Notes on Assessing and Managing Harmful Pollutants in the Aquatic Environment

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Ontario

Overview

- Government
  - Federal and provincial powers with regard to the environment
  - Ministry of the Environment Programs
- Great Lakes Context
- Chemistry/Toxicity Considerations & Challenges
- Future Directions

Federal and Provincial Roles

- Powers between federal and provincial governments assigned by the Constitution
- No explicit authority over the environment
- Federal authority over navigation, fisheries and matters of national interest.
- Provincial authority over natural resources (including water), property and civil rights, local works and undertakings, matters of a local nature.
- Both governments have to cooperate to restore and protect the environment.

Environment Canada

- Two key pieces of environmental legislation:
  - Canadian Environmental Protection Act (CEPA) - joint administration with Health Canada
  - Fisheries Act

- CEPA:
  - Chemical-by-chemical approach to toxics assessment and management
  - Determines whether a substance is “CEPA-toxic” (i.e., requiring risk management) - control may be through voluntary agreements, regulatory controls or bans/phase outs
- Fisheries Act:
  - General prohibition on discharges of harmful pollutants to waters frequented by fish
  - Authorization for discharge through regulations: Pulp and paper and mining sectors

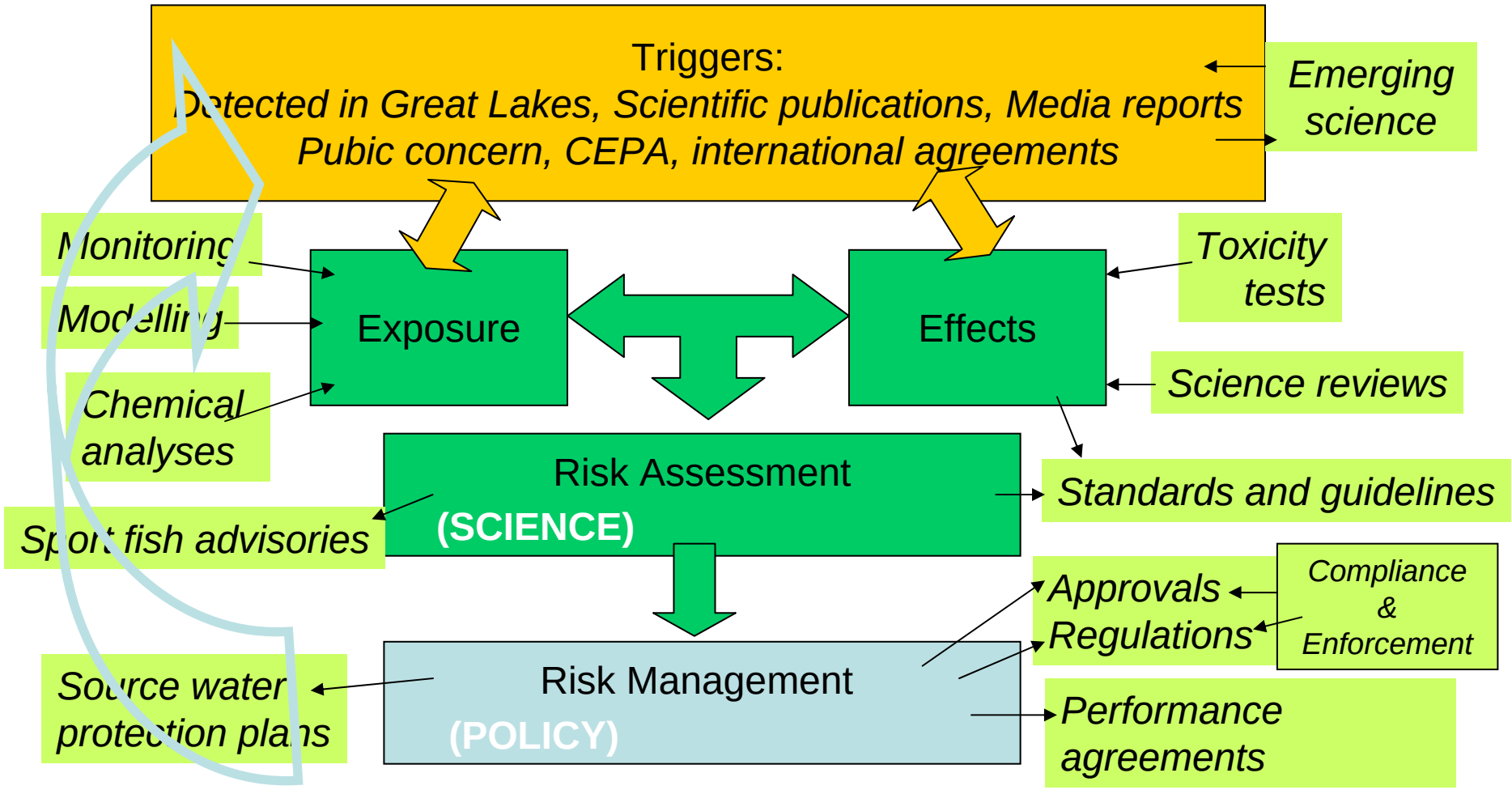
Ontario Ministry of the Environment

- Mandate to restore and maintain the Ontario environment to protect human and environmental health
- Regulates “pipes and stacks”
  - e.g., Environmental Protection Act
    - Municipal industrial Strategy for Abatement (MISA)
    - No discharge of a contaminant above regulated limit; no discharge of a contaminant at a concentration that causes or is likely to cause an adverse effect

MOE Cont'd.

- Selected Programs:
  - Setting standards for environmental media and drinking water
  - Provision of Technical and scientific advice on human health and environmental risks
  - Administration of the Pesticides Act
  - Monitoring and reporting on the state of the environment (air, water, land, biota and sediment)
  - Conducting laboratory studies and analyses
  - Informing and innovating MOE business through science

Addressing Harmful Pollutants - Triggers and Responses



The Great Lakes Context

- **Great Lakes Water Quality Agreement (GLWQA)**
  - 1972, renewed in 1978, amended 1987
  - commitment of Canada and the United States to restore and maintain the chemical, physical and biological integrity of the Great Lakes Basin Ecosystem
  - Started in response to phosphorus – later included persistent toxic substances
  - Policy that "…the discharge of toxic substances in toxic amounts be prohibited and the discharge of any or all persistent toxic substances be virtually eliminated."

Canada-Ontario Agreement

- Implementation of the GLWQA in Ontario through the Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem (COA)
- First signed in 1971
- Most recently in 2002

COA 2002

- Vision:
  - "healthy, prosperous and sustainable Great Lakes Basin Ecosystem for present and future generations"
- Four Annexes:
  - Areas of Concern
  - Harmful Pollutants
  - Lakewide Management
  - Monitoring and Information Management

Harmful Pollutants Annex

- Overall Goal
  - To continue progress towards the virtual elimination of persistent bioaccumulative toxic substances, and the significant reduction of other harmful pollutants

COA Tier 1 and Tier 2 Substances (legacy compounds)

Tier 1	Tier II	Criteria Air Pollutants
benzo-(a) pyrene	1,4-dichlorobenzene	NOx
mercury	anthracene	VOCs
alkyl-lead	4,4”-methylenebis (2-chloraniline)	SO_2
octachlorostyrene	cadmium	PM1O
hexachlorobenzene	3,3’-dichlorobenzidine	PM 2.5
PCDD (dioxins)	PAHs	
PCDF (furans)	pentachlorophenol	
PCBs	tributyltin	
5 pesticides (DDT, mirex, chlordane, toxaphene, aldrin/dieldrin)	dinitropyrene	
	hexachlorocyclohexane	

How to reduce releases?

- Go to the source
  - Continue to work with producers and sources of pollutants using regulatory and non-regulatory tools
- Enhance knowledge
  - Ensure that essential knowledge is available for decision making pertaining to virtual elimination of persistent bioaccumulative toxic substances and reductions of other harmful pollutants

COA - Expected Results (1)

- Quantitative Release Reductions:
  - Reduction targets for PCBs, mercury and dioxins
- Qualitative Release Reductions:
  - No reduction target
  - Applies to “other harmful pollutants including Criteria Air Pollutants”
  - Applies to municipal discharges

COA - Expected Results (2)

- Enhanced knowledge:
  - Results aimed at better, more efficient reporting of emissions and tracking of movements in-basin and out-of-basin
  - Better communication with the public
  - Better understanding of the ecological and human health risks of chemicals of harmful substances

COA - Progress on Legacy Substances

Substance	Goal*	Achieved to Date
High level PCBs	90% reduction of PCBs in storage	89%
Mercury	85% reduction in releases by 2005 90% reduction in releases by 2010	84%
Dioxins /furans	90% reduction by 2005	87%
Mirex, DDT, toxaphene, alkyl lead, chlordane, octochlorstyrene, aldrin/dieldrin	Virtual elimination	Great Lakes sources virtually eliminated

* Compared to a base year of 1988 except PCBs (1993)

Enhancing Knowledge

- Sources, fate and impact studies
  - Monitoring and assessments
  - Analytical method development
  - Standards development
- Development of a Great Lakes Public Health Network (GLPHN)

e.g., Municipal Wastewater Effluent (1)

- Investigations:
  - Technologies for reducing harmful pollutants in municipal wastewater effluent
    - Pathogens
    - Ammonia
    - Pharmaceuticals & other emerging substances of concern
  - Monitoring effluents, sludge, biosolids, receiving environment

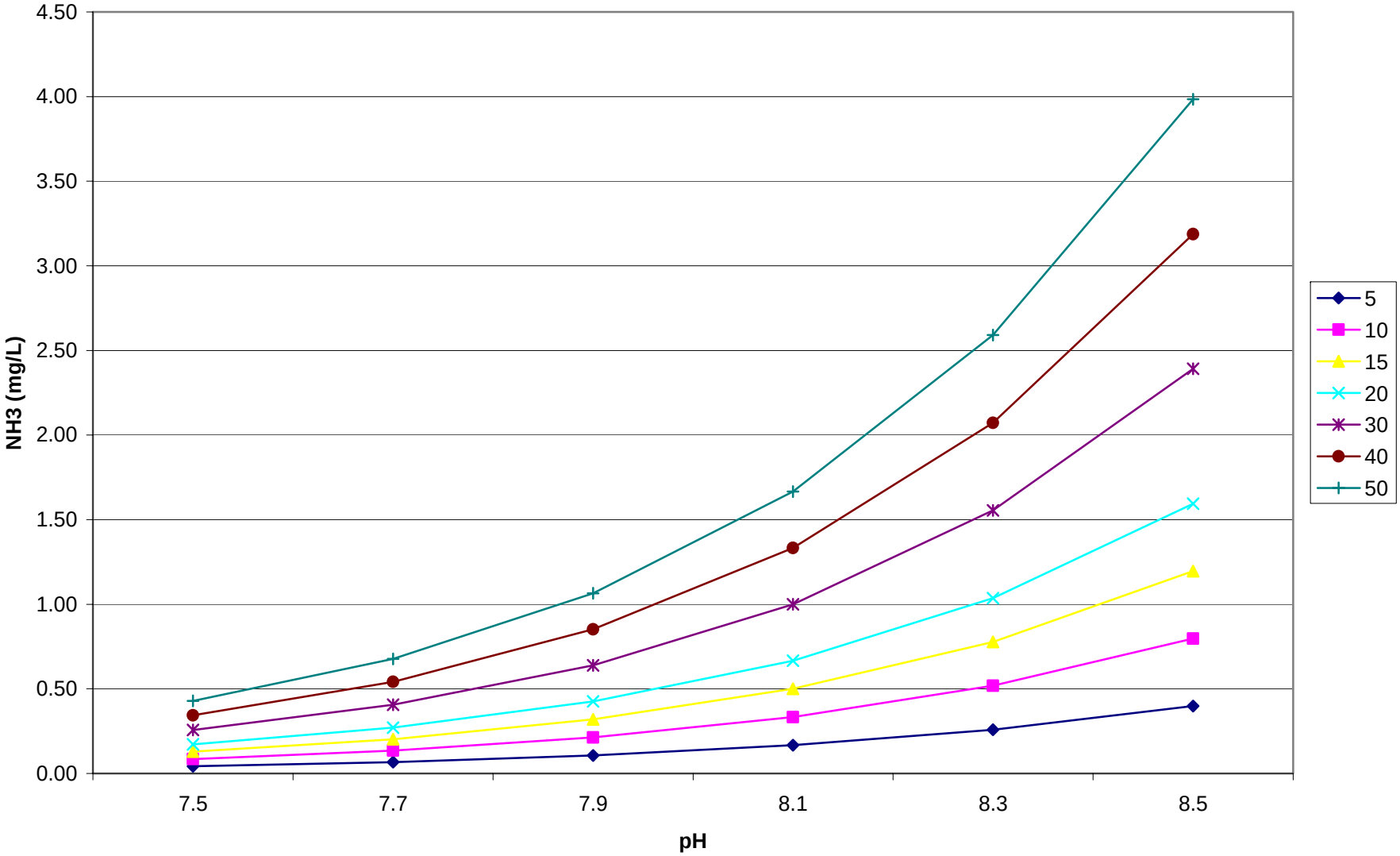
e.g., Municipal Wastewater Effluent (2)

- Ammonia: Major issue in policy development regarding municipal wastewater effluent
  - CEPA Toxic – must be risk managed; guideline under CEPA
  - Acutely lethal to fish
  - Not persistent
  - Acute lethality in effluent vs environmental impact
  - Costs for control of effluent quality vs costs for bypasses and overflows

e.g., Municipal Wastewater Effluent (3)

- Ammonia is a pH sensitive toxicant
- Total ammonia = sum of unionized (NH_3) + ionized forms (NH_4)
- Form most associated with toxicity is NH_3
- As pH rises, the proportion present as NH_3 increases.
- Therefore, pH of discharge is an important factor affecting toxicity due to ammonia

Concentration of NH3 at Various pHs and Total Ammonia Concentratins



e.g., Municipal Wastewater Effluent (4)

- Effluent must not be acutely lethal to aquatic organisms
- Measure of acute lethality is the 96-hr rainbow trout test
  - (Environment Canada RM13)
- Test requires aeration which increases pH of the exposure medium
- Federal government considering pH stabilization in toxicity testing for the municipal sector

e.g., Water Quality Criteria (1)

- e.g., Canadian Water Quality Guidelines (CWQGs); Provincial Water Quality Objectives (PWQOs)
- Numeric or narrative criteria representing a satisfactory level for surface waters.
- Protective of all forms of aquatic life, all life stages, indefinite exposure periods
- Based on current, scientifically defensible toxicological data
- PWQOs may be made enforceable through certificates of approvals

e.g., Water Quality Criteria (2)

- Accounting for Bioavailability:
  - e.g., PWQOs for Metals
    - Most are based on total concentrations – do not represent bioavailability
    - Can account for site specific effects through:
      - Water Effects Ratios
      - Chemical Speciation Models
      - Bio-chemical Models – The Biotic Ligand Model

        free download: www.hydroqual.com/contact.html

e.g., Water Quality Criteria (3)

- Water Effect Ratios
  - Parallel laboratory toxicity tests conducted using a metal in site water and in laboratory water:
  - $WER = \frac{\text{LC50 in site water}}{\text{LC50 in lab water}}$
  - WER>1 – site conditions mitigate toxicity
  - WER<1 – site conditions enhance toxicity
  - WER could be applied on a site specific basis to adjust restrictions on discharges

e.g., Water Quality Criteria (4)

- Chemical Speciation Models e.g., MINTEQA2
  - free download from USEPA: www.epa.gov/ceampubl/mmedia/minteq/index.htm
  - DOS program
  - Provide model with data regarding a water sample (major cations and anions, alkalinity, TOC, pH)
  - Model estimates proportion of metal present in free form
  - Free form – link to toxicity.

e.g., Water Quality Criteria (5)

- WER
  - Measures effects
  - unknown mechanism (don't know why metal is more toxic in one water)
  - has to be repeated for each site
- Chemical Models (MINTEQA2)
  - Exposure model
  - Mechanistic but only accounts for two "Cs": complexation and concentration

e.g., Water Quality Criteria (6)

- BLM – provides the third C: competition
  - Predicts toxicity based on the strength of the binding between the free metal ion and the biological receptor, compared to competing cations.
  - Main Assumptions:
    - Solutions are at equilibrium
    - Body concentration associated with a particular effect is constant
    - Free metal ion is the form associated with toxicity

e.g., Water Quality Criteria (7)

- BLM
  - Considers the biological receptor (e.g., gill) a ligand in solution
  - Uses equilibrium constants for ions binding to the gill
    - K_M = [ML] / [M][L]

      K_M = conditional equilibrium constant

      ML = body concentration of metal (µmol/mg tissue)

      M = water concentration (µmol/L)

      L = concentration of ligand (µmol/mg tissue)
  - Predicts toxicity based on the number of gill sites bound by the metal (fish)

The Math

$$ML = \frac{K_M * M * L_T}{1 + K_M * M + K_X * X + K_Y * Y + \ldots}$$

K_M = conditional equilibrium constant

ML = body concentration of metal (µmol/mg tissue)

M = water concentration (µmol/L)

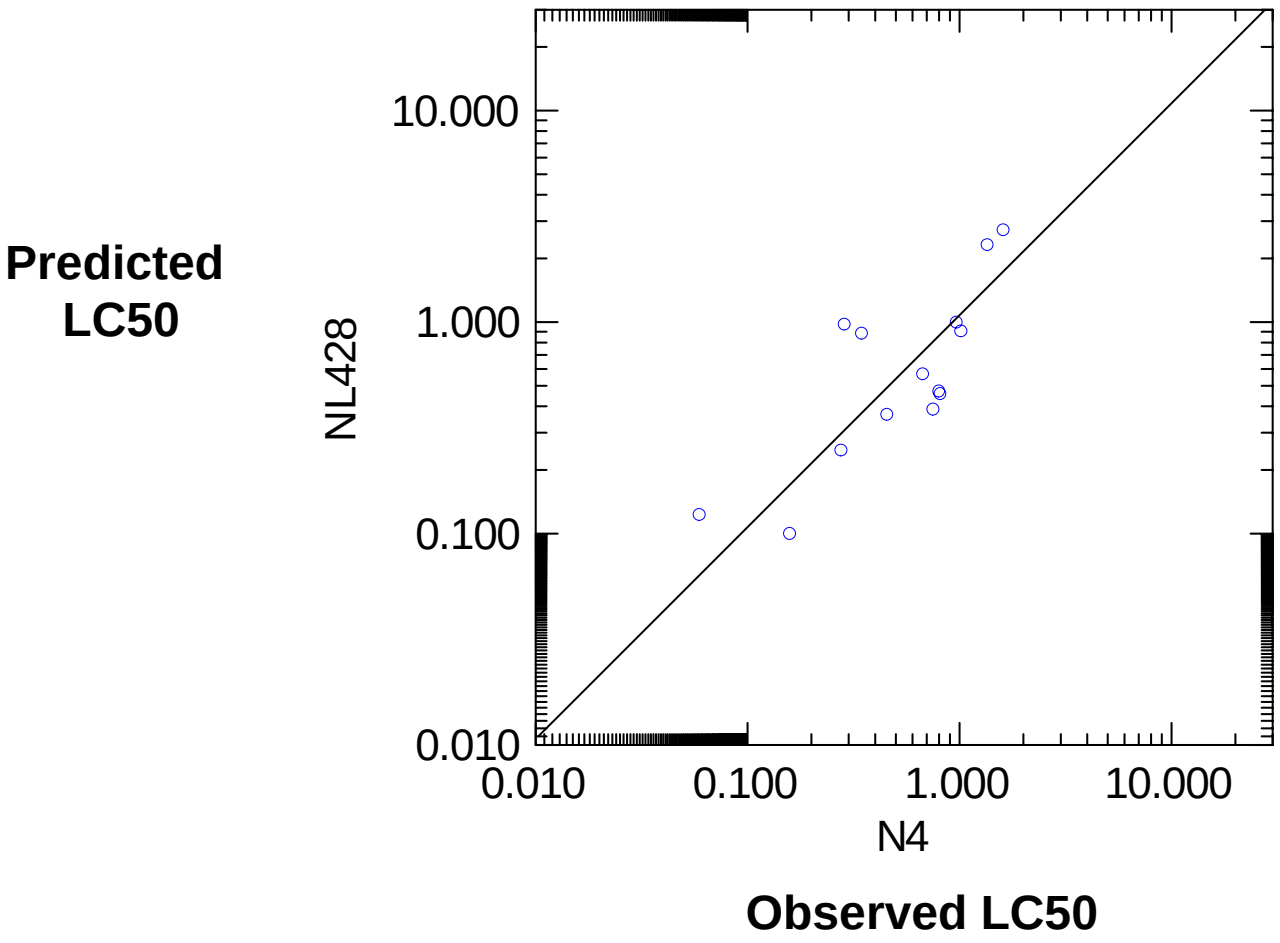
L = concentration of ligand (µmol/mg tissue)

X,Y = competitor cations

$K_{X,}$ = conditional equilibrium constant for X

$K_{Y,}$ = conditional equilibrium constant for Y

Some Hot New Data!

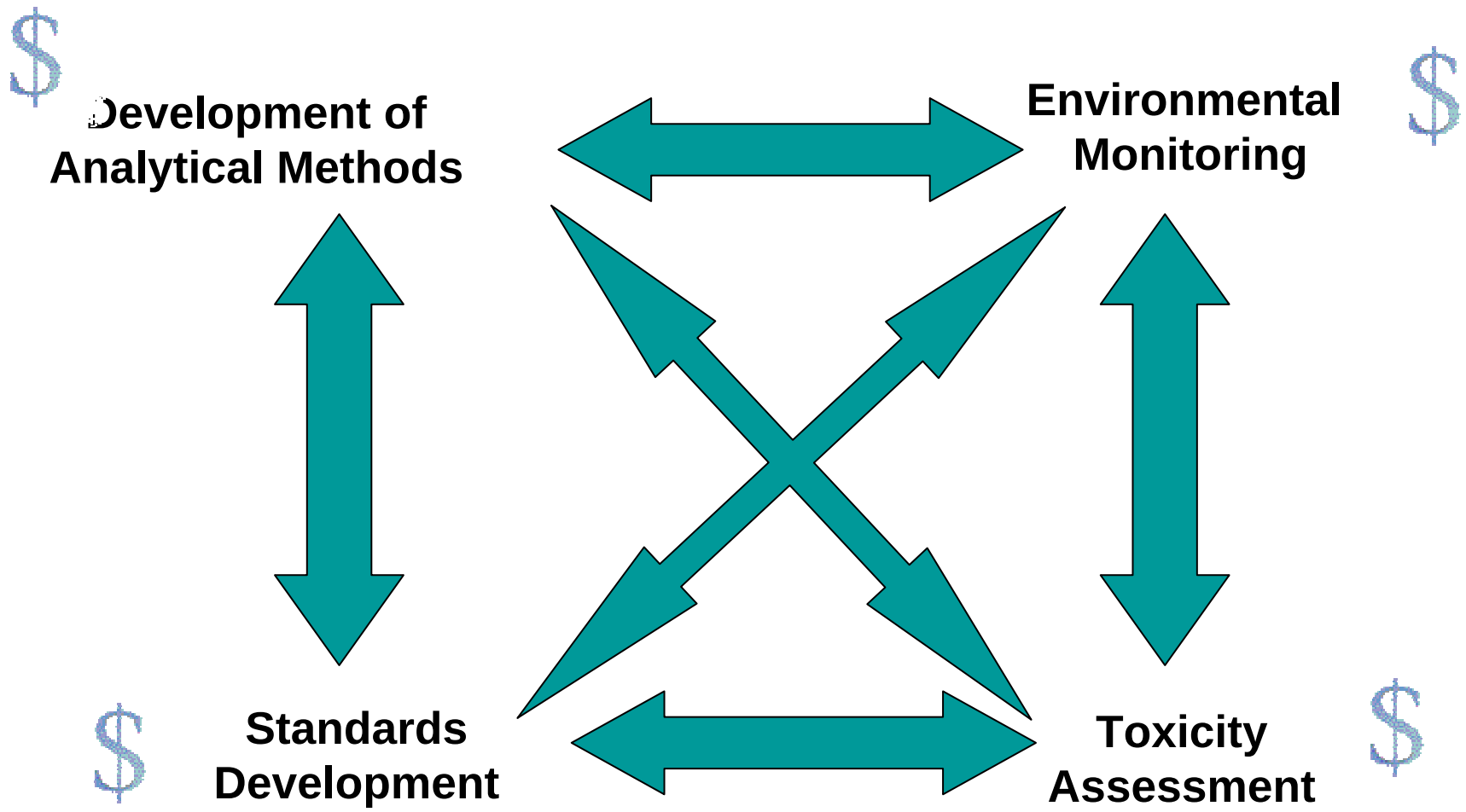


28-d *Hyalella azteca* LC50 tests with Nickel - Predictions using BLM-type model

e.g., Emerging Contaminants (1)

- Reference under COA to substances of "potential concern"
- e.g., fluorinated substances
  - e.g., perfluorooctane sulfonate (PFOS) perfluorooctanoic acid (PFOA)
  - Surfactant – water and stain repellent used in clothing, leather, carpeting etc
  - Carcinogenic in mammals, persistent, bioaccumulative
  - Enter municipal waste stream
  - Currently under CEPA assessment

e.g., Emerging Contaminants (2)



Source – Fletcher, 2006

e.g., Emerging Contaminants (3)

Time line for Criteria Development

Identification of issue	Data Acquisition	Data Dissemination	Criteria Development
• detection in environment • knowledge of release • other identified concern	• Detection refinement •lab toxicity studies • fate and transport work	• Peer review • Report Publication	• Data Review • Report Development • Peer review • Management Approval • Report Publication

Studies needed for WQC development;
3 fish
2 invertebrate
1 algae

e.g., PFOS

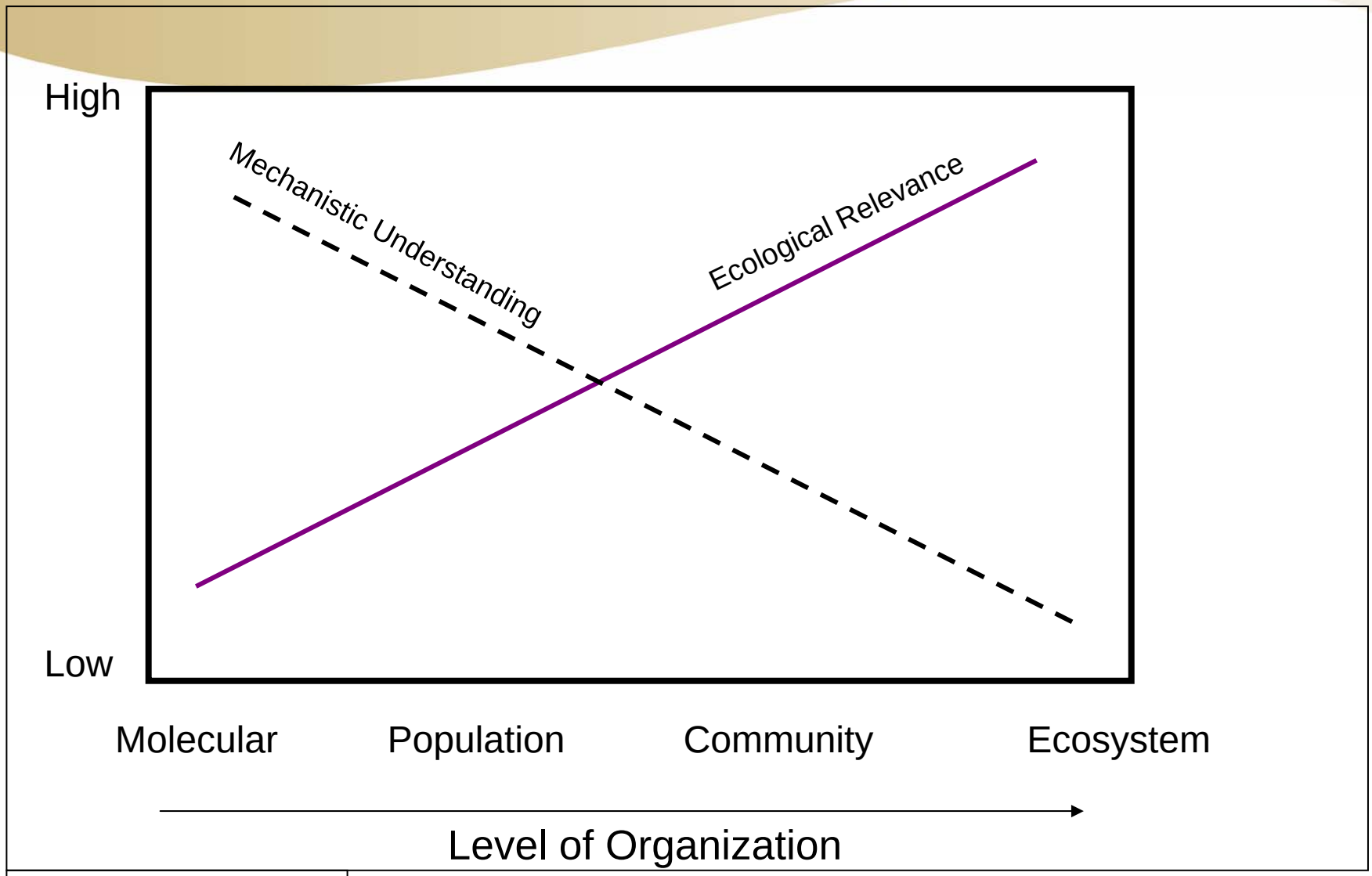
Use	Detection	Toxicol…	…ards
1950/60's	Late 1990's	2003 – 2 studies 2004 – 2 studies 2005 – 2 studies	?	?

Source – Fletcher, 2006

e.g., Emerging Contaminants (4)

- Challenges with Emerging Substances:
  - Traditional Substances
    - Effects measured by whole organism tests – lethal and sublethal response
    - Assumptions:
      - criteria estimated from a subset of species will be reasonably protective of the majority of species
      - Species protection confers ecosystem protection
  - Emerging substances
    - Effects of Emerging Substances may be more subtle:
      - May need different tools to assess – cellular tests
      - More difficult to link cellular response to environmental effects
      - These effects occur at lower concentrations than traditional whole organism tests –would (further) drive down WQC
      - Communicating relevance of the results to non-scientists (decision makers) is more challenging

Source – Fletcher, 2006



From Mount, et al. 2003

Source – Fletcher, 2006

Challenges (1)

- Legacy of Contaminants in the Basin
  - e.g., Sediment
    - Trackdown of ongoing sources
    - Decision making framework for contaminated sediment
- Long Range Transport of Airborne Pollutants
  - Binational Toxics Strategy addresses U.S. and Ontario sources through overall reduction efforts but not international sources.

Ongoing Challenges (2)

- Diminishing returns
  - Initial reduction releases achieved through technologically and economically practicable measures
  - Last 10% is more difficult, requiring greater investment, technological advances, and/or targeting of smaller dispersed sources
- Knowledge gaps in inventories for many substances

Ongoing Challenges (3)

- Many of the emerging substances of concern are contained in products
  - Challenge is the societal and economic value of these products
    - Present in the home (flame retardants/stain repellants on building materials, furniture, carpets)
    - Dumped down the drain (pharmaceuticals)

Opportunities

- Collaboration and communication among provincial and federal agencies to monitor, assess risk and address priority and emerging substances
- Harmonized regulatory and non-regulatory controls
- Increased education and outreach to the public