEMICAL INTEGRITY BREAKOUT SESSIONS – DAY 1

Naturally-Occurring Chemicals – Sessions 1 & 2

Mercury	
What Do We Know?	**What Do We Need to Learn?**
o There are 3 forms in the environment; elemental, methyl, oxidated o Sources are widespread o Smokestacks are a significant source of atmospheric input o There is mercury in zebra mussel tissue o There are no wildlife consumption guidelines so we don't know if anyone has looked at this o Mercury does trigger fish consumption advisories – it's a human health issue	o We need to make an assessment about what the largest mercury contributors are and whether addressing local issues will be enough. We need to determine the amounts being deposited from global, regional and local sources. o We need a better understanding of the mechanisms of how mercury changes form in the environment. o We need to know how to lower fish consumption advisories o What are the sources of bio-available mercury, where are they, and can we remediate? o Can we look at changes in diatom communities (this is difficult) in sediment cores to determine an environmental baseline? o We need to keep looking for potential sources. o We need to research nearshore affects in addition to open lake. o We need to research affects on fish behavior and wildlife.

Phosphorus	
What Do We Know?	**What Do We Need to Learn?**
o We are able to control it. o We have made good decisions about controlling loads and concentrations beginning in the 1970s, but are they still good decisions? o We know the life histories of Great Lakes fish depend on pulses in phosphorus levels. 80% of the phosphorus loads to Lake Erie occur in 20% of the year. o There is variability in phosphorus concentrations by region, lake and season. o The season that the pulse occurs is significant. Late summer fish production is determined by phosphorus cycling. o Over the long term, phosphorus is a lake-specific issue. o In Lake Erie, the sediments are closely coupled with the water column. Because the Lake is shallow, the phosphorus is redistributed more quickly. o Residual phosphorus being recycled is a concern and tied to tributary sources. o Residual phosphorus is lake specific. o Phosphorus is controlled from point but not non-point sources.	o Target loadings and endpoints • We don't know whether the decisions made in the 1970s about acceptable levels are valid today with a changed ecosystem. Are our decisions about target levels, which were based on what we were looking at then, still valid today? • What are appropriate loads by watershed? • How are we going to pick desired endpoints? o Bioavailability of phosphorus • We don't know whether it is important to look at proportions of soluble to total phosphorus. The soluble portion has been increasing recently. • We don't know about changes in bioavailability. • We need to research total and soluble phosphorus in this new environment. o Environmental fate and loadings • Naturally occurring pulses – do we know about them? We don't know whether we have changed the phosphorus pulses. • We need to look at phosphorus on a

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Phosphorus	
What Do We Know?	**What Do We Need to Learn?**
o Tributaries are the largest sources, whereas in the past the largest sources were municipal. o In Lake Erie there has been a reduction in non-point source loads. o In the Maumee River there are not enough point sources upstream to account for the phosphorus load. Some is from non-point sources. o We have good information on how hydrology of the system affects phosphorus loads.	watershed by watershed basis because the mechanisms making phosphorus available to aquatic systems are unique to each. • How is the residual phosphorus in systems recycled and then eventually sequestered? • No model now exists that deals with nearshore vs. offshore loading. • Round out SOLEC reports so we communicate the difference between offshore and nearshore loads, including tributaries. o Monitoring issues • We need to look at a finer scale to determine whether phosphorus levels are in balance. • Are we monitoring enough of the watershed and the correct sites to get accurate results? • Storm drainage, aging infrastructure, etc., are not monitored, and we need to determine if they are contributors. • What is the accuracy of the monitoring networks that are in place? Do we need to change, increase frequency of monitoring, etc.? • We need better phosphorus data from Canada and Michigan. Concentrations in tributaries may have been measured but have not been made available. o We need to focus on regulations for non-point sources.

Bio-toxins – Cyanobacteria	
What Do We Know?	**What Do We Need to Learn?**
o We know that we are measuring high concentrations that cause issues in drinking water and wildlife. o Chlorophyll is one measure or part of the measure of photosynthetic capacity but it doesn't give you biomass. o Human ingestion of algal blooms promotes tumors and affects the liver. o Less than 20% of water treatment plants remove microcystins. This requires tertiary treatment.	o Occurrence in the environment • We do not know which species is making the toxins, and it is different in every basin. • We don't know how it is getting into the system or whether this is a natural phenomena. • What is a bloom? There is no accepted definition. What promotes an algal bloom and what promotes toxin production? • What are the factors of bloom formation from one species to another? • Need to know the taxonomy of algae/phytoplankton, not just chlorophyll type and amount. o Monitoring and measurement

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Bio-toxins – Cyanobacteria	
What Do We Know?	**What Do We Need to Learn?**
	• We need a finer scale analysis of the problems and integrated monitoring. • There may be a bias in how we are measuring the toxins. • A phosphorus level of 20 micrograms/liter and increasing precedes a bloom. We need an early warning indicator. There is no predictive measure right now. o Human health effects • We need human health, epidemiological studies about acute and chronic toxicity. • We may not have established a maximum acceptable contaminant level in the US for microcystins. There are questions about exposure for humans. Do we know exposure levels • What are the effects of small exposures for long periods of time • We need to establish basic understanding of exposure routes.

Nitrates	
What Do We Know?	**What Do We Need to Learn?**
o Once it is in the system, it is there for good. Prevention is preferred. o At most environmental levels it is not toxic, but it is soluble. o 75-80% of total nitrogen is nitrates in tributaries o It does present problems in groundwater. It is being monitored in Ontario and maybe in Michigan, but not regularly in the US o Municipalities test for it in drinking water o 10 mg per liter is the guideline for nitrates and 1 mg for nitrites in the US for drinking water o Nitrate concentrations are going up in all the lakes. o Lake Superior paper from 1970 sites an increase over the last century. o Loading is increasing since phosphorus is decreasing. o The sources of nitrates are acid rain, Concentrated Animal Feeding Operations (CAFOs), sewage treatment plants, (correlations exist between nitrate increases and the amount of it sold for fertilizers. The Lake Superior basin is not predominantly agricultural, so the source of the increase in Lake Superior might be acid rain.) o Management tradeoff between phosphorus in sediments and nitrates	o Presence, fate and transport in the environment • We do not fully know the nitrogen transformations in the system, i.e., the nitrogen cycle. • We do not know why concentrations are changing. Is it still an issue? • We need to know where the main inputs are and how much is coming in before it gets diluted. • What is the extent of internal loading through nitrification of sediment? What is the ratio of nitrate to nitrogen gas? • Is agriculture a major source? (Corn and soybean production have increased in the basin) o Effects on human health • Our knowledge of human health dietary impacts are incomplete. o Environmental effects • Are nitrates affecting the hatchability of fish eggs close to storm sewer outlets? • What effects are there on certain species? • What effects are occurring at wetland (or other systems) vegetative margins? Could increases in nitrates be explaining population shifts of some species?

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Ammonia	
What Do We Know?	**What Do We Need to Learn?**
o This form of fixed nitrogen is released by biota in a nitrogen cycle. o Fish are sensitive to un-iodized ammonia. o There have been Green Bay beach closures because of toxic ammonia levels. o In most areas, concentrations in the water are at or near detection limits. o Concentrations are not high in tributaries unless there is a local point source o There are still incidences of where ammonia may affect algal growth.	o Where are the major sources of ammonia in the watershed, e.g. sewage treatment plants?

Chloride	
What Do We Know?	**What Do We Need to Learn?**
o This is an indicator of anthropogenic impact on the ecosystem o It naturally existed at 1 mg per liter, but now concentrations are much higher o There is an argument that an increase in chloride concentrations may provide a friendlier environment for [marine] species to acclimate to fresh water. o There has been a decrease in chloride concentrations in the Lower Lakes. o The last studies were from the 1970s. o 750 stormwater ponds are sequestering brackish water. Late-1990s Toronto studies are raising concerns because brackish water is coming into sensitive areas o True marine organisms would not survive with these levels, only brackish creatures.	o What are the ecological impacts of increased chloride concentrations? o We don't know what the cumulative impacts might be basinwide. We need to revisit because the data are 30 years old. o We should look at loading issues and salt chloride relationships. o Are there issues of cross contamination in aquifers of brine? o Is sodium a limiting nutrient for blue-green algae?

Anthropogenic Chemicals – Session 1: What Do We Know?

<u>Presence of anthropogenic chemicals in the Great Lakes basin</u>

- Discussion included the definition of what we mean by "what do we know?" Full certainty is not possible, but we have strong evidence about certain classes of chemicals.
- We need to be discussing actual constituents of all of these chemicals; and not just the classes of chemicals.
- Sources of Contaminants
  - Waste water effluent is a source of emerging contaminants and we have not typically looked at waste water for legacy contaminants.
  - There are data about emerging compounds that we can consult from studies conducted outside the basin.
  - Groundwater contains radon and arsenic
  - We know some sources of contaminants (for example, mercury) are long-range. Regulatory action outside of the Great Lakes basin is needed.
  - "New" sources of chemicals are not being monitored
- Regarding the "dirty dozen" (legacy chemicals)
  - See Binational Toxics Strategy documentation for more information. A lot of research has been done on these contaminants.
  - We have the data to show downward trends but they are still present in the environment, even after events such as the banning of DDT.

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        - Are the current regulations sufficient? If consensus is that they are sufficient, then why are we still addressing issues associated with these contaminants in the environment?
        - Regulation does not equal virtual elimination.
    - Modeling
        - We can predict/model contaminant presence and trends before we measure them in the environment (this is true for some, not all)
        - We need better models and the data to input into the models.

<u>Observed or potential impacts on Great Lakes ecosystem health</u>

- The highest priority contaminant class to be focused on in terms of input and quantity should be PBDEs
    - Their toxicology is unknown
    - Sediment cores show exponential increases in the 1990s
    - Are we lacking data about trends of contaminants in the sediment?
- Observed feminization in fish and amphibians. Fish are functioning differently but complete feminization is not evident. Are there ecosystem effects though? No effects have been documented on Great Lakes function.
- Perfluorinated Compounds (PFCs) are persistent in the water column.
    - Is this a worse problem than persistence in the sediments?
- Wildlife are recovering from known legacy contaminants since environmental concentrations of POPs have decreased.
- It is unknown as to whether wildlife are recovering from chemicals of emerging concern. One theory is that the "new" chemicals are not as "bad" as the legacy contaminants.

<u>Observed or Potential Impacts on Human Health</u>

- We know that a healthy ecosystem is important to maintain healthy people.
- It is harder to detect trends in human health because concentrations of some toxic chemicals are decreasing in the environment (see Daniel Hryhorczuk's talk). Therefore, should we now focus studies on fetal exposure AND specific times during people's lives when they are more sensitive to exposure, i.e. study PCB levels of people born in the 1950s or teenagers going through puberty? There are many potential confounding factors. (A study would need archived cord blood or archived breast milk samples to be rigorous.) Current exposure might not be the important exposure to focus on and larger populations need to be surveyed in the future.
- Some members of the discussion group claimed we know little about direct exposures of mercury on human health in the Great Lakes basin; others claimed that we do know that there are direct effects of mercury exposure (via consumption of Great Lakes fish) on human health when a certain does is ingested. This statement was challenged by some members who stated we do not have data to support this claim. It was agreed that we think we know that there is some sort of problem from eating Great Lakes fish and that the government is using the advisories in an attempt to inform the public about the situation and potential impacts. The existence of fish consumption advisories does not mean that exceeding the advice will result in an impact. Some believe that most people don't eat Great Lakes fish (as most fish purchased in supermarkets comes from other locations) and therefore the contamination is not from these fish but from air emissions.
- The health of the general population in the Great Lakes basin is based on life expectancy. Since life expectancy in the Great Lakes basin has increased over the years, it can be inferred that the health of Great Lakes basin residents is also improving/increasing. However, we know very little about actual chemical exposure from the Great Lakes and the health impact on basin residents.
    - This trend could also be due to better health care.
    - To make this claim, we need to separate fish ingestion from exposure to other media.
    - Overall population health is not a good indicator for certain at-risk populations that consume a lot of fish.
    - Studying subsets of populations is the key. We can't generalize across the Great Lakes basin regarding exposure.
    - The Great Lakes basin is contaminated from a lot of different sources. Accumulation of contaminants [in humans] does not occur primarily via fish consumption.

Anthropogenic Chemicals – Session 2: What Do We Need to Learn?

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- There is a need to determine what is in the lakes in terms of chemicals, what the effects of these chemicals are and what are the risk assessment paradigms with respect to these chemicals working synergistically. There is a difference between documenting the presence of chemicals and risk assessment.
- The trends, sources, loads, etc for each chemical is important information that needs to be determined.
- We need to know more about the "mixture" or synergistic effects of these chemicals and the impacts on the ecosystem and human health.
- Need to develop a priority list of chemicals that need to be addressed. We cannot look at every chemical being used, but we can develop a list of priority chemicals to look at and research.
- The list of chemicals [presented to the workshop] is not accurate as it stands now.
- Need to learn how to categorize these chemicals. For example, in Canada the Domestic Substance List is under review. PBT properties, risk assessments, management action required and data gaps for these chemicals are being identified. Chemicals with unknown information are also being included on this list.
- Endpoints. SOLEC was never given the charge to determine and set endpoints. Endpoints help to determine whether management action or programs are working or need to be modified. Since the Great Lakes Water Quality Agreement will be under review, the issue of a lack of endpoints for the Great Lakes indicators should be brought forward as a discussion item that needs to be addressed during this review process.
- Need timeframe to meet endpoints.

<u>Presence in the Great Lakes watershed</u>

- SOLEC reports on a small percentage of compounds – consider expanding the list.
- Chemicals that are or should be added to the list are below. The comments related to each chemical can often apply to one or more classes of chemicals in the list.
    - Pharmaceuticals (including SSRIs)
        - Other countries have conducted risk assessment studies on pharmaceuticals. No harmful effects were detected.
        - No studies showed health impacts by pharmaceuticals.
        - USGS conducted a study regarding pharmaceutical products in water supply.
    - Non-prescription drugs (use is completely unknown)
    - Legacy contaminants
    - Mercury – global transport and in basin sources are both sources of mercury
    - PBDEs
        - More exploratory work is needed, more analytical methods are needed.
        - Fish consumption in the Great Lakes is not the main route of exposure for PBDEs in humans (currently).
        - There are data showing PBDEs are increasing exponentially in rainbow smelt.
        - The longer we continue to use PBDEs, this risk could increase.
        - We need to prevent PBDEs from entering the food chain.
    - Pesticides – global and in-basin sources are both sources of pesticides.
    - Polymers (brominated) – breakdown rate in the environment is unknown
    - Agricultural chemicals (registered and veterinarian drugs) – screening needed in agricultural and urban areas as there is a time lag between emissions and absorption by fish. Temporal trends are needed. Need tissue samples and archives to determine temporal trends.
    - Nanomaterials – not easy to monitor, ubiquitous, non-biodegradable, pass through membranes, bioconcentrate
    - Perfluoride compounds – breakdown rate in the environment is unknown
    - Leachate from landfills
    - Surfactants (alkyl phenols)
    - Metabolites of hormones, pharmaceuticals, mirex, atrazine, etc.
    - Water effluent
    - Metals – naturally occurring but when chemical reactions occur, they can change their structure and speciation – free metal ions (Ca and Mg)
    - Personal Care Products (PCPs)
        - Antibacterial surfactants in PCPs are causing bacterial resistance.

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        - These bacteria might not survive in the environment (studies show survival in the lab but not in the field).
    - Endocrine disruptors – Many chemicals comprise this group; "endocrine disruptors" are an endpoint classification
    - Androgenic and estrogenic-mimicking compounds
        - These compounds can cause the effects attributed to endocrine disruptors.
        - Estrogen sources can be from farm animals, agriculture, chemicals, etc.
    - Musks
    - Carcinogens and mutagens
    - Road salt (anti-slip agents)

Impacts on Great Lakes basin ecosystem function

- A contaminant concentration that may not be high enough to pose risks to humans *could* cause risk to aquatic biota. Do we know or not know this?
- General statements about ecosystem function
    - We know that at high concentrations and exposures of certain chemicals, there are toxicity impacts on ecosystem health and function and effects on organism reproduction. Inhibition of lake trout reproduction (in the past) is an example.
    - "Critter level" impacts apply to populations, not individuals.
    - Ecosystem effects definition needs to include the spatial scale and area affected.
    - If you don't know if there is an impact, can you say that there is a *potential* impact?
    - Keep in mind that just because there is a risk, it doesn't mean that there is a problem.
    - There are regulations in other nations for some of these chemicals. We might not need to reinvent the wheel.
- How do we move into risk management? What is the expectation of where we are going?

Summary of what we need to learn

- Need to be vigilant because we have done a lot of work on chemicals to get where we are today. Learn from this process and react quicker next time. For example, human population growth and vehicle miles traveled are important indicators of an increase in the release of PBDEs, therefore the trends in usage/emissions need to be considered.
- If we aren't finding problems, then do we assume that the issues do not exist or do we need to look harder?
- We have improved methods to detect chemicals, but still need to determine endpoints so that progress towards a goal can be measured..
- Need more money so research can continue, especially long-term monitoring.
- Need to expand the list of compounds being reported on.

CHEMICAL INTEGRITY BREAKOUT SESSIONS – DAY 2

Naturally-Occurring Chemicals – Session 3: Key Issues and the Path Forward

Need studies/research about the systems/parameters.

- The nearshore is the center of most problems.
- We need to assess loadings into the lakes by tributary.
- What are the interactions of nutrients in ecosystem function? We need to assess functional approaches, productivity, biomass, growth rates within systems.
- We need accurate information about primary production

Need risk assessments and cost benefit analyses to prioritize what to study further and monitor—decisions need to be based on agreement by scientists and managers.

Need long term monitoring of parameters that have been prioritized.

- In general, we need long term monitoring on all naturally occurring chemicals.
- We need monitoring on radon/arsenic/nutrients.
- Restore long term monitoring to tributaries.

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- Expertise is lost when you lose monitoring years. Then there is no message.
- We need more atmospheric deposition monitoring, especially for mercury.
- Measure the right things. Take into account "Type 3" questions (what are we really looking for?).
- Increase replication not duplication.
- We don't know what the future is, therefore long term monitoring is essential.
- Long term monitoring is undervalued by agencies.
- Long term monitoring needs to be better coordinated between Environment Canada and EPA. If methods differ but results are similar, that is ideal.
- Data can be shared through the monitoring inventory on binational.net.
- Unrealistic expectations about binational monitoring coordination may actually provide a check and balance in the long term.
- Monitoring can be opportunistic, e.g., vessels on the lakes can measure more than one thing at a time.
- Nearshore monitoring is expensive but necessary.
- We need indicators for mass balance and rate of accumulation of phosphorus (e.g., lawn care, fertilizers, urban areas, groundwater, inland lake eutrophication, feed lots).

<u>Need to inhabit appropriate models with data from the studies and monitoring</u>

- We need data on all naturally occurring chemicals for the models.
- We need models that are hypothesis driven.
- We need to be able to parameterize the models.
- Previous models aren't appropriate today due to invasive species and loadings.
- Models need to be holistic enough to include the entire food web.
- We need wetlands and riverine modeling.

<u>Need to determine bounded endpoints based on science for those parameters that are important or prioritized.</u>

<u>Manage systems based on the studies, monitoring, and models. This requires communication</u>**.**

- Laws exist for arsenic but not for phosphorus, which is just as important.
- Monitoring is useless unless it becomes information and is shared.
- Coordination and management needs dollars and people. Funding requirements need to be well stated and directed at the appropriate agency. A contingency fund for unexpected problems needs to be included in cost estimates.
- Agricultural systems are primarily voluntary. Therefore, we need a watershed approach and additional information for managers regarding best management practices.
- Managers need to understand the importance of letting researchers meet and talk.
- Researchers need to talk frequently with environmental managers about problems and needs (e.g., Lake Erie Millennium).
- We need to inform managers about connection between groundwater, nearshore, and open lake.
- We need to get information out there on a constant basis. We need to be more articulate.
- NEMO (non-point education for municipal officials) is a model we should look at.

<u>This is a continuing process requiring vigilance.</u>

- It will be necessary to continue long term studies, modeling, and monitoring, because while we will solve some problems, new ones will emerge.
- Each Lake needs to have an equivalent of the Lake Erie Millennium group.

<u>Summary</u>

- Long term assessment programs need to be maintained.
- Old models need to be revamped because of changes in the system. We need models to integrate what we are learning, so we better understand the system. How serious is this for decision making?
- Researchers need to be funded to share information and to keep funders' concerns in mind.
    - Make better use of binational.net.
    - There is a need for researchers to talk. Establish a Millennium-like equivalent for each lake.
    - Maintain adequate and consistent funding.
    - Translate information and present it to managers.

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Anthropogenic Chemicals – Session 3: Key Issues and the Path Forward

Priority Chemicals List

- Find a process to identify and prioritize these chemicals and processes. This could be a useful piece for the replacement of Annex 1 in the GLWQA. Current Annex is static and needs to be updated and revised.
- We need to identify the chemicals that we have consensus on and get the funding.
- Set aside chemicals that are not problematic. Perhaps we are including chemicals in the list that don't need to be researched. However, it is a waste of resources looking at a very specific suite of chemicals just because they are easy to measure.
- As we prioritize the list, we can remove chemicals during this process as well. Don't get caught up in making lists. Don't be afraid to de-list. The removal of chemicals may show progress.
- Economic analyses: cost effectiveness / cost benefit analyses to be included in these prioritization approaches.
- Use the Domestic Substance List to identify existing chemical compounds and to assist with the development of the priority chemical list for the Great Lakes.

Human Health Issues

- Finish the job on legacy contaminants. As long as there are fish consumption advisories, there is the perception that there is a problem. Is there a reference or an endpoint?
- We need to be better at developing messages for the public. The public is very confused, for example, about pesticide bylaws and advisories and whether or not they should use pesticides or eat fish from the Great Lakes. Clear and concise messaging is needed.
- Trends in cancer rates are leveling out (incidences) except for lung and skin cancer. Refer to the Center for Disease Control (CDC) website. There is a causal relationship between skin cancer and the sun and lung cancer and smoking. If our drinking water was causing these things, we would see it.
- There are increased incidences of cancer rates in young people, increased cancer rates in non-smoking people, etc., that are a result of multiple causes.
- We are dealing with a chemical soup in the environment. Epidemiology is associated with statistics that cannot determine causality. We should not be encouraged to be able to identify one chemical that is hurtful from epidemiological studies when exposure is to many chemicals.
- Epidemiological language may not be the best to use, but rather human health effects in response to chemicals, not based on cancer endpoints, but rather neuro, renal results, etc.
- Studies in recent years show that thallium acts like methyl mercury. Sediment core studies from Switzerland show neurotoxin issues similar to methyl mercury.

Ecosystem Health Issues

- There seems to be reduced interest in ecosystem health. Much money is going into human health, but not ecosystem health.
- We need to legitimize the importance of ecosystem health and science.
- We should move towards a sustainable environment.

Remediation and Environmental Control

- Try to pull in economical analysis when determining priorities for Great Lakes remediation or other management actions. Any prioritization that is done needs an economical assessment.
- There is a whole range of things [chemicals and issues] in the environment and we can't look at them all on the same level. We need to focus on things now that can be addressed in the future. Managers want to get the most "bang for their buck".
- We need to look at the things that need to be done (based on the priority chemicals list), evaluate the cost effectiveness of different approaches, and then show the benefits of the most efficient approaches.
- Governments are spending millions on restoring the ecosystem. Sixty million dollars spent on sediment remediation. Did it work? Governments need to go back and evaluate effectiveness.
- A timeline for Area of Concern (AOC) cleanup is needed.

Indicators and Endpoints

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- Legacy contaminants require endpoints and a timeframe for reading these endpoints.
- What are the human health indicators that we should be reporting on? What is it that you would like to see done with the existing information?
- Reference toxicity values are not agreed to, i.e., no consensus, but if you look at metadata, you can look at trends and see that things are happening.
- We have to worry about too high of levels [of chemicals], but also too low of levels. Does this come into play with endpoints?
- The assessment of biological health is an indicator of chemical impairments. Linkage is needed with biological and chemical integrity. Biological health can serve as a warning of chemical problems.
- When is clean, too clean?

Research Issues

- Research priorities need to be reviewed. Is the list in Annex 17 of the GLWQA still relevant? Where is the research on climate change, energy sources, etc? Through the process of defining chemical integrity, there is an opportunity to look at research agendas, and this could happen with the review of Annex 17. Use the messages that are coming out of SOLEC (i.e. chemical integrity) and consider them very seriously in the review of the GLWQA.
- There is a lot of tension when we talk about the effects on humans related to chemicals. Research is unclear, but what is this tension conveying to managers? Epidemiological research is needed that is designed to be conclusive, i.e., the right cohorts, right exposure. Ecosystem and human health work is not an epidemiological study. Health effects are unclear, and scientists disagree. Federal governments have a responsibility to get this research done.
- Where do we need research? We should not use a fear approach because it is not sustainable. If we identify unknowns that we are all trying to research, we may have more leverage to receive funding.
- Rather than referring to "environmental research," we should revise our lexicon to help focus more towards "sustainability."
- Let us caution against "Type 3" errors, i.e., we think we know what we are looking for, but we are trying to answer the wrong question. Are there ways to help recognize this error?
- We need more research on chemical mixtures (additive or synergistic effects)
- More university involvement in research occurring in the Great Lakes is needed.

Monitoring

- Continuing long-term data sets is important. We can't put all of the money into PCB research, but it is still important to be able to look at PCB trends.
- The foundation for all of this [evaluating chemical integrity] is monitoring. It is our way of measuring our successes and determining where problems are.
- The Council of Great Lakes Research Managers is trying to develop a monitoring strategy to compete for research money.
- We can use many different approaches to additional research that is necessary, but we need to continue monitoring. If all stakeholders communicate that we need to continue monitoring, then the chance of funding is higher.
- There are issues concerning archiving environmental samples
    - We must create an archive tool for fish tissue and/or sediment NOW! There are chemicals that we don't know about now that we will need to test for in the future.
    - The 30 year old archive of fish tissue in Canada is threatened.
    - The fish archive in U.S. is held by U.S. Geological Survey, and every year the question is raised about whether money is available to keep the freezers running.
    - We don't have a good mammal archive in Canada. We don't routinely store air, water and sediment extracts.

Funding

- In terms of funding and research, we know what we need to do, but we need to identify who is doing this research, i.e., we need a common research strategy and an overall funding program.
- There is no [centralized] fund in the Great Lakes to which researchers can apply for funding. There should be a source for basin-wide, competitive, research funding. For example, IADN is run by a university contractor.

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- There are very large amounts of money being put into [Great Lakes research] that has nothing to do with human/public health. Very little money is put into research to identify relationships between chemicals in the environment and public health.
- Prevention is a very wise way of spending money. We have intervention programs that have been successful and can translate into human health improvements and remediation. Perhaps we have not seen the human health improvements because of time lags.
- An underlying theme for these points is the lack of money. Eco-evaluation is going on internationally. You should care for the organisms because they need it, but money is one of the considerations that is looked at when determining research.
- If this were your last chance to get funding for the future, what would you convey to managers?
- What does it mean when we say that 98% of our samples have "x" in it, but it may not be something that causes harm. We can't use scare tactics to get research grants.
- There are many examples of a shortage of funding for Great Lakes research:
    - In many cases, research and monitoring budgets are either static or declining. The continuation of the Canadian fish monitoring program is questionable.
    - Why are *Diporeia* declining? We came up with some good ideas, but where is the money going to come from to determine why they are declining? Millions of dollars are needed for research.
    - Unless you have dead bodies, there is no political motivation to get funding for research.
    - A lot of environmental research has been "crying wolf" for a long time. Now we need to show ways of cost savings to get funding money.

<u>Great Lakes Governance</u>

- Taxpayers and politicians are overwhelmed and don't know what to pay attention to. We [stakeholders] may be passionate about some issue, but it is not always an issue for government. How do you convey this message?
- Build in for SOLEC participants, how the governments are dealing with issues related to chemical sources that are affecting the Great Lakes. There are mechanisms, but they are not well understood.
- Cost benefit analysis does not capture everything. We need adaptive management tools to take the cost benefit analysis and make it relevant in the ecosystem.
- We have been successful with POPs (Persistent Organic Pollutants), because we ultimately came to a near consensus decision that all stakeholders needed to work towards the same goal.
- A multi-stakeholder approach is needed, as well as being aware of public perception.
- The main messages from the U.S. Great Lakes Regional Collaboration included:
    - We need to finish the job related to existing problems (still need to reduce legacy contaminants) and be aware of chemicals (grandfathered chemicals) that need to be tracked and reported
    - We need funding. We have a big job ahead of us to reduce existing chemicals in the environment.
- Specific agency challenges that lie ahead include:
    - U.S. EPA – GLNPO is sub-optimizing its monitoring program. Funding has been constant for years. To monitor new chemicals requires trade-offs within the existing program to stay within budget.
    - Beginning in 2006, Environment Canada will be charged to use the LIMNOS, which they had used for free in the past. No one has this cost included in their budgets.
    - Many Great Lakes scientists within Environment Canada are retiring, which will affect not only Environment Canada but other Great Lakes institutions as well.

<u>Communications and Reporting</u>

- Defining Chemical Integrity
    - We need one definition of chemical integrity in the Great Lakes basin so everyone can work towards this one definition. We want to make sure that there is a consistent message about what chemical integrity means.
- Improving Communications with the Public
    - Things are getting better in the Great Lakes for the compounds that we are measuring. Where is this information being provided to the public? Maybe those things aren't so bad, but what other things do we need to be worried about? We need to do a better job of communicating the science.
    - We need to better communicate the status of certain chemicals in the Great Lakes which isn't going to change quickly because of retention time. We still need to monitor those chemicals, but maybe our focus

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should change. How much effort do we put into tracking and reporting on these slowly-changing chemicals?-

- How do you convey the message regarding human health issues? In the 1950s-1960s, the exposure to anthropogenic chemicals was higher, but now the general population is living longer and leading healthier lives. How do you compel the public to see that there is a health issue? Some of the chemicals that we talking about in the system are also the drugs that are helping people live longer.
- It is also important to communicate to the public about what contaminants we are NOT finding through our monitoring programs.
- We need to better report on the implications of trends of contaminants

- Getting press release attention from the Media
  - When we have a success, it should be blasted out to the public. Lack of media interest should not waylay communicating good news to the public.
  - Success is a tough term. SOLEC can demonstrate where there have been successes, but what newspaper will carry the message that a 98% reduction of loadings to the Niagara River has occurred? Someone else needs to commend the government(s) for doing a good job, e.g., the Sierra Club might announce that the government did a good thing.
  - You get media attention by putting key words in a press release, e.g., "DEAD ZONE" in Lake Erie.

<u>SOLEC-related Comments from Workshop Participants</u>

- What are the future trends? SOLEC is an opportunity to get some big issues into the arena in a multi-stakeholder forum. For example, what is going to happen when we run out of oil? Will major restructuring be occurring? What about climate change? Forecast the trends.
- SOLEC should not marginalize issues.
- As you think about SOLEC 2006 messaging, ensure that ecosystem function assessments are included. Prioritization of issues such as lumps and bumps versus *Diporeia* is important.
- SOLEC is a process to evaluate the effectiveness of the programs. Therefore you need to monitor the effects of the interventions. What has been spent on the Great Lakes in terms of monitoring to track improvements? You may find that the money spent on monitoring is nothing compared to the money spent on remediation.
- For SOLEC Success Stories, try to identify local, state/provincial, and regional levels that have done something successful. No one has recognized what the governments have done that has benefited industry, etc.
- The Binational Toxics Strategy group produced a good report on how reductions are happening. Maybe we need to find a better way of reporting.
- If we believe that governments need to invest more money, then maybe SOLEC should invite keynote message-givers who are not government staff, but are industrial representatives, ENGOs, etc.
- The public perceives that there is a strong link between the Great Lakes and human health impacts. SOLEC could help focus the message around this strong perception, including research that is being conducted and the scientific results that are available.

<u>Summary of Main Messages to Relay to Decision Makers in the Great Lakes Basin</u>

- Monitoring: long-term monitoring is essential. It is cheaper to monitor then remediate. Monitor ecosystem function, not just human health impacts.
- Prioritization of chemicals is needed. We need consensus on the chemicals to monitor.
- Funding for research is needed.
- Endpoints are required for the Great Lakes indicators in order to see progress and successes.
- Messaging is important. We need to better communicate messages to the public, including success stories.
- Sustainability is a goal that we should be aiming towards.

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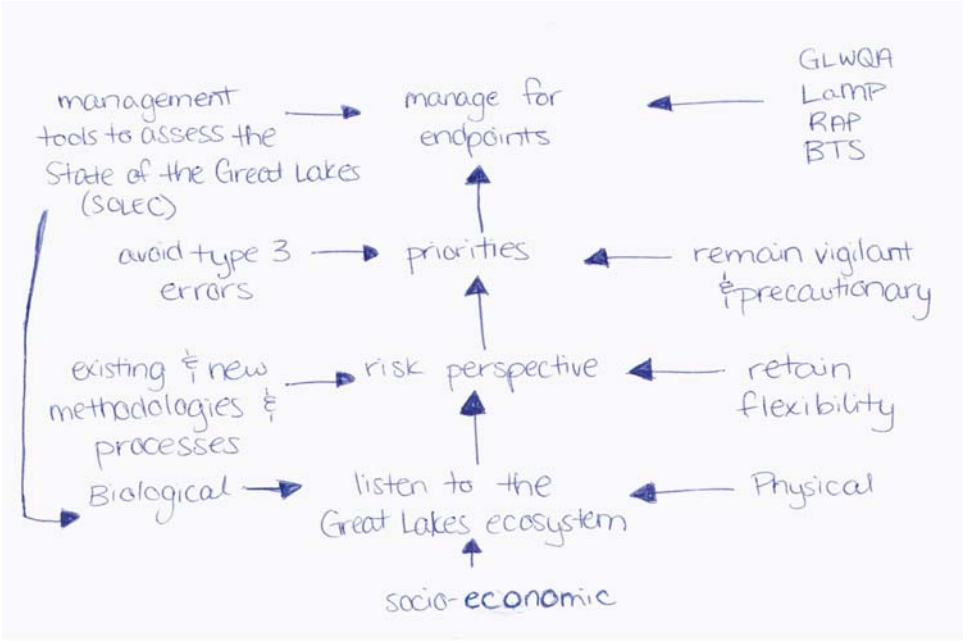
A summary flow chart of the components that are involved with assessing the state of the Great Lakes.



Summary Thoughts (Murray Charlton)

Naturally-occurring Chemicals

- Nitrate and chloride loadings are out of control. Road salt is now a toxic chemical! Nitrate concentrations in groundwater are now an issue.
- Phosphorus loading estimates have not been confirmed. Non-point loads may be increasing, but around the lakes the monitoring data are sparse.
- Don't put too much effort into studying and explaining the annual variability of the "dead zone" in Lake Erie. It may very well be reflecting variations in meteorological events.
- Mercury in the Great Lakes ecosystem needs further assessment, especially perspectives on global sources. What further actions can be taken?
- Cyanotoxins are an issue. Blue-green algae occur where total phosphorus concentrations are greater than 20 micrograms/liter. This concentration creates an aesthetic problem and a potential human health issue.
- We may need renewed attention to nearshore effects. Shoreline algae are a problem in some areas again, and there may be a nearshore shunt of nutrients due to zebra and quagga mussels. We may need to lower phosphorus loads and pay attention to urban runoff and lawn fertilizers.
- We need an indicator of whether nutrients are accumulating in the basin. Data for the Lake Erie watershed show that phosphorus may be accumulating in the soils.

Anthropogenic Chemicals

- Assessing the presence, transport, fate and effects of chemicals in the Great Lakes ecosystem is a capacity issue. It takes people, equipment and money.
- A stable, credible, long-term science effort is needed, and it needs to be sustained.
- We have had considerable success reducing the quantity of anthropogenic chemicals in the Great Lakes basin ecosystem. But remember that PCBs were not banned, just their production was, and the in-use stock is still a threat.
- There needs to be biological monitoring to indicate integrated effects of exposures to toxic chemicals. For example, reproduction impairments can signal a chemical cause.
- Restricted areas such as AOCs may represent important biological production resources. EDCs and pharmaceuticals, etc., may be their most destructive in these areas.

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- New and emerging chemicals need to be monitored. We need to assess the degree of their threats. Their sources may be ubiquitous. They may be less toxic than the legacy chemicals, but we need to check to see if an assessment about emerging chemicals of concern can be made.
- Regarding contaminants in fish, we need to bring into the discussion the numbers of people affected by fish consumption. What is the source of contamination for the majority?

General Observations

- Environmental models are out of date. More work is needed to understand the effects of new non-native species and to integrate physics, hydrodynamics and hydrology.
- Is there a chance for early warning monitoring? How would that be done?
- We need to market and articulate science needs to Great Lakes management.
- Don't rule out problems by thinking that they are already solved.

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APPENDIX A – WORKSHOP AGENDA

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SOLEC Chemical Integrity Workshop
November 29-30, 2005
Windsor, ON

Tuesday November 29, 2005

9:00 Welcomes and Overview of Workshop
Paul Bertram, U.S. Environmental Protection Agency
Douglas Dodge - StreamBenders (Workshop Master of Ceremonies)

9:15 *What is chemical integrity?* (Includes a summary of the Chemical Integrity workshop held at SOLEC 2004, the working definition of chemical integrity and the relative importance of chemical balance and integrity vs. physical and biological integrity with respect to maintaining ecosystem integrity)
Brian Eadie – NOAA/GLERL

9:40 *Naturally-occurring chemicals in the Great Lakes basin – Part 1* (Includes trends in loadings of naturally occurring chemicals (phosphorus and nitrogen) as measured over the last thirty years in Lake Erie tributaries)
Peter Richards – Heildelberg College.

10:05 *Naturally-occurring chemicals in the Great Lakes basin – Part 2* (Includes environmental health effects resulting from loadings of naturally occurring chemicals, based on expected outcomes from ecosystem models)
Joe DePinto – LimnoTech Inc.

10:30 Break

11:00 *Anthropogenic chemicals in the Great Lakes basin – Part 1* (Includes relationships to chemical integrity; observed and potential impacts; environmental concentrations and trends; factors which impact risk (toxicity and exposure); sources, loadings, transport, fate with a focus on **human health**)
Daniel Hryhorczuk – University of Illinois at Chicago

11:25 *Anthropogenic chemicals in the Great Lakes basin – Part 2* (Includes relationships to chemical integrity; observed and potential impacts; environmental concentrations and trends; factors which impact risk (toxicity and exposure); sources, loadings, transport, fate with a focus on **ecosystem health**)
Scott Brown – National Water Research Institute

11:50 *Assessing chemical integrity in the Great Lakes basin* (Includes a discussion on information needs defined through LaMPs, GLBTS, other plans; status of current monitoring and **Great Lakes indicators**; factoring in risk assessment; integrating chemical integrity with overall Great Lakes basin ecosystem assessment)
Keith Soloman – University of Guelph

12:15 *Charge to Participants*
Doug Dodge

12:30 Lunch

1:30 *Breakout sessions I* – Themes, Issues and Conclusions: What Do We Know?

3:00 Break

3:30 *Breakout sessions II* – Themes, Issues and Conclusions: What Do We Need to Learn?

5:00 Adjourn for the day

Wednesday November 30, 2005

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8:30 *Summary of Day 1*
Doug Dodge

9:00 *Breakout sessions III* - Key Issues and the Path Forward for Assessing Chemical Integrity

10:30 Break

11:00 *Plenary Discussion* - Key issues, management questions, suggested actions
Moderated by Doug Dodge

12:15 *Workshop Wrap-Up* - An overall perspective of what was heard at the workshop, summary of what messages we need to take into SOLEC 2006
Murray Charlton - National Water Research Institute

12:30 Workshop Adjourns

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APPENDIX B – SOLEC 2006 DRAFT AGENDA

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SOLEC 2006 Conference Agenda
(Draft—August 2005)

Day 1—State of the Great Lakes

Morning—Plenary

9:00-9:30 Welcomes & Introductions [*Responsibility of the SOLEC Steering and Executive Committees*]

9:30-10:45 State of the Great Lakes [*Responsibility of the SOLEC Steering and Executive Committees with input from LaMP Managers*]
Condition of Great Lakes human health, land use-land cover, contamination, biotic communities including fisheries, invasive species, aquatic habitats, coastal zones, resource utilization, and climate change based on indicators. To the extent possible, the presentations will report conditions at a Lake level as well as convey the overall basinwide status.

10:45-11:15 Break

11:15-12:30 Management implications for the Lakes, the St. Clair-Detroit ecosystem, and the St. Lawrence River [*Responsibility of the LaMP Managers in coordination with the SOLEC Executive Committee*]
Lake by Lake management implications resulting from the state of the Great Lakes based on the condition reports and supplemental information.

12:30-2:00 Lunch
- 12:30-2:00 Networking – for all attendees
- 1:30-2:00 Introduction to Indicators session – for all attendees [*Responsibility of the SOLEC Steering and Executive Committees*]

Afternoon—Breakout Sessions

2:00-4:30 Lake by Lake sessions to discuss the next steps needed to address condition and management implications. [*Responsibility of the LaMP Managers with assistance from the SOLEC Executive Committee*]

Evening—Dinner/Reception

6:00-8:30 Success Story presentations will take place from 8:00-8:30, after the dinner. [*Responsibility of the SOLEC Steering and Executive Committees*]

Day 2—Chemical Integrity

Morning—Plenary

9:00-9:15 Highlights from Day 1 [*Responsibility of the SOLEC Steering and Executive Committees*]

9:15-9:30 Chemical Integrity overview. [*Responsibility of the SOLEC Steering and Executive Committees with input from the Chemical Integrity Working Group and the LaMP Managers*]

The following six presentations [*Responsibility of the Chemical Integrity Working Group with assistance from the SOLEC Executive Committee*] will attempt to include Lake-specific examples:

9:30-9:50 TOXICS – Impacts and Issues
9:50-10:10 TOXICS – Sources, Loads and Transport
10:10-10:30 TOXICS – Management Response/Actions and Environmental Changes
10:30-11:00 Break
11:00-11:20 NON-TOXICS – Impacts and Issues
11:20-11:40 NON-TOXICS – Sources, Loads and Transport
11:40-12:00 NON-TOXICS – Management Response/Actions and Environmental Changes
12:00-1:30 Lunch
- 1:00-1:30 Keynote address—invited speaker

Afternoon—Chemical Integrity Workshops

1:30-4:30 Workshops will include additional presentations and discussions of specific issues including: municipal sector issues (pesticides, pharmaceuticals, groundwater contamination, ecological footprint, and cycling

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of contaminants among others (topics will be determined by the experts attending the November 2005 workshop). [*Responsibility of the Chemical Integrity Working Group*]

Day 3—Cross-Cutting Issues

9:00-12:00 Ideas include: beaches, groundwater, forestry, brownfields, eco-footprint, climate change, GLWQA, societal values, land use/zoning. Sessions will be determined by the SOLEC Steering Committee. [*Responsibility of the SOLEC Steering and Executive Committees*]

12:00 **Adjourn**

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APPENDIX C – WORKSHOP ATTENDEES

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Chemical Integrity Workshop Attendees

NAME	AFFILIATION
Jackie Adams	U.S. Environmental Protection Agency – GLNPO
Doug Alley	International Joint Commission
Bill Alsop	AMEC Earth and Environmental Consulting
Frank Anscombe	U.S. Environmental Protection Agency – GLNPO
Paul Bertram	U.S. Environmental Protection Agency – GLNPO
Giselle Bouchard	Environment Canada
Scott Brown	National Water Research Institute
George Bullerjahn	Bolling Green University
Murray Charlton	Environment Canada
Stacey Cherwaty	Environment Canada
Jan Ciborowski	University of Windsor
David Culver	Ohio State University
Sarah Da Silva	Environment Canada
Marcia Damato	U.S. Environmental Protection Agency – GLNPO
Nicole Davidson	Environment Canada
Joe DePinto	LimnoTech Inc.
Jon Dettling	Great Lakes Commission
Miriam Diamond	University of Toronto
Doug Dodge	Streambenders
Jack Dutra	Industry Task Force
Brian Eadie	National Oceanic and Atmospheric Administration
David Flakne	Syngenta Crop Protection
Diana Graham	Contractor to Syngenta Crop Protection
Beth Hinchey-Malloy	U.S. Environmental Protection Agency – GLNPO
Paul Horvatin	U.S. Environmental Protection Agency – GLNPO
Daniel Hryhorczuk	University of Illinois at Chicago - School of Public Health
Matt Hudson	Great Lakes Indian Fish and Wildlife Commission
Melissa Hulting	U.S. Environmental Protection Agency – GLNPO
Allan Jones	Canadian Chlorine Coordinating Committee
Rimi Kalinauskas	Environment Canada
Bruce Kirschner	International Joint Commission
Paul Klawunn	Environment Canada
Gail Krantzberg	McMaster University
Edwina Lopes	Environment Canada
Jianmin Ma	Meteorological Service Canada
John Marsden	Environment Canada
Gerald Matisoff	Case Western Reserve
Ann McConnell	Proctor & Gamble Canada
Michael McKay	Bowling Green State University
Derek Muir	Environment Canada
Beth Murphy	U.S. Environmental Protection Agency – GLNPO
Melanie Neilson	Environment Canada
Todd Nettesheim	U.S. Environmental Protection Agency – GLNPO
Jerry Niemi	National Regulatory Research Institute
Carolyn O'Neill	Environment Canada
Dan O'Riordan	U.S. Environmental Protection Agency – GLNPO

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NAME	AFFILIATION
Dale Phenicie	Council of Great Lakes Industries
Lou Pocalujka	Consumers Energy
Peter Richards	Heidelberg College
David Rockwell	U.S. Environmental Protection Agency – GLNPO
Karen Rodriguez	U.S. Environmental Protection Agency – GLNPO
Dan Salvito	Research Institute for Fragrance Materials
Hans Sanderson	The Soap and Detergent Association
Barbara Scudder	U.S. Geological Survey
Ted Smith	U.S. Environmental Protection Agency – GLNPO
Keith Solomon	University of Guelph
Dee Ann Staats	Crop Life America
Nancy Stadler-Salt	Environment Canada
Jay Unwin	National Council for Air and Stream Improvement, Inc.
Srinivasan Venkatesh	Environment Canada
Donald Versteeg	Proctor & Gamble U.S.
Jennifer Vincent	Environment Canada
Alan Waffle	Environment Canada

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APPENDIX D – PLENARY PRESENTATIONS

(Note: Plenary Presentations are also available online at: http://www.epa.gov/glnpo/solec/solec_2006/presentations/index.html)

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‘Chemical Integrity’ of the Great Lakes?

Brian J. Eadie
NOAA - GLERL

Windsor Nov 29, 2005

Summary of the 2004 Chemical Integrity Workshop in Toronto

Chemical Integrity is the capacity to support and maintain a balanced, integrated and adaptive biological system having the full range of elements and processes expected in a region’s natural habitat.

• Is Chemical Integrity the capacity to maintain Biological Integrity?

* What about the capacity to maintain the sustainability of human uses of the habitat?

What Items should be included in Chemical Integrity?

- The current suite of chemicals of concern are declining
- Toxicology information is needed, not just concentrations
- Very weak information on the toxicology of mixtures
- Focus on assessment not monitoring
- How well do we find new chemicals of potential concern ?
- Perturbations (e.g.,Invasives, Climate, Land use)

What Items should be included in Chemical Integrity?

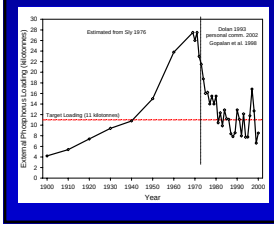
* Nature of the chemical
  - * Persistence
  - * Toxicity
  - * Quantity/concentration
* Chemical sources and loadings
  - * Atmosphere
  - * Tributary
  - * Non-point Sources
  - * Point Sources
  - * Internal
• Habitat
  - * Tributary
  - * Wetland
  - * Nearshore
  - * Off-shore
* Effects on Biological Integrity

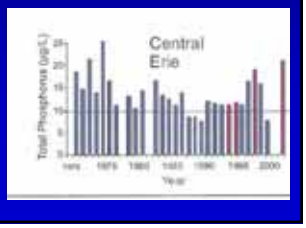
What Chemicals are of Concern

Nutrients (P; **Nitrate**, Fe?)

Phosphorus has generally declined, but:

- P is increasing in the central basin of Lake Erie
- Internal recycling has changed (dreissenids)
- N is increasing everywhere





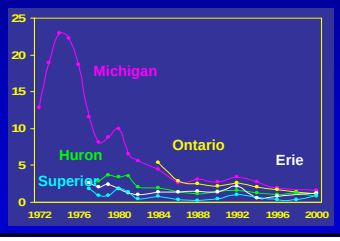
What Chemicals are of Concern - cont

Organic Contaminants (PBTs; pesticides, PCBs, PAHs, dioxins)

PBTs have declined, but:

- some still result in restrictions
- internal reservoirs and recycling may dominate loads
- some controls are beyond the Great Lakes Basin

PCBs in Lake Trout (Walleye in Lake Erie)



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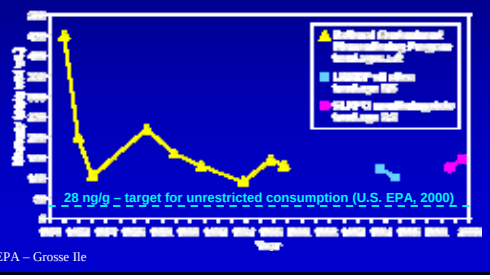
What Chemicals are of Concern - cont

Metals (Hg,[methyl-Hg], Pb, etc.

Total Mercury in Lake Michigan Lake Trout Median of Composites)



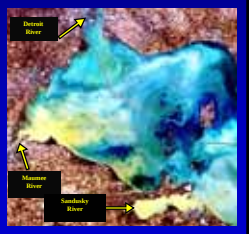
EPA – Grosse Ile

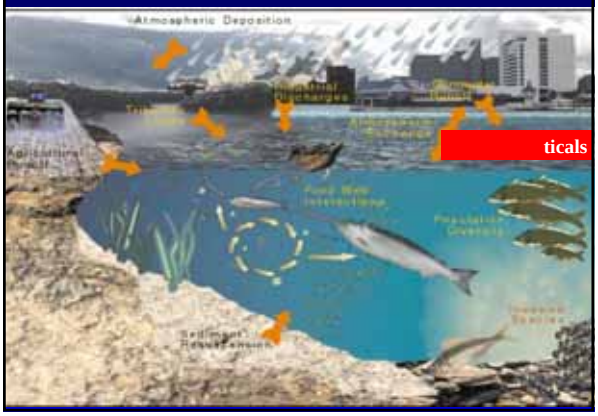
What Chemicals are of Concern – cont.

- Taste/Odor
- **HABs (e.g., microcystins)**
- Pharmaceuticals
- Road Salt
- Caffeine / other WWTP discharges
- Biohazards (viruses)
- Medical wastes

Seasonal HABs

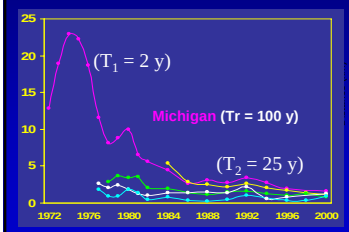
High concentrations of toxins microcystin > 1µg/l

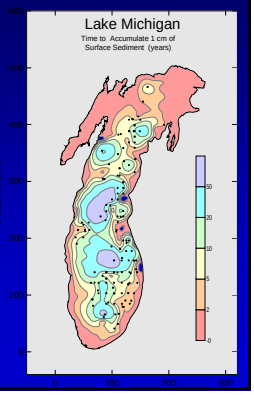


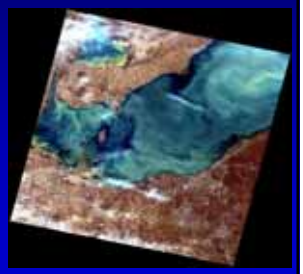


Fundamental information needed for each lake

PCBs in Lake Trout (Walleye in Lake Erie)







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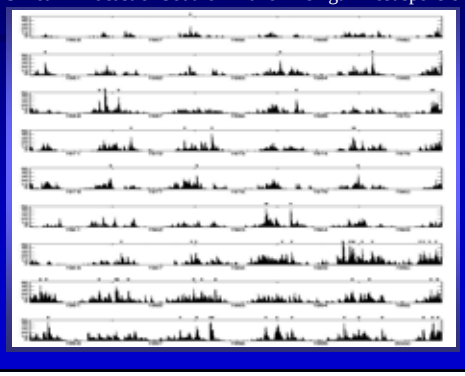
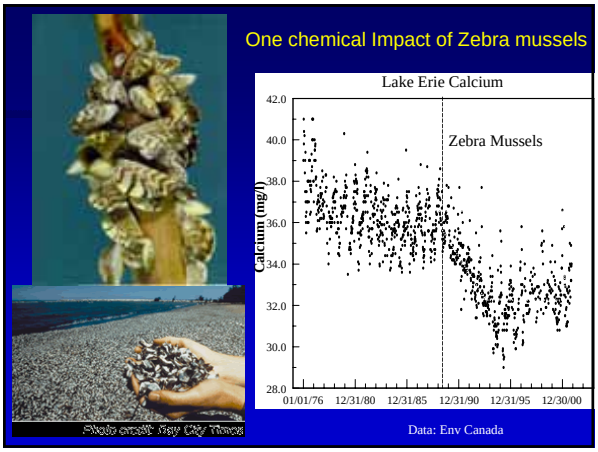
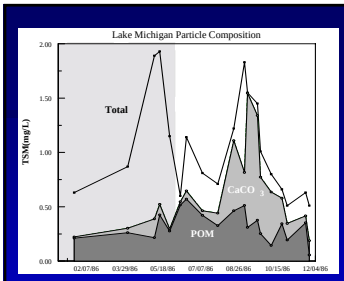
Climate Change ?

45 Year Hindcast of Southern Lake Michigan Resuspension

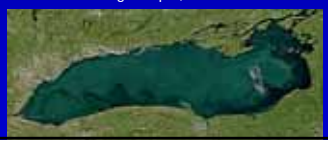


One chemical Impact of Zebra mussels





'Whiting' Sep 6, 2000



'Whiting' Sep 7, 1999

Summary - Issues relating to Chemical Integrity

PBTs have declined, but some still result in restrictions

Nutrients

- P increasing in the central basin of Lake Erie
- N is increasing everywhere

Pharmaceuticals – low levels detected – Impacts ?

Impact of Climate Change

Aging infrastructure

- Sewage and water treatment facilities
- Recruitment and retention of younger Great Lakes scientists

Summary - Issues relating to Chemical Integrity - contuied

Areas of Concern

Constituent loads

- Local (Tributary P, pharmaceuticals)
- Regional (Combustion products)
- Global (Hg, DDT)

Processes → Ecosystem Models

Improving Risk Assessment Tools

Algorithm improvements for satellite imagery

Development of automated observing systems

ACKNOWLEDGEMENTS

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Ron Rossmann – EPA/Grosse Ile

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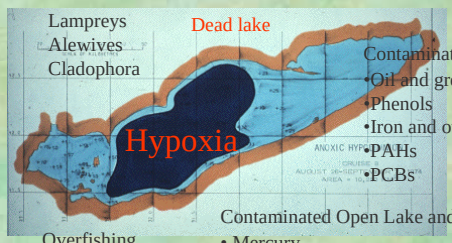
Trends in Water Quality in Lake Erie Tributaries, 1975-2004

R. Peter Richards
National Center for Water Quality Research
Heidelberg College
Tiffin, Ohio 44883

Outline

- The "death" and rehabilitation of Lake Erie
- Trends in nutrient loads
- Causes?

What's wrong with Lake Erie?



Lampreys
Alewives
Cladophora

Dead lake

Contaminated Harbors
•Oil and grease
•Phenols
•Iron and other metals
•PAHs
•PCBs

Overfishing
•Blue Pike
•Walleye

Contaminated Open Lake and Fish
• Mercury
• PCBs
• DDT, DDE

No more mayflies...

Strategy for reducing hypoxia

- Reduce phosphorus
  - Sewage Treatment Plant upgrades
  - Phosphorus detergent ban
  - Non-point source programs, especially aimed at agriculture
    - Nutrient management
    - Reduced tillage

Tributary Loading Studies

- Army Corps Wastewater Management Study
- Heidelberg Tributary Sampling Program
  - Major Lake Erie Tribs
    - Sandusky 1974
    - Maumee 1975
    - Cuyahoga 1982
    - Raisin 1982
    - Grand 1986
  - Autosamplers at "integrator" stations, 3 samples/day
  - USDA-LEASEQ Trend Analysis 1975-1995 (Mau, Sand)
  - USDA-CEAP Trend Analysis 1975-2004

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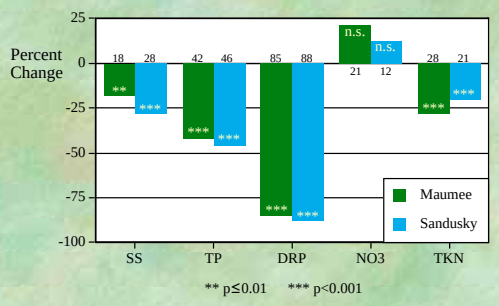
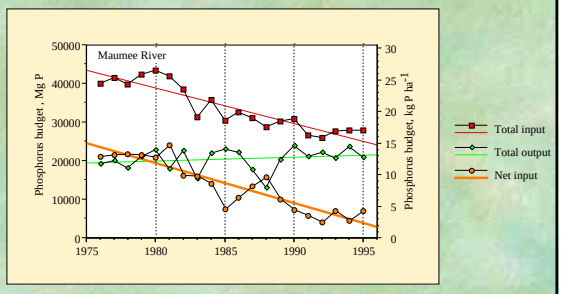
Trends in Water Quality, 1975-1995



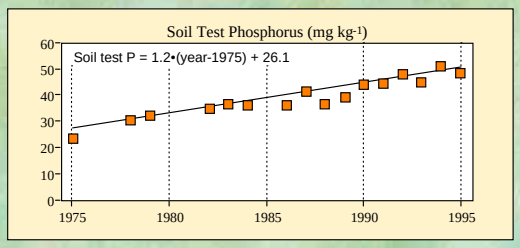
Trends in phosphorus mass balance

…substantial decrease, but always input>output



Trends in soil fertility

…nearly doubled between 1975 and 1995



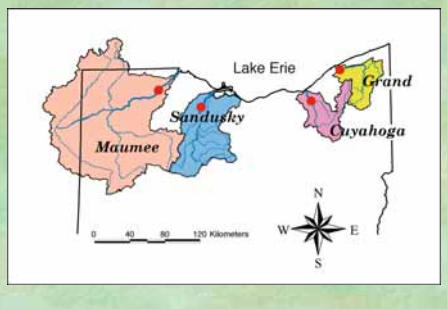
LEASEQ Conclusions

- Water quality trends are toward improved conditions (except nitrate)
- Water quality trends result from intentional changes in use of the land
- A major victory for environmental science and management

Trends 1995-2004:

- How do trends in the last 10 years compare with trends in the previous 20 years?
- Also extend analysis to Cuyahoga and Grand

Station Locations



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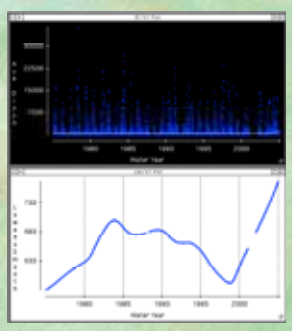
Trends in Water Quality, 1975-2004

- Methods: Formal Analysis
  - Adjust concentrations for flow effects, using LOWESS smoother
  - Analyze trend in flow-corrected, log-transformed concentrations using ANCOVA-based two slope model
  - log(c)=fn[log(q), t, sin(2πt), cos(2πt), PrePost, PrePost*t]
  - Results expressed as % change over 10 years
- Today: LOWESS smooths of unmodified daily flows and daily loads (bin width 20%)
- LOWESS: LOcally WEighted Scatterplot Smoother

I. Loads vs. Concentrations, Sandusky

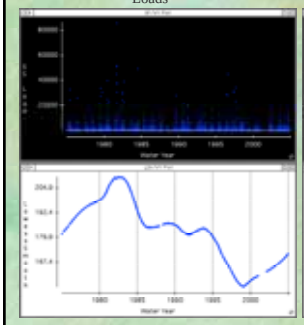
- Goals
  - Illustrate similarities/differences in trends for loads as opposed to concentrations
  - Illustrate magnitude of trends relative to day-to-day fluctuations
  - Avoid trying to show you 100+ different trend graphs!

Discharge

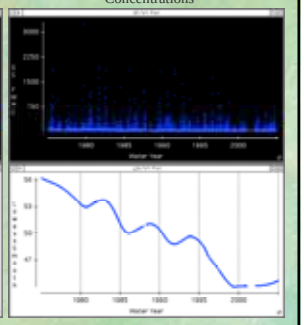


Suspended Sediment

Loads

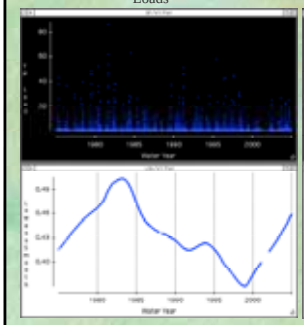


Concentrations

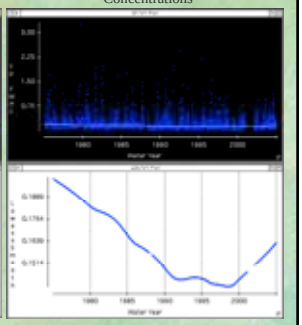


Total Phosphorus

Loads

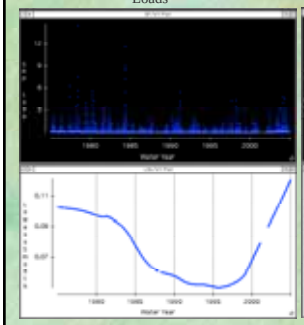


Concentrations

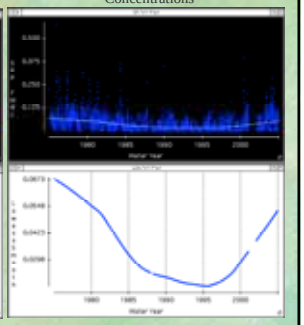


Dissolved Reactive Phosphorus

Loads



Concentrations



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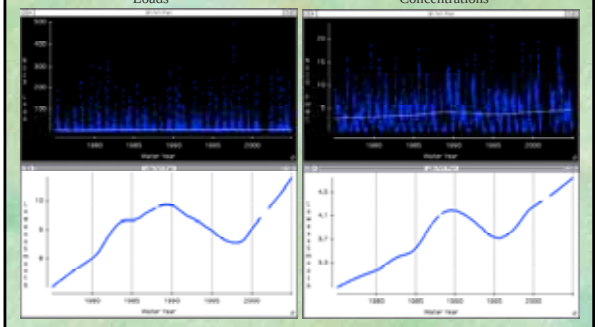
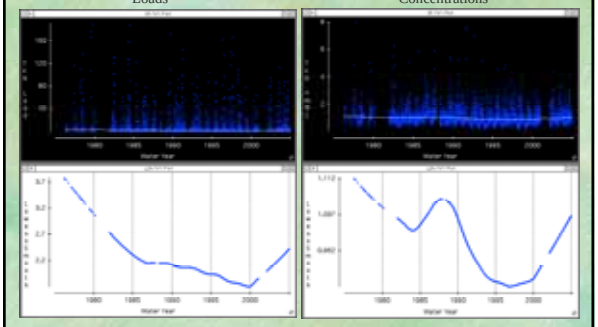
Nitrate

Loads | Concentrations



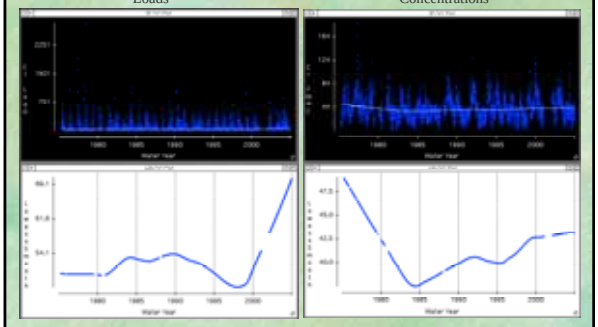
Total Kjeldahl Nitrogen

Loads | Concentrations



Chloride

Loads | Concentrations



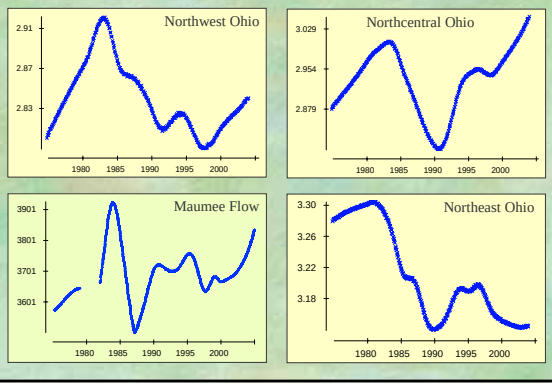
Patterns, Loads vs. Concentrations

- Loads and concentrations for a given parameter tend to have similar trends
- But there can be important differences as well
- SS and TP load trends track flow strongly, others less so or not at all
- Trends reflect “something real” and important, but…
- Generally the 30-year trends are small compared to the short-term variability, especially for loads
- (What does this imply for management?)

II. Loads, parameter by parameter

- Flow, SS, nutrients, derivative parameters
- LOWESS values are essentially locally weighted averages, tend to be intermediate between the median and the mean

Precipitation (cm/month)



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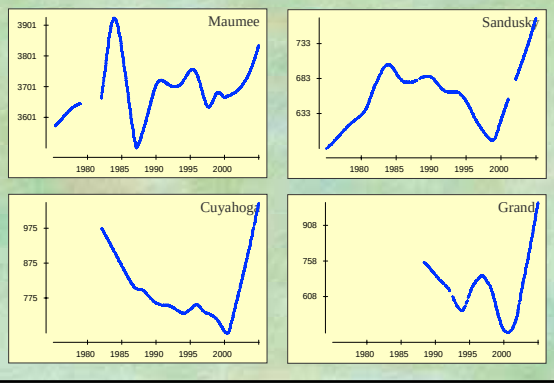
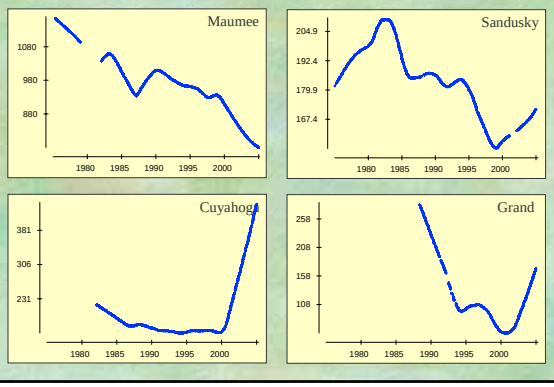
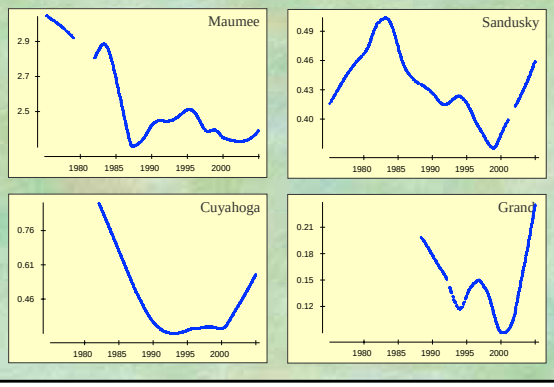
Discharge (cubic feet/second)



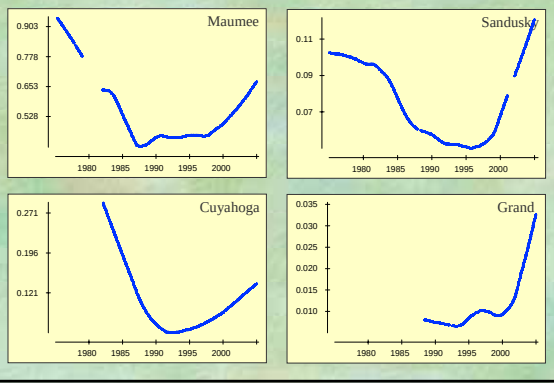
SS Load (metric tons/day)



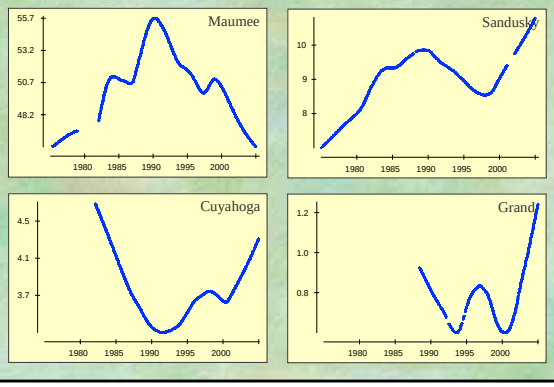
TP Load (metric tons/day)



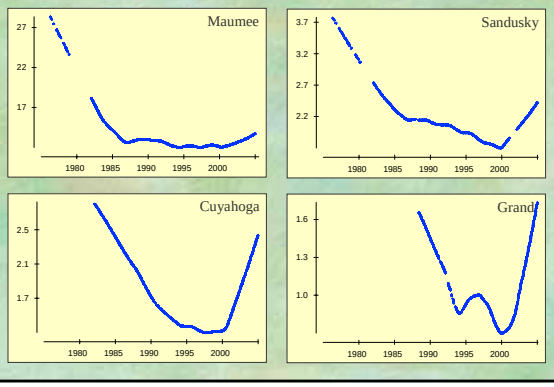
DRP Load (metric tons/day)



Nitrate Load (metric tons/day)



TKN Load (metric tons/day)



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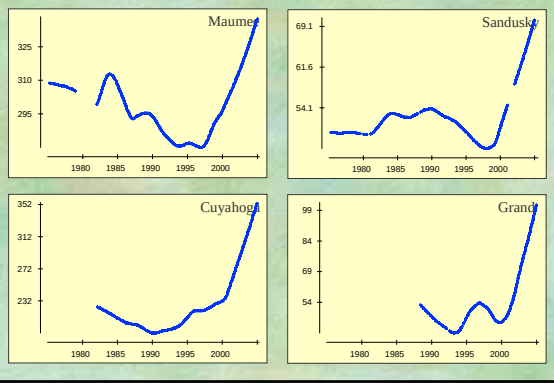
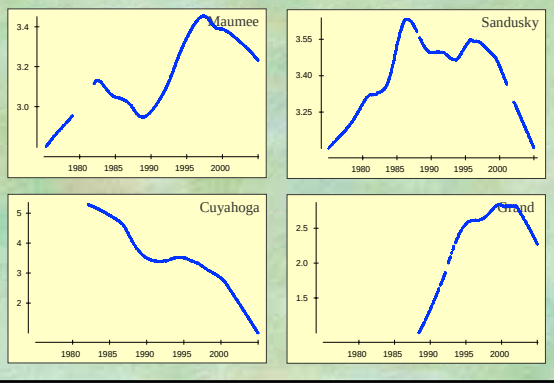
Chloride Load (metric tons/day)

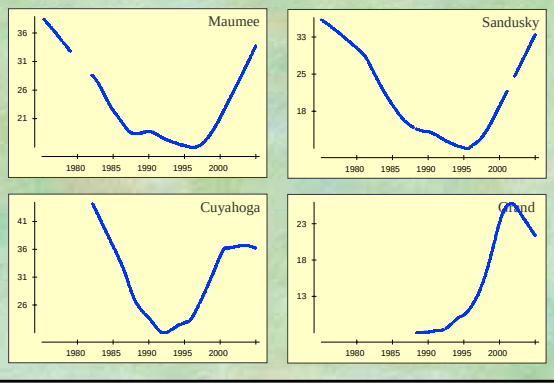


"PP"/SS ratio (g/kg)

("PP"=TP-DRP)

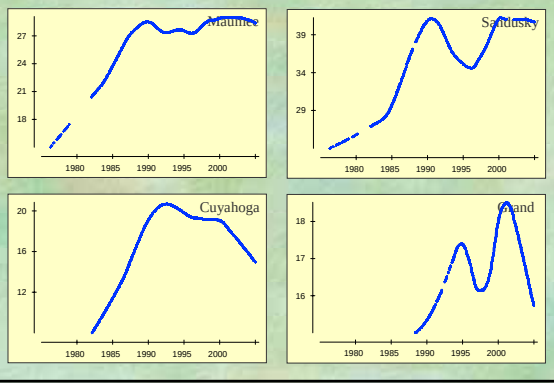


DRP/TP (%)



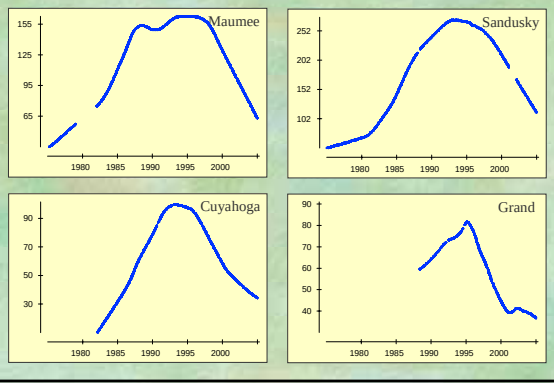
TN/TP ratio

(Redfield Ratio ~ 7)



NO3/DRP ratio

(Redfield Ratio ~ 7)



Summary

- General improvements (except nitrate) during 1975-1995, most params/most rivers
- Worsening in TP, DRP, TKN since then; inflection point between 1993 and 2000
- Continued improvement in Maumee SS but not in other rivers
- Mixed results for NO3

Summary

- PP/SS ratio (sediment "richness") improving recently, but perhaps for bad reasons
- Recent increases in %P that is dissolved
- TN/TP and NO3/DRP decreasing or no longer increasing, but ratios are appropriate for phosphorus limitation

Causes?

- Weather? More important for loads than concs?
- Population growth and exurbanization?
- No-till concentrates nutrients at surface?
- Concentrated animal agriculture?
- Winter spreading of manures?
- Global climate change?
- Whew! It could be all of them….

Impacts?

- Renewed problems in Lake Erie
  - Increased in-lake phosphorus concentrations
  - Hypoxia in summer in Central Basin
  - Microcystis and other cyanobacteria
- Tributary inputs are not the sole cause, but are likely contributors to these problems

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Chemical Integrity in the Great Lakes
Pre-SOLEC workshop
Windsor, ON – November 29-30, 2005

Chemical Integrity of Naturally-occurring Substances in the Great Lakes

Joseph V. DePinto
Limno-Tech, Inc.
Ann Arbor, MI

Acknowledgements

- USEPA – Great Lakes National Program Office
  - David Rockwell, other staff
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  - Murray Charlton
- NOAA-GLERL
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- UW-Green Bay
  - Dave Dolan
- SUNY – CESF
  - Greg Boyer, MERHAB-LGL PI
- New York Sea Grant
  - Helen Domske, NYSG specialist

Presentation Outline

- Naturally-occurring Substances
- Chemical Integrity Analysis Logic
- How to manage phosphorus in a changed Great Lakes ecosystem?
- Are there undesirable trends in general water chemistry?
- What bio-toxins should we worry about?

Categories of Naturally-occurring Substances

- Nutrients and eutrophication
  - Macro-nutrients (P, N, Si)
  - Micro-nutrients (Fe, Zn, etc.)
  - Chlorophyll *a*
  - Dissolved oxygen
- Metals (Pb, Cd, Hg, etc.)
- General water chemistry
  - Major ions/salinity/hardness
  - pH – Alkalinity – DIC system
- Taste/odor compounds (MIB, geosmin)
- Biota-produced toxins
  - Cyanotoxins
  - *Botulinum* toxins

Sources of Naturally-occurring Substances

- Naturally occur in earth's crust
  - Leached and eroded from soil
- Formed by natural chemical and biochemical reactions in soil, water, sediments
- Humans can accelerate cycling and entry into the Great Lakes
  - Mining and application of road salt
  - Mining and manufacturing processes
  - Application of fertilizers
  - Creation of conditions that accelerate natural chemical and biochemical reactions

What is Chemical Integrity?

- Chemical Integrity of the Great Lakes
  - The chemical composition of a lake ecosystem that provides all of the chemical needs for that system to maintain overall *ecosystem integrity*.
  - Chemical concentrations are bounded such that there is not too much or too little relative to other chemicals and relative to the ecosystem's needs for maintaining its integrity.
- Chemical integrity must be understood and evaluated in terms of sources, loadings, transport, fate, and ecological effects (humans are part of the ecosystem).

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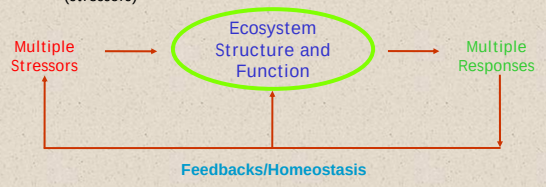
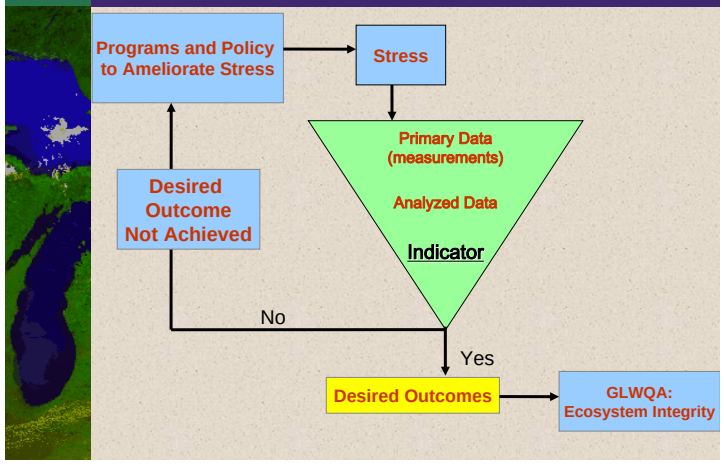
What is Ecosystem Integrity?

- An aquatic ecosystem is judged to have integrity when its physical, chemical, and biological structure is such that it is functioning as a complete and healthy ecosystem.
- "Complete" and "healthy" can only be determined in terms of indicators of that ecosystem's performance relative to a performance goal
- Measures of ecosystem performance
  - Biologically diverse/complexity
  - Evolving toward a more stable system
  - Resilience/Homeostasis
    - resistance to irreversible change in response to external perturbations (stressors)



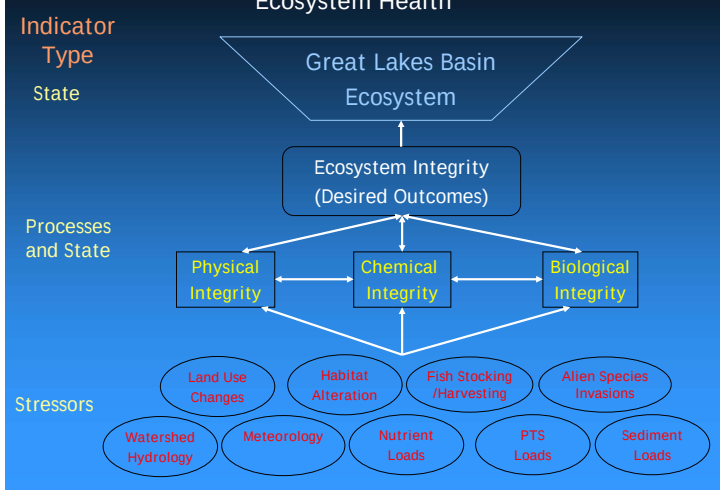
Framework for Evaluating Ecosystem Integrity (from IETF-IJC)



Indicators of Ecosystem Performance

- Ecosystem Indicator: A measurable feature, or one derivable from measurements, which singly or in combination provides managerially and scientifically useful evidence of ecosystem integrity, or reliable evidence of progress toward one or more ecosystem objective.
  - Indicator can be a physical, chemical, or biological measurement that can be related in a meaningful and understandable way to ecosystem performance.
  - Indicator can be a *stressor*, a *process*, or a system *state variable*
- Ecosystem models are a tool for relating indicators to ecosystem performance.

Model for Measuring and Understanding Ecosystem Health

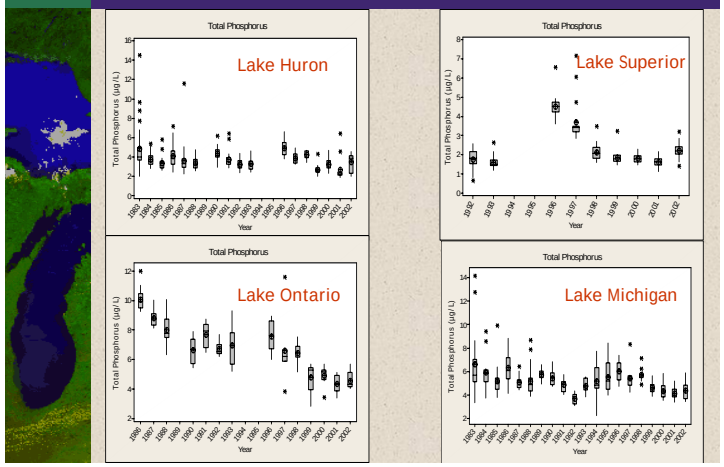


Nutrients and Eutrophication

- Phosphorus is limiting nutrient and is controlled in Great Lakes
- Nitrogen (as N/P ratio) can impact algal speciation
- Phosphorus management in 1970's and '80s was based on chlorophyll *a* targets
  - Very successful outcome
- Now other factors raised as issues in P control
  - Fish production
  - Invasive species impacts
  - Still seeing water quality impacts in Lake Erie – hypolimnion DO

Total Phosphorus Trends in Great Lakes

(GLNPO spring data)



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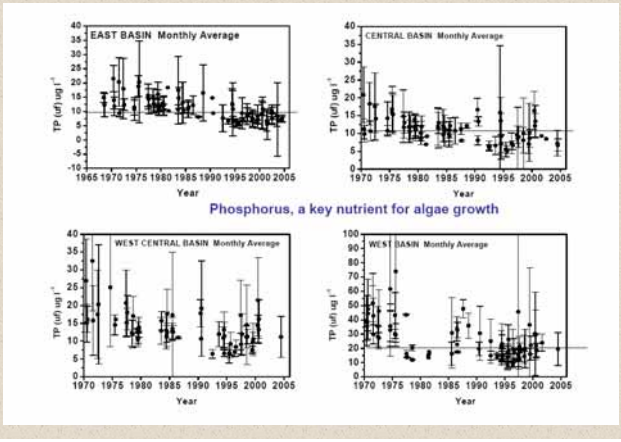
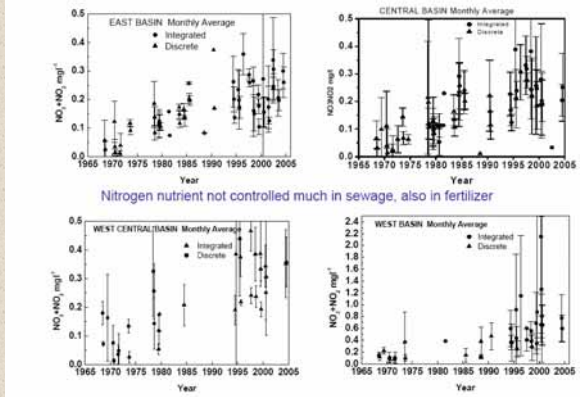
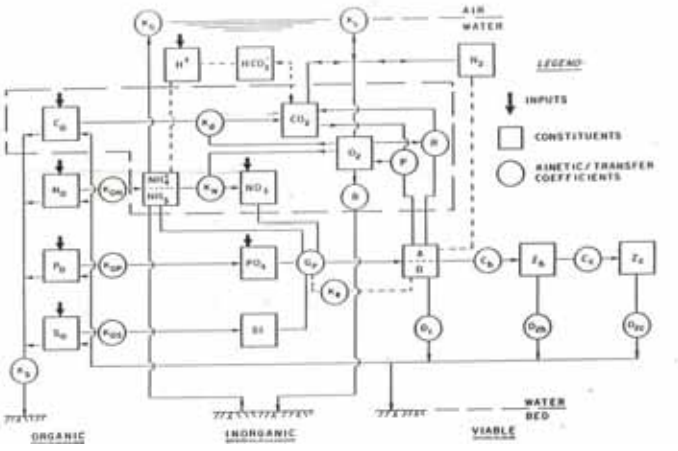
Environment Canada TP Data for Lake Erie
(Charlton, 2005)



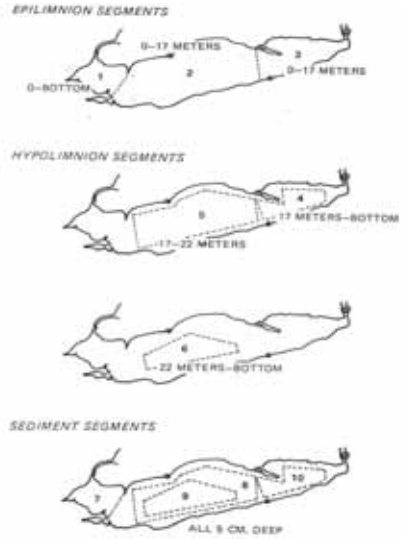
Environment Canada NO_3-NO_2 Data for Lake Erie
(Charlton, 2005)

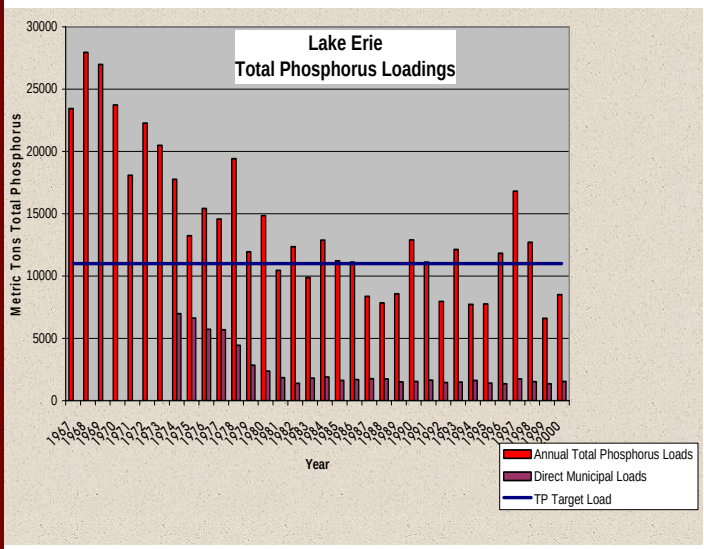


DiToro, et al. Lake Erie Eutrophication Model (1976)

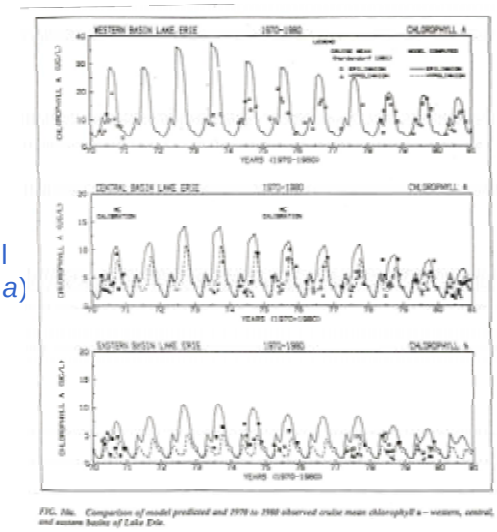


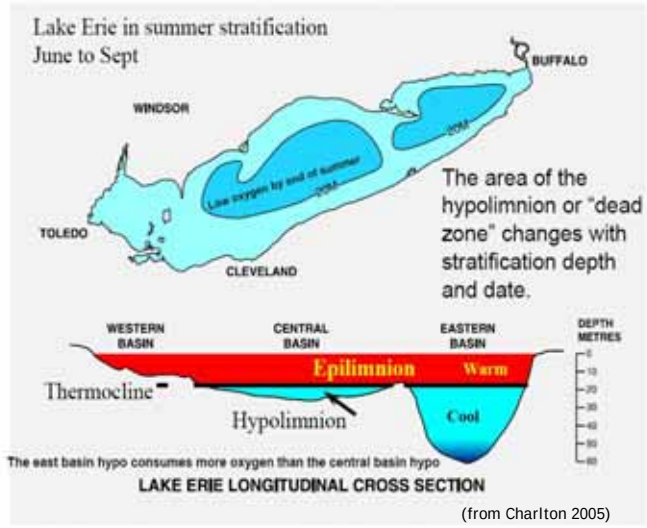
Segmentation for 1976 Lake Erie Model





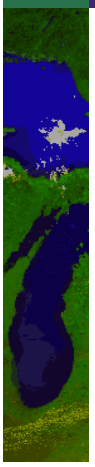
Lake Erie Model Post-audit (Chl *a*)
(DiToro, et al. 1987)

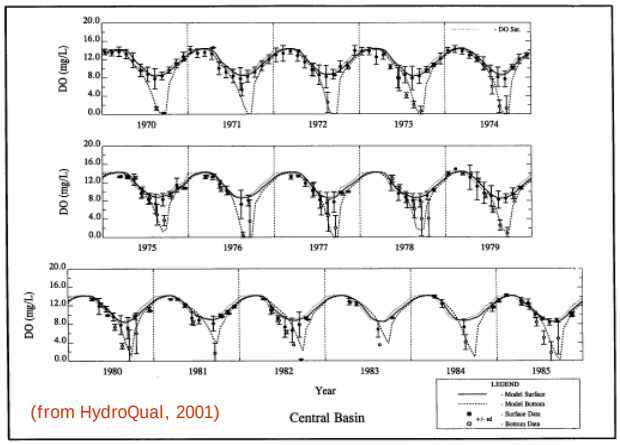




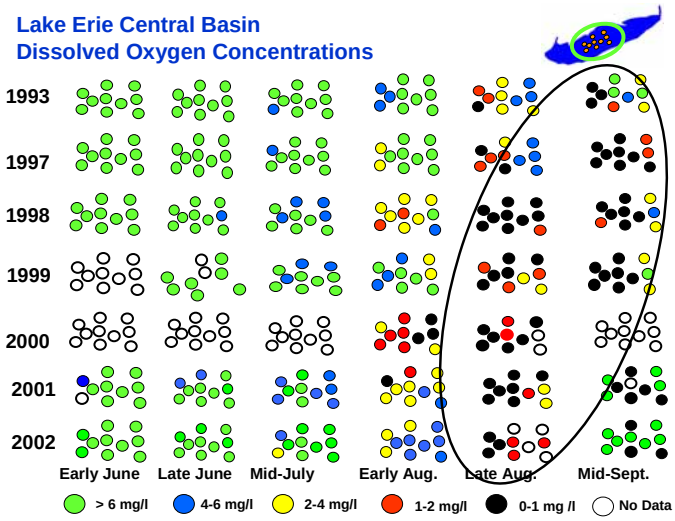
(from Charlton 2005)

Lake Erie Model Post-audit
(tested through 1985)

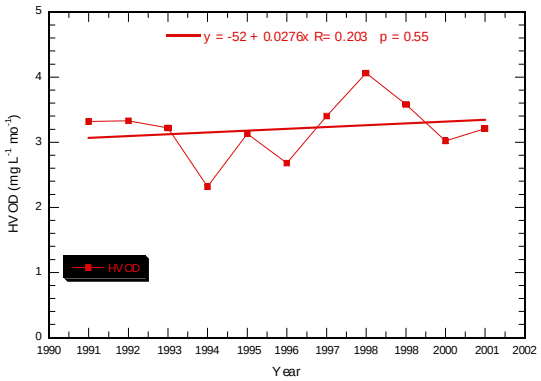




(from HydroQual, 2001)



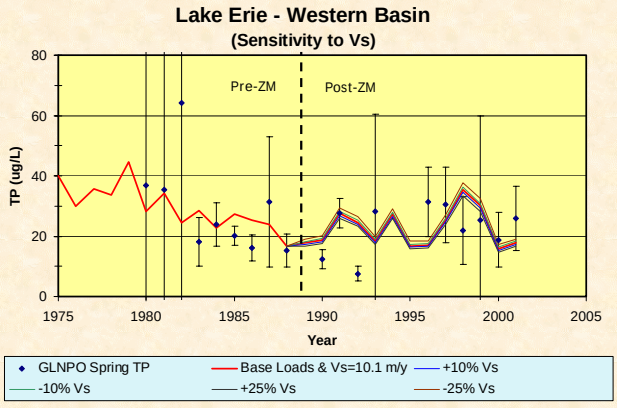
HVOD rates for the Central Basin from 1991 to 2001 corrected for temperature, vertical mixing and hypolimnion thickness.



Hypothesis

- There is always zebra mussels
- Due to a de-coupling of the phosphorus-chlorophyll *a* relationship in Lake Erie caused by the *Dreissena* invasion, the ***net loss rate of total phosphorus from the water column*** (*i.e.*, net apparent phosphorus deposition rate to sediments) has decreased.

Model Sensitivity to Net Vs (WB)



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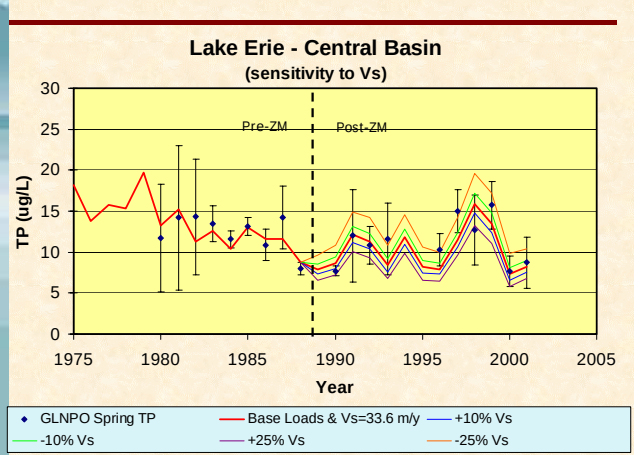
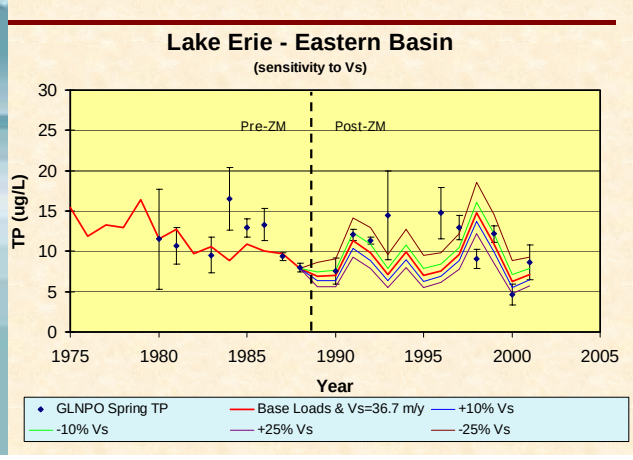
Model Sensitivity to Net Vs (CB)

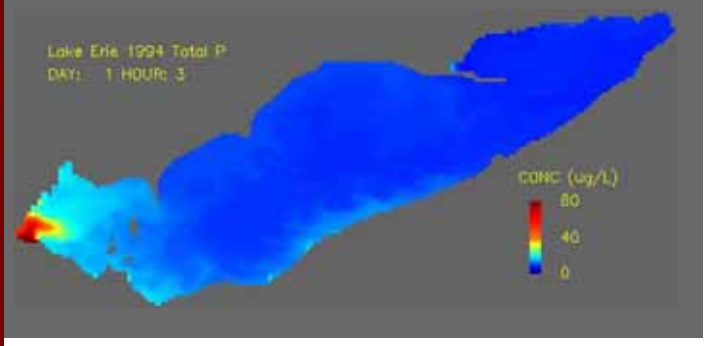


Model Sensitivity to Net Vs (EB)

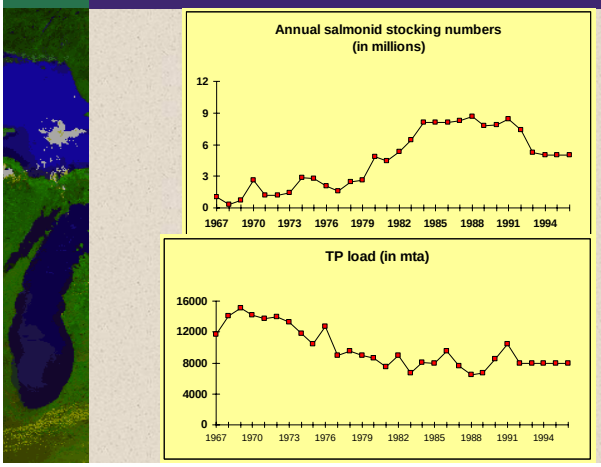


Computer animation of model results:

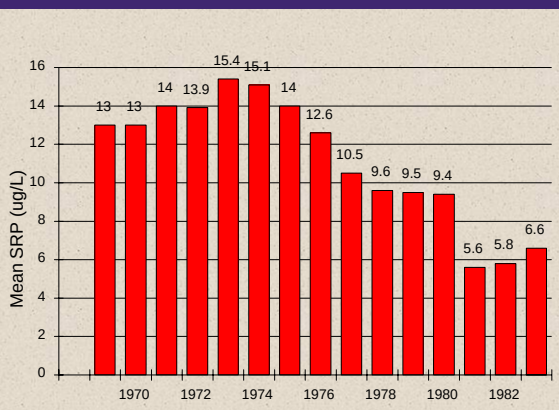
- -Starts in January, 1994
- -Uses 2d currents from hydrodynamic model
- -Time dependent P loads
- -Combination Lax-Wendroff and upwind advection scheme
- -No horizontal diffusion
- -Initial condition: C = 10 ug/L
- -Settling velocity = 6.8E-7 m/s (21 m/yr)



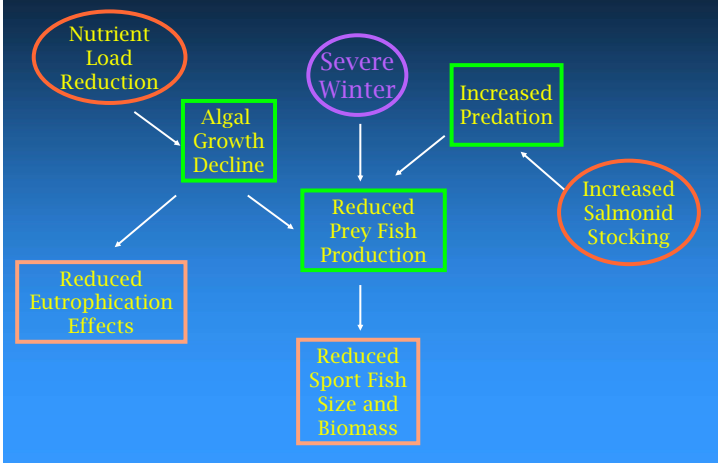
Historical Trends of Key Stressors in Lake Ontario



Spring Whole-lake Average SRP for Lake Ontario



Nutrient Control versus Sport Fishing - Lake Ontario



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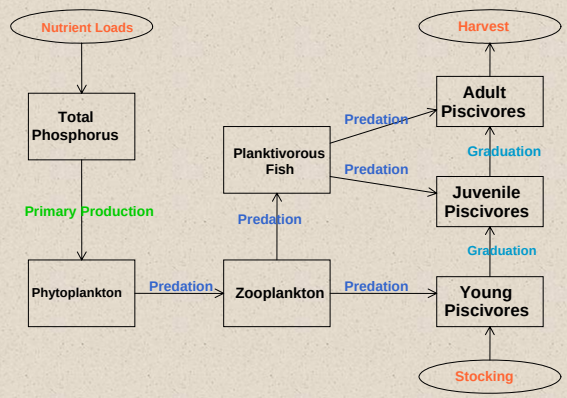
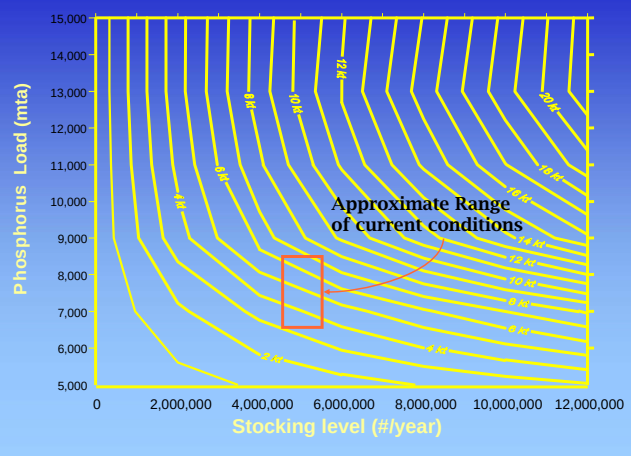
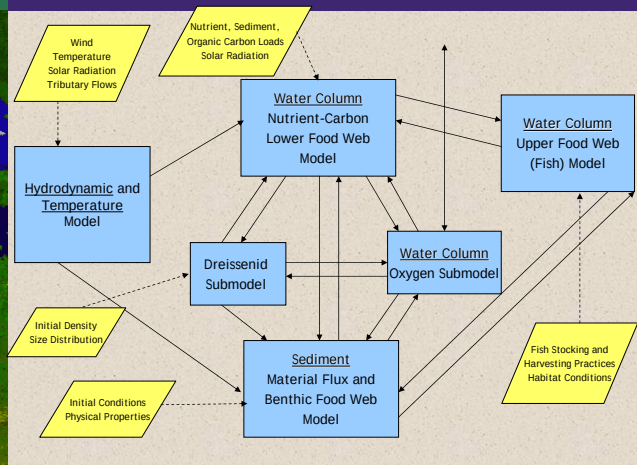
Conceptual Model of Simplified Lake Ontario Ecosystem Model



Adult Piscivore Biomass in Lake Ontario

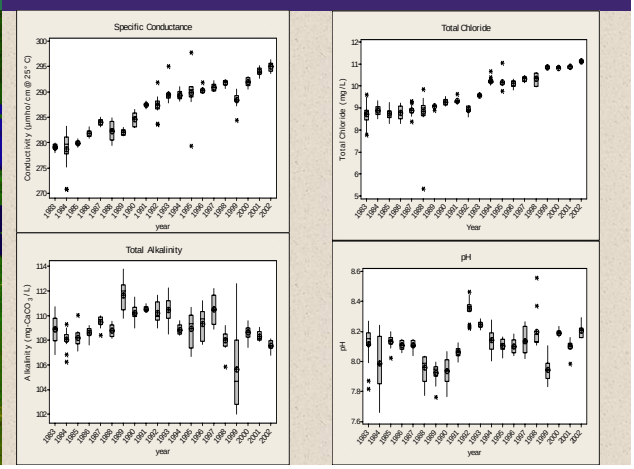


Model Linkages to P Management Questions



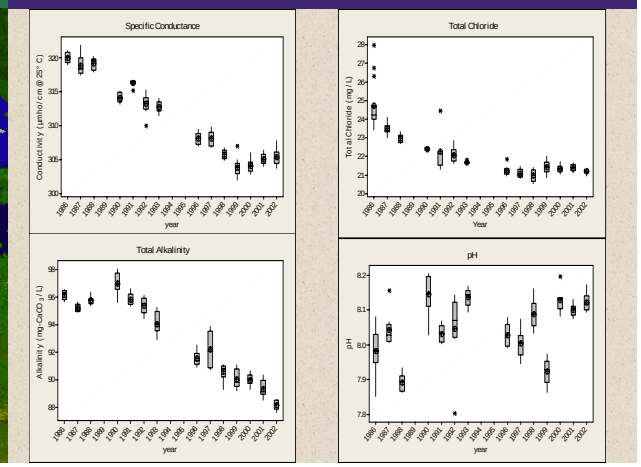
Lake Michigan Water Chemistry (1983-2002)

(GLNPO spring data)



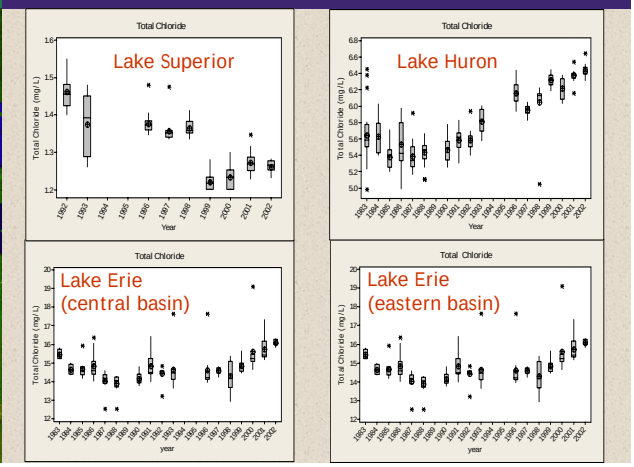
Lake Ontario Water Chemistry (1983-2002)

(GLNPO spring data)



Chloride in Other Lakes (1983 – 2002)

(GLNPO spring data)



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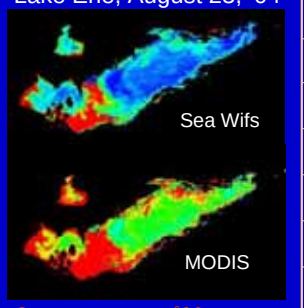
Cyanotoxins in the Lower Great Lakes

- MERHAB-LGL Study
  - PI: Greg Boyer, SUNY-ESF
- Produced by cyanobacteria (blue-green algae)
- Four primary classes of toxin compounds
  - Microcystin
  - Anatoxin-a
  - PSP toxins
  - Cynlindospermopsin
- Neurotoxicity and hepatotoxicity in
  - Fuana coming in contact with blooms
  - Can exceed WHO limits in drinking water intakes

MERHAB-LGL
Harmful Algal Bloom
Monitoring and Event Response in the Lower Great Lakes

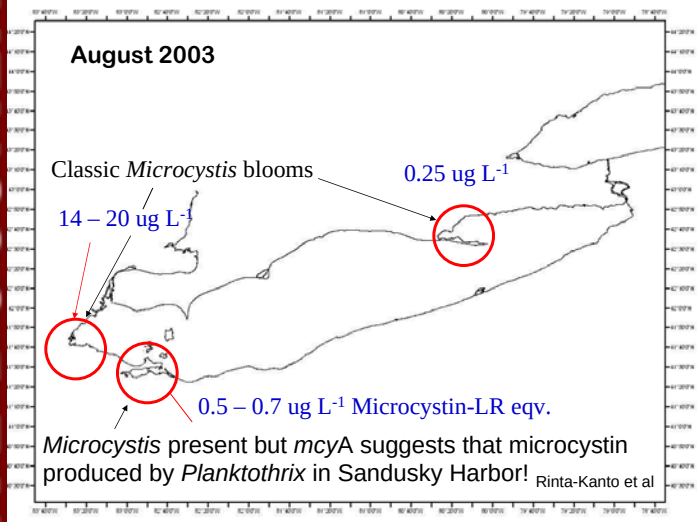
Cyanobacterial blooms are becoming commonplace in Lake Erie.

Lake Erie, August 23, '04



Imagery courtesy of M. Sultan, WMU

Year	(n)	% toxic >0.1 ppb	Highest value, ppb
1996 Sept	44	~10%	3.4
2002	119	7%	0.79
2003 July	59	41%	0.65
2003 Aug	48	60%	21
2004 July	40	38%	>1
2004 Aug	13	85%	2.4
2005	315	(3%)	0.27 (June)



Toxic Blooms in Lake Ontario

(not as severe as in Lake Erie)

Cruise date	# sta	Toxin ? (%)	Highest values	Notes
2000 (Aug)	2	0%	MC: < 0.02 μg l^{-1}	Eastern end
2001 (late July)	52	2% (MC) 4% (ATX)	MC: 0.15 μg l^{-1} ATX: 0.05 μg l^{-1}	Whole lake
2002 (late June)	7	0% (MC) 70% (ATX)	MC: 0.007 μg l^{-1} ATX: 0.006 μg l^{-1}	Henderson Bay
2003 (July, August)	80 63 17	>25% (MC) 0.5% (ATX)	MC: 1.06 μg l^{-1} ATX: 0.01 μg l^{-1}	Whole lake + Eastern shore
2004 (Aug-Sept)	81	17% (MC) 16% (ATX)	MC: 0.85 μg l^{-1} ATX: 0.02 μg l^{-1}	Whole lake

Clostridium botulinum

- Bacterium that produces botulism toxin
- Anaerobic bacterium- it grows in the absence of oxygen
- Forms endospores- dormant structures that remain viable for years
- The endospores quite resistant to temperature extremes and drying.

Where are the bacteria found?

- Spores of both type C and type E Botulism are naturally found in anaerobic habitats:
  - Soils
  - Aquatic Sediments
  - Intestinal tracts of live, healthy animals

- In the absence of oxygen, with a suitable nutrient source, and under favorable temperatures and pH, spores can germinate and vegetative growth of bacterial cells can occur. (Brand, et. al 1988).
- Botulism toxin is only produced during vegetative growth, not when the bacterium is in its spore stage.

Botulism Outbreaks in Lower Lakes

Lake Erie

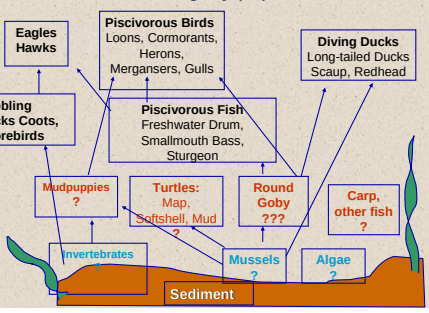
- 1999-2002- Large Outbreaks
- Confined primarily to Eastern Basin
- Smaller Outbreak in 2003
- Minimal reports of fish mortality in 2004, but a larger die off of birds in November and December during migrations.
- Nov 3 - 15 (ongoing) approximately 200 Common Loons found at Long Point National Wildlife Area, Ontario.

Lake Ontario

- 2003 – First small recorded outbreaks
- Outbreaks first confined primarily to Western Basin – some fish and birds
- 2004 - Outbreaks continued, birds and fish
- September 2004 - central portion of Lake Ontario, over 500 double-crested cormorants collected, tests were positive
- October 2004 - several hundred dead long- tailed ducks along the Hamilton/Burlington beaches
- Summer 2005 - over 1,400 double-crested cormorants collected on the islands along the Central-Eastern shore in Ontario.

Botulism – Many unanswered questions

- Is the outbreak caused by a new strain?
- Do algae blooms (Cladophora) play a role?
- Do Dreissenids play a role?
- Why have fish die-offs decreased since 2003?
- Is the decrease related to goby populations?



Lessons

- Ecological integrity cannot be achieved simply by managing chemical integrity
  - Physical and biological integrity matter
  - Scale matters
- Cannot understand chemical integrity in an ecological vacuum
  - Ecosystems have many feedback mechanisms that provide resilience; these must be understood in order to define bounds of chemical integrity
- Ecological integrity cannot be achieved by managing single issues independently of understanding interactions with other management issues
- Require coordinated modeling, monitoring, and research programs
- If we have learned anything over the last 30 years, it is that we need a *Great Lakes Basin Ecosystem Agreement*

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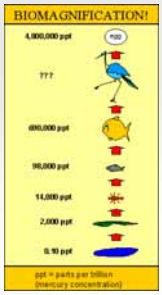
Anthropogenic Chemicals in the Great Lakes Basin: Human Health Effects

Daniel Hryhorczuk, MD, MPH

Persistent Toxic Substances in the Great Lakes Basin

- Organochlorine compounds
  - PCBs
  - Hexachlorobenzene
  - DDT and metabolites
  - Dioxins and dibenzofurans
  - Mirex
  - Dieldrin
  - Toxaphene



Persistent Toxic Substances in the Great Lakes Basin

- Heavy metals
  - Alkylated lead
  - Methylmercury
- Polycyclic aromatic hydrocarbons
- Emerging contaminants
  - Polybrominated diphenyl ethers (PBDEs)

Key Findings

- Elevated body burdens of contaminants in persons who consume large amounts of Great Lakes fish
- Developmental deficits and neurologic problems in children of some fish-consuming parents
- Endocrine dysfunction among fish eaters
- Disturbances in reproductive parameters

At Risk Populations from Contaminated Fish Consumption

- Native Americans and other indigenous peoples
- Sports anglers
- Subsistence fisherman
- Pregnant women, fetuses
- Nursing infants

Human Health Studies:
Fish consumption vs contaminant levels

- Michigan Sport Fisherman Study (Humphrey, 1976, 1983, 1988; Tee et al, 2003)
  - First demonstration of association between consumption of contaminated Great Lakes sport fish and serum levels of PCBs
  - Persons who annually consumed $\geq$ 24 lbs of fish had serum PCB levels 4x higher than controls
  - Monotonic decline in serum PCB levels among all participants from mean of 24 ppb in 1980 to 12 ppb in 1994 paralleled by and 83% decrease in fish consumption
- Wisconsin Fish Eater Study (Fiore et al, 1989)
  - Serum levels of PCBs and DDE statistically correlated with amount of Great Lakes fish consumed

Human Health Studies:
Fish consumption vs contaminant levels

- Great Lakes fish eaters, age 50 years and older (Schantz et al, 1996)
  - Those who consumed ≥ 24 lbs of sport fish for more than 15 years had higher levels of PCBs and 2x higher levels of DDE and mercury
- Great Lakes Consortium fish eaters (Turyk et al, 2005)
  - Blood samples from fish eaters obtained in 1993-95
  - Noncoplanar PCBs higher in fish eaters than in referent population, associated with fish consumption, and varied by lake

Human Health Studies:
Children's growth and development

- Michigan Maternal and Infant Study (Fein et al 1983, 1984; Jacobson et al, 1983, 1984, 1988)
  - Intrauterine exposures to diet of contaminated Lake Michigan sport fish (PCBs) associated with:
    - Decreases in infants birth weight
    - Decreases in gestational age
    - Decreases in head circumference
    - Infants exhibited neurodevelopmental and behavioral deficits on tests of visual recognition and memory at 7 months and 4 years of age
    - Poorer short- and long-term memory and lower IQ scores at 11 years of age

Human Health Studies:
Children's growth and development

- Newborns of Great Lakes fish eaters (Lonky et al, 1996)
  - Neurobehavioral deficits at 12-24 hours and 25-48 hours after birth from mothers who consumed on average 2.3 fish meals per month
- New York State Angler Cohort Study (Buck et al, 2003)
  - Absence of an adverse relation between Lake Ontario fish consumption and reduced birth size as measured by weight, length and head circumference
- Michigan Anglers Study (Karmaus and Zhu, 2004)
  - Maternal PCB concentration ≥ 25 mcg/l associated with reduced birth weight of offsrping

Human Health Effects:
Endocrine disruption

- New York State Angler Cohort Study (Bloom M et al, 2003)
  - Hexachlorobenzene inversely associated with T4
- Great Lakes Consortium fish eaters study (Persky et al, 2001)
  - Serum PCB levels and fish consumption inversely associated with T4 and Free thyroxine index in women and T4 in men
  - Among men, there were significant inverse associations of both PCB and fish consumption with sex hormone-binding globulin (SHBG)-bound testosterone, but no association with SHBG or free testosterone

Human Health Studies:
Reproductive health

- New York State Angler Cohort Study (Mendola et al, 1997; Buck et al, 2000)
  - Consuming more than one fish meal per month associated with reduction in menstrual cycle length in women
  - Maternal consumption of fish for 3-6 years associated with reduced fecundability

Human Health Studies
Community Health Profile of Windsor

- Windsor AOC ranked among the highest of 17 AOCs on Canadian side of the Great Lakes for selected health end points potentially related to pollution
- Health outcomes data
  - Mortality
  - Hospitalizations
  - Congenital malformations
- Local industrial sources and transboundary air and water pollution from Detroit

Gilbertson and Brophy, EHP 109:827,2001

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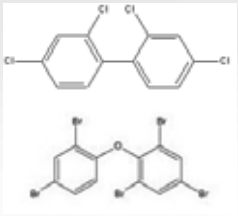
Human Health Studies
Fish consumption and breast cancer risk

- Wisconsin population-based case control study
- Relative risk for recently consumed sport-caught fish
  - Overall: 1 (0.86-1.17)
  - Postmenopausal: 0.78 (0.57-1.07)
  - Premenopausal: 1.70 (1.16-2.50)
- Frequency of and location of consumption not associated with breast cancer risk

McElroy et al. EHP 112:156, 2004

Emerging Pollutants

- While concentrations of most organochlorines in fish in the Great Lakes declined as first order decay from 1983-1999, the concentration of polybrominated diphenyl ethers (PBDEs) increased exponentially (Chernyak et al, 2005)
- PBDEs used as flame retardants
- Can bioconcentrate and bioaccumulate



Emerging Pollutants

- Toxicologic effects of PBDEs
  - Thyroid hormone imbalance (reduction in T4)
  - Developmental neurotoxicity
  - Estrogen disruptors
  - Increased liver tumors

Great Lakes Centers
Environmental Profile of PCBs

- Joyce Foundation
- Canadian Environmental Law Foundation and GLC
- www.uic.edu/sph/glakes

Great Lakes Centers
Environmental Profile of PCBs

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Wildlife and Fish Health Effects in Canadian AOCs

Scott Brown, National Water Research Institute

Environment Canada Environnement Canada

Jim Sherry, Mark McMaster, Joanne Parrott, Mark Hewitt, Derek Muir, National Water Research Institute, Environment Canada

Alice Dove, Scott Painter, Melanie Neilson, John Struger Ecosystem Health Division, Environment Canada - Ontario Region

Kim Fernie, Pamela Martin, Canadian Wildlife Service, Environment Canada-Ontario Region

Glen Fox, Liard Shutt, C. Hebert, Canadian Wildlife Service, National Wildlife Research Centre, Environment Canada

A. McNabb, Virginia Tech, Blacksburg, VA, USA

K. Grasman, Wright State U., Dayton, OH, USA

Environment Canada Environnement Canada

Great Lakes Areas of Concern

- In 1987, the International Joint Commission designated 43 areas of concern in the Great Lakes Basin
- To qualify as an AOC, the area contained one or more beneficial use impairment

Environment Canada Environnement Canada

Beneficial Use Impairments

- restrictions on fish and wildlife consumption
- tainting of fish and wildlife flavor
- degradation of fish and wildlife populations
- fish tumors or other deformities
- bird or animal deformities or reproduction problems
- degradation of benthos
- restrictions on dredging activities
- eutrophication or undesirable algae
- drinking water restrictions, or taste and odor problems
- beach closings
- degradation of aesthetics
- added costs to agriculture or industry
- degradation of phytoplankton and zooplankton
- loss of fish and wildlife habitat

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Past Effects

Reproductive Impairment In Fish-Eating Predators

- In the 1960s, Great Lakes fish were implicated in a large number of diet-related reproductive failures in ranch mink
- LOEL for mink kit survival associated with maternal liver PCBs=2.2 mg/kg
- Congenital malformations/GLEMEDs in fish-eating birds was associated with exposure to persistent organic contaminants such as dioxins and PCBs
- Reproduction in shore-line nesting eagles and cormorants failed
- Egg-shell thinning and hatching failures associated with DDT/DDE

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Developmental abnormalities found in 9 species of fish-eating birds and in hatchling snapping turtles

Environment Canada Environnement Canada

A combination of factors led to the decline of lake trout such that by 1960 they were extirpated from the Great Lakes; sea lamprey, overexploitation, changes in forage base, pollution

From mid 50's to mid 70's, Blue-Sac from exposure to TCDD-like contaminants was sufficient account for 100% offspring mortality in Lake Ontario (Cook et al. 2003)

Environment Canada Environnement Canada

Effects of POPs on wildlife have been recognized and there has been action taken to reduce exposure

Good NEWS!!!

No Blue-Sac, Return of Fish-Eating Bird Populations

Concerns Leading to Recent Studies

- **Health Canada Reports released in 2000 suggest some human health outcomes were more prevalent in certain AOCs**
- **What, if any, are the present Wildlife and Fish Health Effects in AOCs?**
  - **Last assessment summarizing known spatial and temporal trends in environmental contaminants and associated effects in fish & wildlife in 1991 "Toxic Chemicals in the Great Lakes and Associated Effects"**

Environment Canada Environnement Canada

Fish and Wildlife Health Effects and Exposure Study

Objectives

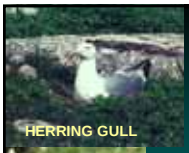
- **Update understanding of the state of fish and wildlife health**
- **Determine if effects are similar to those in human population**
- **Measure current concentrations of chemicals (old and new) in aquatic environment and tissues that could be associated with heath outcomes**

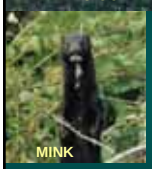
Phase I (2001-2005)

- **Canadian AOCs in the lower Great Lakes**
- **Benthic and pelagic fish, Snapping Turtles, Herring Gulls and mink**

Environment Canada Environnement Canada

Wildlife Assessments





- **Laboratory analyses:**
  - **histology**
  - **enzyme activity**
  - **estrogenicity assays**
  - **immunotoxicity**
  - **hormone function**
- **Field assessments:**
  - **sex ratios**
  - **embryonic viability**

Environment Canada Environnement Canada

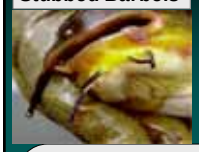
US EPA ARCHIVE DOCUMENT

Assessment of Effects in Wild Fish

- Examination of gonad development, egg size, fecundity, expression of secondary sexual characteristics
- Measurement of circulating Vg, reproductive steroid hormone levels and thyroid hormones
- Determination of steroid and thyroid biosynthetic capacity
- Liver mixed-function oxidase (index of exposure to dioxin-like organochlorines)
- Histology of endocrine and other tissues (gonads, thyroid, liver, gills)
- Deformities and other anomalies

External Abnormalities in Brown Bullheads

Stubbed Barbels



Melanoma

Focal Discoloration

Surface lumps and bumps in Western Lake Erie are more prevalent 2001 than in 1990.
Association between sediment contaminants (e.g. PAHs & metals) and higher incidence of external abnormalities – particularly barbel and raised growths.

Raised Growth - Lip

Environment Canada

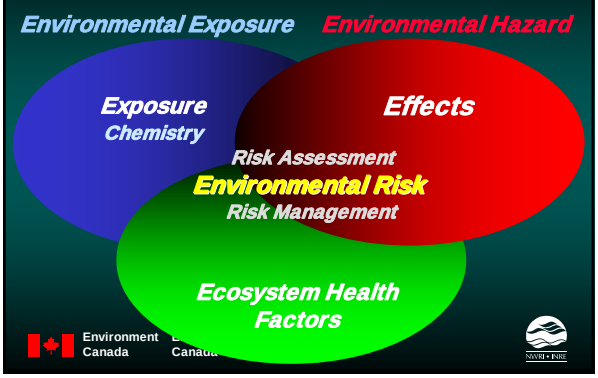
Stephen Smith, USGS

Health Changes Are Detectable!

- SNTUs, HERGs, Mink, Fish;
- subtle effects on thyroid, reproduction, physiology, morphology;
- all age stages, from embryos to young to adults;
- likely not just a OC issue, effects suggest impacts from other contaminants like EDSs
- effects mostly found at sites nearest to the AOCs.

What has wildlife told us about the current Great Lakes environment?

Assessment of Effects



Environment Canada

Ecosystem Health Factors

- Alien species have appeared at the rate of one per year since Dreissena invasion, "controls" not working.
- Assessment of effects of alien species impeded by lack of basic annual data on distribution and numbers.

Environment Canada Environnement Canada

Overview of Great Lakes Salmonids Today

- With exception of Lake Superior and parts of Lake Huron still recruitment bottleneck for lake trout
- Early mortality syndrome in salmonids
- Major prey species for salmonids
  - alewife, rainbow smelt, and bloater chub
- Thiamine deficiency is a major factor
- Alien invasive species contain thiamine degrading activity
  - alewife and rainbow smelt

Environment Canada Environnement Canada

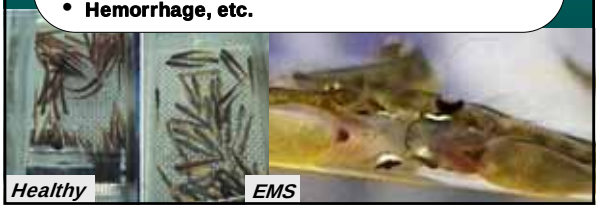
US EPA ARCHIVE DOCUMENT

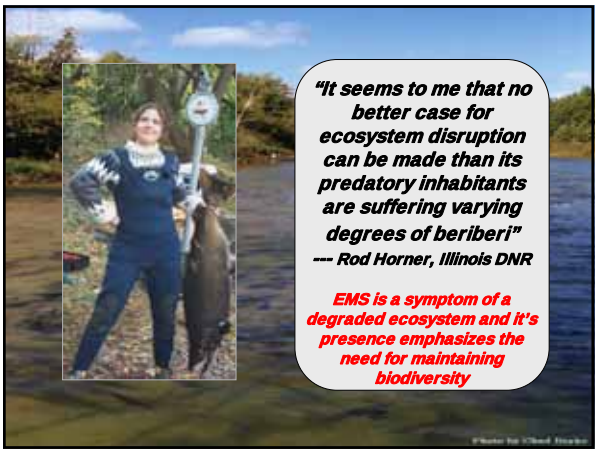
What is Early Mortality Syndrome (EMS)?

Observed between hatch and first feeding in Great Lakes salmonids and is characterized by:

- **Loss of equilibrium**
- **Swimming in a spiral pattern**
- **Lethargy**
- **Hyperexcitability**
- **Hemorrhage, etc.**

} *Neurological Symptoms*





"It seems to me that no better case for ecosystem disruption can be made than its predatory inhabitants are suffering varying degrees of beriberi"

--- Rod Horner, Illinois DNR

EMS is a symptom of a degraded ecosystem and it's presence emphasizes the need for maintaining biodiversity

Great Lakes Food Web Effects

"Nearshore Shunt"

Harvesting of offshore waters by mussel filtration nearshore may alter food web, affect YOY fish survival, increase/decrease export of nutrients and contaminants.

Environment Canada Environnement Canada

Food Quality Issues (nutrition)

- **Need to assess impacts of dreissenids and *Bythotrephes* on production at higher trophic levels.**
- Since the mid 1990's *Diporeia*, normally about 70 % of the biomass on the bottom, has disappeared in parts of the Great Lakes, except Superior, including all suitable habitat in Lake Erie, and above 80 m depth in Lake Ontario, Lake Michigan and southern Lake Huron.
- **Need to examine the flow of essential nutrients from the base of the food web to key species.**
- **Gizzard shad and gobies now major components.**

20:5n-3 = EPA (Ecosapentaenoic acid)

Other Effects

- **Shoreline filamentous algae - research largely dropped but problem has re-occurred.**
- **Sporadic blue-green algae blooms sporadic – taste/odor compounds and toxins produced.**
- **Botulism outbreak: why now? linkage with gobies, blue-green algae toxins?**

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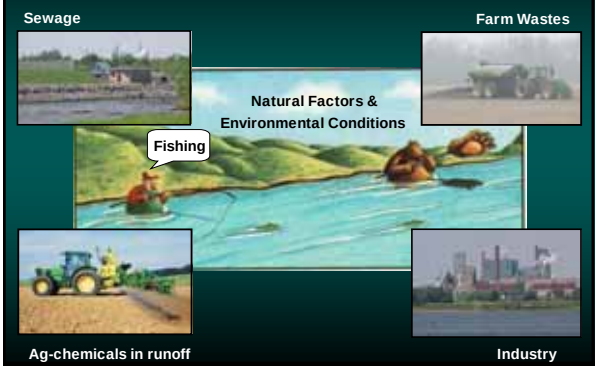
There are Many Potential Causes for Declines in Wildlife and Fish Populations



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ASSESSING CHEMICAL INTEGRITY IN THE GREAT LAKES BASIN

Keith Solomon
University of Guelph
ksolomon@uoguelph.ca

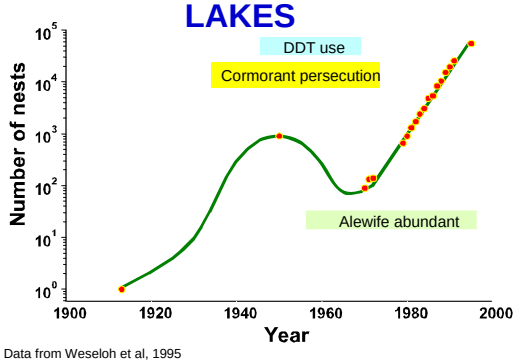
OUTLINE

- Identifying chemicals of concern
- Identifying sources
- Assessing effects
- Assessing risks of chemicals of concern
- Toxicity, hazard and risk
- Dealing with mixtures
- Conclusions

IDENTIFYING CHEMICALS OF CONCERN

- The chemical is in the system
  - So what?
- By analogy because the chemical is in other systems
  - Other systems are different?
- Must avoid Type-3 errors

CORMORANTS IN THE GREAT LAKES

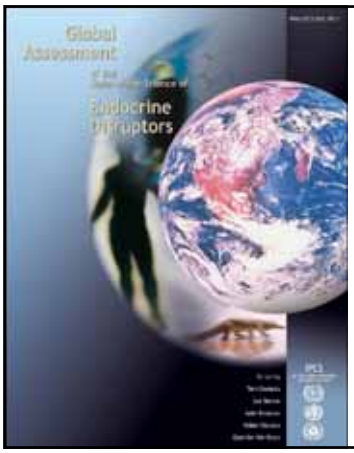


Data from Weseloh et al, 1995

RESIDUES IN ORGANISMS

- Presence in the organism does not mean that it is causing a problem.
  - Canadian "Toxic Nation" report.
- Presence in the matrix does not mean that it is causing a problem.

US EPA ARCHIVE DOCUMENT



CAUSAL CRITERIA FOR ASSESSING ENDOCRINE DISRUPTORS: A PROPOSED FRAMEWORK

IPCS. 2002. Global Assessment of the State-of-the-Science of Endocrine Disruptors. Geneva, Switzerland: International Programme on Chemical Safety of the World Health Organization Report No. WHO/PCS/EDC/02.2. August 2002. http://www.who.int/pcs

GUIDELINES FOR CAUSALITY

- Temporality
- Strength of association
- Consistency
- Biological plausibility
- Recovery

Koch

Hill

Doll

Koch R. 1882. Die Aetiologie der Tuberculose. In: Clark DH, ed. *Source Book of Medical History*. Dover Publications, Inc. p 392–406
Hill AB. 1965. The environment and disease: association or causation? *Proc. Roy. Soc. Med.* 58:295-300

CAUSE FOR WORRY

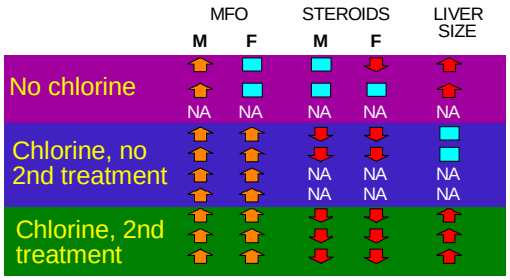
- The concentrations are increasing
  - PBDEs
  - PFOA and PFCs
  - Pharmaceuticals
- The substance biomagnifies
  - PBDEs, not tetrabromobisphenol A
  - PFOA/ long chain PFCs
- The substance is persistent or pseudopersistent
  - PBDEs
  - PFCs
  - Pharmaceuticals

IDENTIFYING SOURCES

- Where is it coming from?
- Can we do anything about it?
  - Process changes
  - Source mitigation

PULP MILL EFFLUENTS

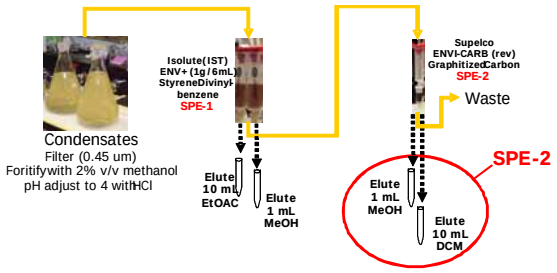
EFFECTS IN FISH



Data from Robinson et al, 1994

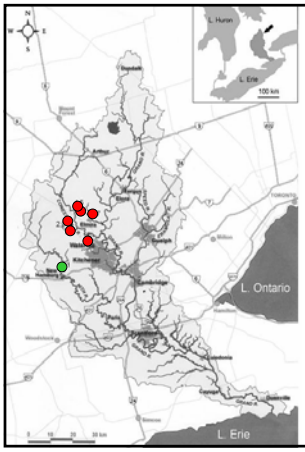
US EPA ARCHIVE DOCUMENT

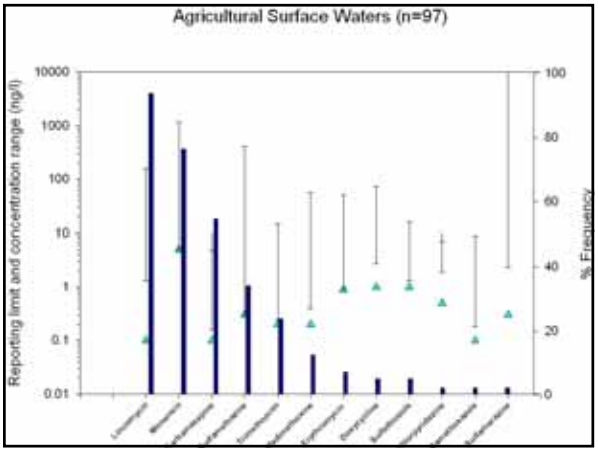
IDENTIFYING THE KEY FRACTION



Hewitt ML, Smyth SAM, Dube MG, Gilman CI, Maclatchy DL. 2002. Isolation of compounds from bleached kraft mill recovery condensates associated with reduced levels of testosterone in mummichog (*Fundulus heteroclitus*). Environ Toxicol Chem 21:1359–1367.

AGRICULTURAL PHARMACEUTICALS

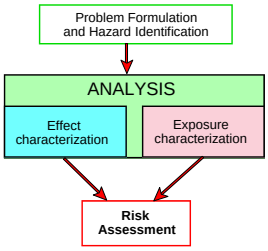




ASSESSING RISKS OF CHEMICALS OF CONCERN

- Frameworks for risk assessment

RISK ASSESSMENT



USEPA 1998

US EPA ARCHIVE DOCUMENT

TOXICITY, HAZARD, AND RISK

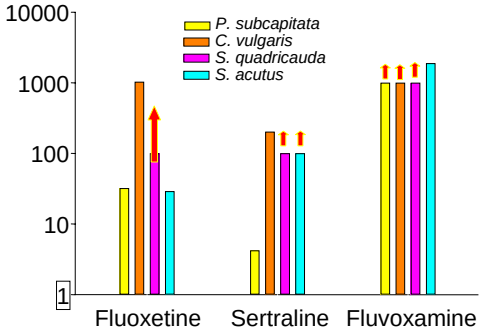
- Toxicity is not Hazard is not Risk

Ranking of concerns in the absence of exposure information

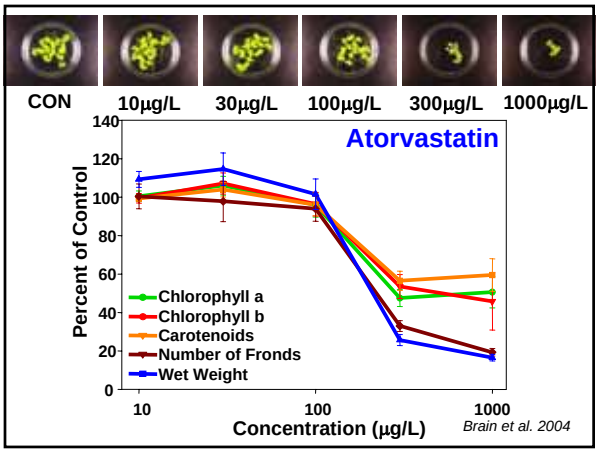
EFFECTS CHARACTERIZATION

- Laboratory studies
  - Surrogate species with standard protocols
  - Mechanisms of action
  - Simple mixtures

ACUTE GROWTH INHIBITION ASSAYS



Johnson 2004



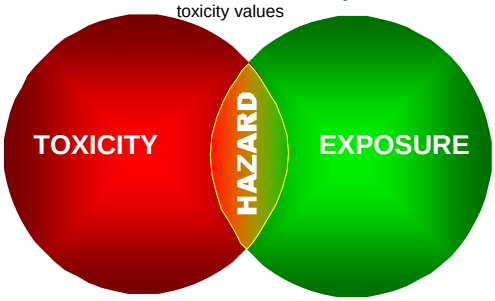
Brain et al. 2004

PARACELSUS,1493-1541

"All substances are poisons: there is none which is not a poison. The right dose differentiates a poison and a remedy"

US EPA ARCHIVE DOCUMENT

Assessment of hazard based on a ratio of single deterministic toxicity values

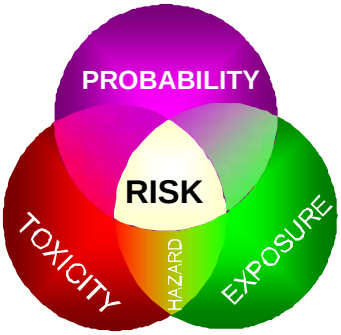


QUOTIENTS

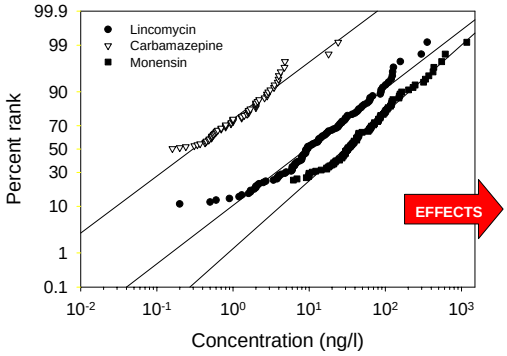
$$\text{HAZARD (LOC)} \approx \frac{\text{EXPOSURE CONCENTRATION}}{\text{EFFECT CONCENTRATION}}$$

CARL FRIEDRICH GAUß
30 April 1777 - 23 Feb 1855

Assessment of risk based on likelihood of exposure and/or toxicity



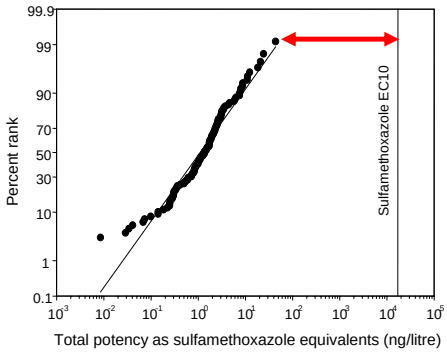
PROBABILITY OF EFFECT



DEALING WITH MIXTURES

- Additive toxicity and using potency addition (TE).
- Whole effluent testing

TOTAL POTENCY AS TOXIC UNITS



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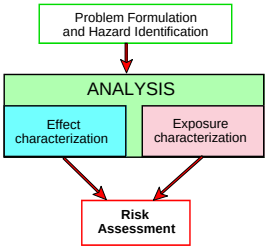
RISK ASSESSMENT

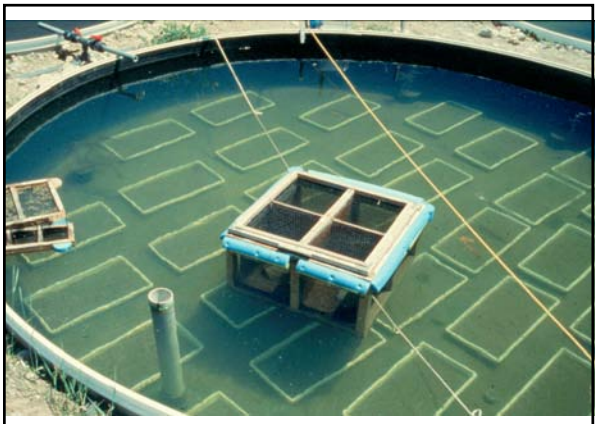


- Special considerations
  - Chronic exposures from pseudopersistence
  - Non-traditional endpoints
  - Mixtures a reality and additivity likely

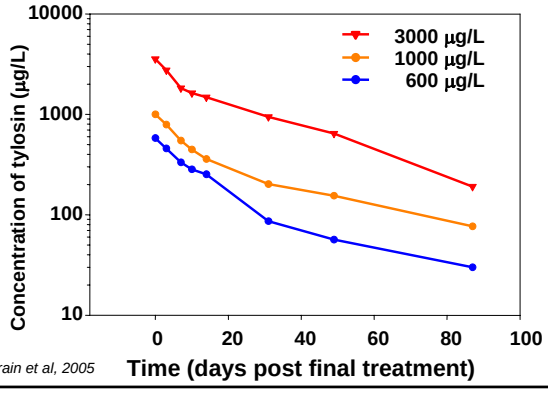
AQUATIC COSMS

EFFECT CHARACTERIZATION IN COSMS

- Community-down approach - rapidly identify sensitive species in several trophic levels
- Observation of direct and indirect effects
- Structural and functional endpoints
- More realistic stressor exposure
- Range of concentrations - upper and lower thresholds - multiple species - multiple responses
- Synthetic mixtures (Whole Effluent Test)

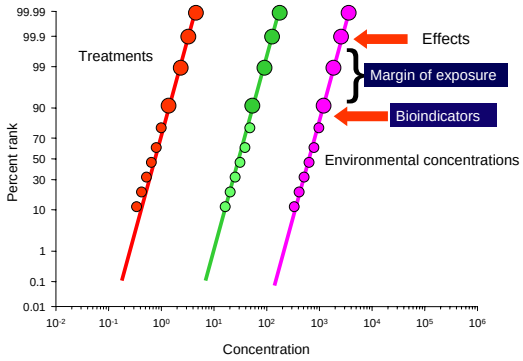


FATE OF TYLOSIN IN AQUATIC MICROCOSMS



Brain et al, 2005

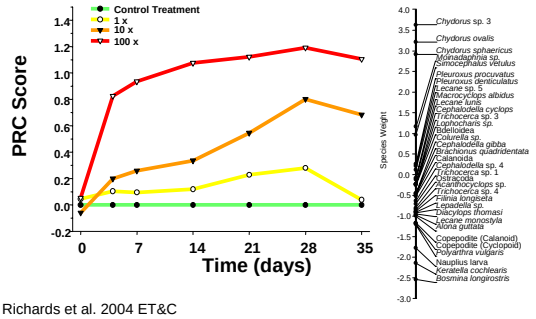
MIXTURE CONCENTRATIONS



US EPA ARCHIVE DOCUMENT

Zooplankton Community Response

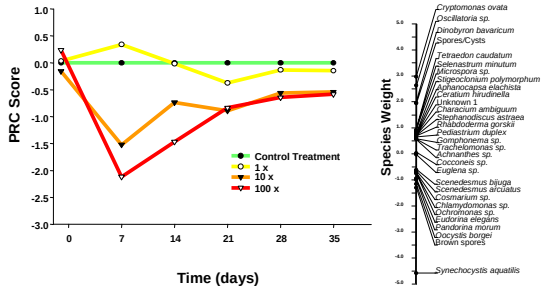
Ciprofloxacin, Fluoxetine, Ibuprofen



Richards et al. 2004 ET&C

Phytoplankton Community Response

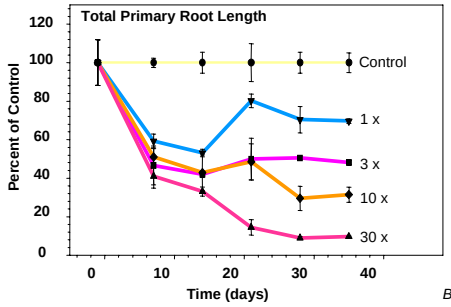
Ciprofloxacin, Fluoxetine, Ibuprofen



Richards et al. 2004 ET&C

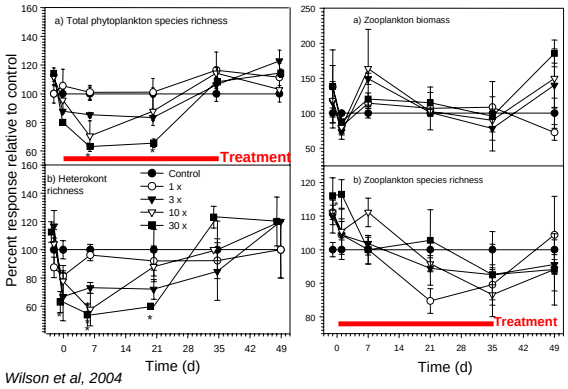
RESPONSE OF *MYRIOPHYLLUM SIBIRICUM*

Tetracycline, oxytetracycline, chlortetracycline, and doxycycline



Brain et al, 2005

RESPONSE OF PLANKTON



Wilson et al, 2004

CONCLUSIONS

- Identifying chemicals of concern
  - Need to consider causality
- Identifying sources
  - Not always easy
- Assessing effects
  - Need to consider effects above the level of the organism
- Assessing risks of chemicals of concern
  - Cannot rely on traditional tests with traditional endpoints
- Toxicity, hazard and risk
  - Probabilistic approaches are promising
- Dealing with mixtures
  - Complex but whole effluent testing offers advantages

THANK YOU

ksolomon@uoguelph.ca