

Overview of current studies to understand sources, fate and impacts of contaminants in the Great Lakes

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Purpose of the Presentation

To provide:

- An update on the Ministry of the Environment's (MOE) municipal wastewater study and,
- An overview of new MOE projects related to the Great Lakes:
 - Monitoring pharmaceuticals and other emerging contaminants in an urban sewer shed;
 - Use of Polar Organic Chemical Integrative Samplers (POCIS) in Drinking Water plants;
 - Hazard Screening of Selected Contaminants in the Great Lakes Basin;
 - Chemicals of Concern in Nearshore Waters and,
 - Chemicals of Concern in the Great Lakes Environment.



ETERCE

- Evaluation of Treatment Efficacy for the Reduction of Chemicals and Environmental impacts (ETERCE) in water and wastewater
- Pilot- and full-scale study of 3 Ontario STPs
- Evaluates removal of harmful pollutants (legacy and contaminants of emerging concern) by 8 different sewage treatment technologies
- Assesses toxicity of STP effluent using whole organism tests (standard tests; life cycle tests) and micro-scale endocrine disruption test
- Investigates links between treatment, chemistry and effluent toxicity
- Baseline study: characterizes conventional activated sludge nitrifying technology without disinfection, and associated effluent toxicity.
- Pilot and Full-Scale study: evaluates relative effectiveness of different conventional and advanced treatment technologies in reducing chemical contaminants and environmental impacts.



Baseline Study

 Concurrent 6-month background evaluation of two Ontario STPs both operating as nitrifying activated sludge systems without disinfection (UV only in Summer to early Fall)





Baseline ECOTOX Summary STP#1

- Acute Toxicity:
 - No acute toxicity (100% survival) to rainbow trout or *Daphnia magna* following exposure to 100% effluent
 - Chronic Toxicity:
 - No longer-term toxicity following exposure to 100% effluent to:
 - Fathead minnow survival or biomass (7-d)
 - Ceriodaphnia dubia survival (7-d) (except one event)
 - » Ceriodaphnia dubia reproduction: $IC_{25} < 1.56\%$ in one sampling event
 - Lemna minor frond number or dry weight (7-d) algae growth noted in several sampling events
 - Pseudokirchneriella subcapitata growth Enhancement of growth in all sampling events
 - No estrogenic, androgenic or thyroid activity measured in all sampling events



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Baseline Chemical Summary

 ~50% of the chemicals analyzed for were not detected in either influent or effluent samples.

Metals:

- Most frequently detected metals were: sodium, calcium, magnesium, potassium, strontium, iron, barium, zinc and manganese.
- Arsenic, beryllium, cadmium, lead, selenium, silver and vanadium were not detected in any effluent samples.

Microcontaminants (MCs):

- Most frequently detected were: bisphenol A, diclofenac, carbamazepine, lincomycin, sulfamethoxazole, ciprofloxacin, erythromycin, naproxen, benzafibrate, gemfibrozil, ketoprofen and ibuprofen.
- 4 nonylphenol, 4 nonylphenol monoethoxylates and 4 nonylphenol diethoxylates were frequently detected in all samples, whereas octylphenol was infrequently detected.



Full Scale / Pilot Studies Phase 1 – STP#1



Sewage Treatment Pilot Plants (STP) #1



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Chemical Summary

Conventionals:

BNR was the most effective at reducing NO_3 -N, TN, TP and PO_4 -P.

Metals:

No difference between treatments except Cr where CAS-N > CAS-BNR ~ CAS.

Microcontaminants (MCs):

- No statistical difference between the 3 treatment for 14 MCs (25 total).
- CAS-BNR routinely had the lowest concentrations detected.
- Some MCs were not reduced (<0%) by any of the treatments (carbamazepine, erythromycin, warfarin, carbadox).
- Ibuprofen was effectively reduced (>95%) by all of the treatments.

Ecotox Summary – STP #1

CAS:

- Acute toxicity: Rainbow trout lethality was observed 2/3 sampling events (LC $_{\rm 50}$ ~58%v/v and 83%v/v).
- Acute toxicity: All effluents were non-lethal to Daphnia magna.
- Chronic toxicity: Mixed effects (no effect, inhibition, stimulation) were observed.
- In vitro Screening:
 - Significant estrogenic, androgenic or thyroid competition was only observed in December samples.

CASN:

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- No acute toxicity was observed for either rainbow trout or *Daphnia magna*.
- Chronic toxicity: Mixed effects (no effect, inhibition) were observed.
- In vitro Screening:
 - Significant estrogenic, androgenic or thyroid competition was only observed in December samples.

CAS BNR:

- No acute toxicity was observed for either rainbow trout or Daphnia magna.
- Chronic toxicity: Mixed effects (no effect, stimulation, or stimulation at low conc + inhibition at high conc) were observed.
- In vitro Screening:
 - Significant thyroid competition was only observed in the December sample.



Rainbow Trout 96h Exposure

	CAS	CAS-N	CAS- BNR
September	$\frac{LC_{50}}{NH_{3(0h)}} = 0.44 \text{ mg/L} (T^{\circ}=14.4, \text{pH}=7.6)$ $NH_{3(96h)} = 0.47 \text{ mg/L} (T^{\circ}=15.1, \text{pH}=8.1)$	No mortality NH _{3(s)} = 0.0026 mg/L	No mortality NH _{3(s)} = 0.0064 mg/L
October	No mortality	No mortality	No mortality
	$NH_{3(0h)} = 0.09 \text{ mg/L} (T^\circ=15.1, pH=7.4)$	NH _{3(s)} =	NH _{3(s)} =
	$NH_{3(96h)} = 0.28 \text{ mg/L} (T^\circ=14.1, pH=8.0)$	0.00086 mg/L	0.0027 mg/L
December	LC ₅₀ 83% v/v	No mortality	No mortality
	NH _{3(0h)} = 0.17 mg/L (T°=15.1, pH=7.4)	NH _{3(s)} =	NH _{3(s)} =
	NH _{3(96h)} = 0.53 mg/L (T°=14.9, pH=8.1)	0.0034 mg/L	0. 0027 mg/L



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Growth in effluent-exposed FHM

Dr. Joanne Parrot (Environment Canada)

- 70-50 % CAS effluent
 - Surviving CAS adult fish growth normal
 - Males increased liver size, increased ovipositor size
- 100 % CAS-N effluent
 - CAS-N adults reduced growth (length of males)
 - Males increased liver size, increased ovipositor size, fewer male sex characteristics
- 100 % CAS-BNR effluent
 - Fish growth = or better than controls (larger females, larger gonads in males and females)



New projects related to the Great Lakes



Monitoring Pharmaceuticals in an Urban Sewer shed

Purpose:

- To investigate source loadings of pharmaceutically active compounds (e.g. pharmaceuticals, antibiotics, x-ray contrast media, hormones) and other emerging contaminants (e.g. disinfectants, anti-microbial agents), to a STP from various institutions.
- Monitoring direct effluent discharge from 3 hospitals, a Long-Term Care Facility, a Veterinary clinic and the influent and effluent of the receiving STP over 5 consecutive days.

Status

• Sampling complete, chemical analysis underway.





Evaluating the use of POCIS at Drinking Water Treatment Plants

Purpose:

 To evaluate the potential use of POCIS at 2 drinking water plants to quantify exposure levels of pharmaceuticals, personal care products and endocrine disrupting compounds in raw and treated drinking water.



- List of indicator compounds include: carbamazepine, gemfibrozil, sulfamethoxazole, trimethoprim, ibuprofen, estrone, acesulfame and sucralose.
- Deployment using both conventional HLB resin and Horizon disks.
- First round of sampling complete. Second round of sampling in the spring 2012.





Hazard Screening of Selected Contaminants in the Great Lakes Basin

Purpose:

- Using the ICJ summary report "*Review of Chemicals of Emerging Concern and Analysis of Environmental Exposures in the Great Lakes Basin*" of ~300 chemicals as the foundation, identify substances that are present in Great Lakes waters & sediment at concentrations that can potentially cause ecological impairment (HQ>1).
- Phase 1: The focus was on substances from the database that were detected in Canadian waters and were detected in greater than 10% of the samples and in <10 samples in the database.</p>
 - Substances identified to have a HQ>1 (exceeded derived NOEC benchmarks) were: Azinphos-methyl, Diazinon, Carbamazepine, Clofibric acid, Naproxen, Ibuprofen and Nonylphenol-TEQ
- Phase 2: Complete the screening exercise to include the remaining substances from the database (those substances detected only in US waters and in <10% of the samples.
 - for substances with a HQ>1, determine the substances quantity, use, sector and application in Ontario.
 - Project initiated.





Chemicals of Concern in Nearshore Waters



Project 1:

- Deployment of nearshore passive samplers (air/water) to screen for alternative halogenated flame retardants.
- Collaborating with the University of Rhode Island.

Project 2:

- Urban Contaminant Influences in the Great Lakes.
- POCIS and polyethylene samplers in urban impacted waters (Thunder Bay, ON & Sault Ste Marie, ON).

• Focus on: legacy compounds, pharmaceuticals, hormones.



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Chemicals of Concern in the Great Lakes Environment – Non Target Screening



Purpose: Using advanced instrumentation to screen for and identify compounds frequently present or more abundant in Great Lakes samples

e.g. Two-dimensional GC chromatograms from Etobicoke Creek

Yellow dots – unknowns; Black dots – target analytes (PCBs, OC pesticides, chlorobenzenes)



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Questions or Comments?

Thank you for your time.

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