MICROCONTAMINANTS IN IN WASTEWATER TREATMENT PLANTS: STATUS IN CANADA

Fate in Wastewater

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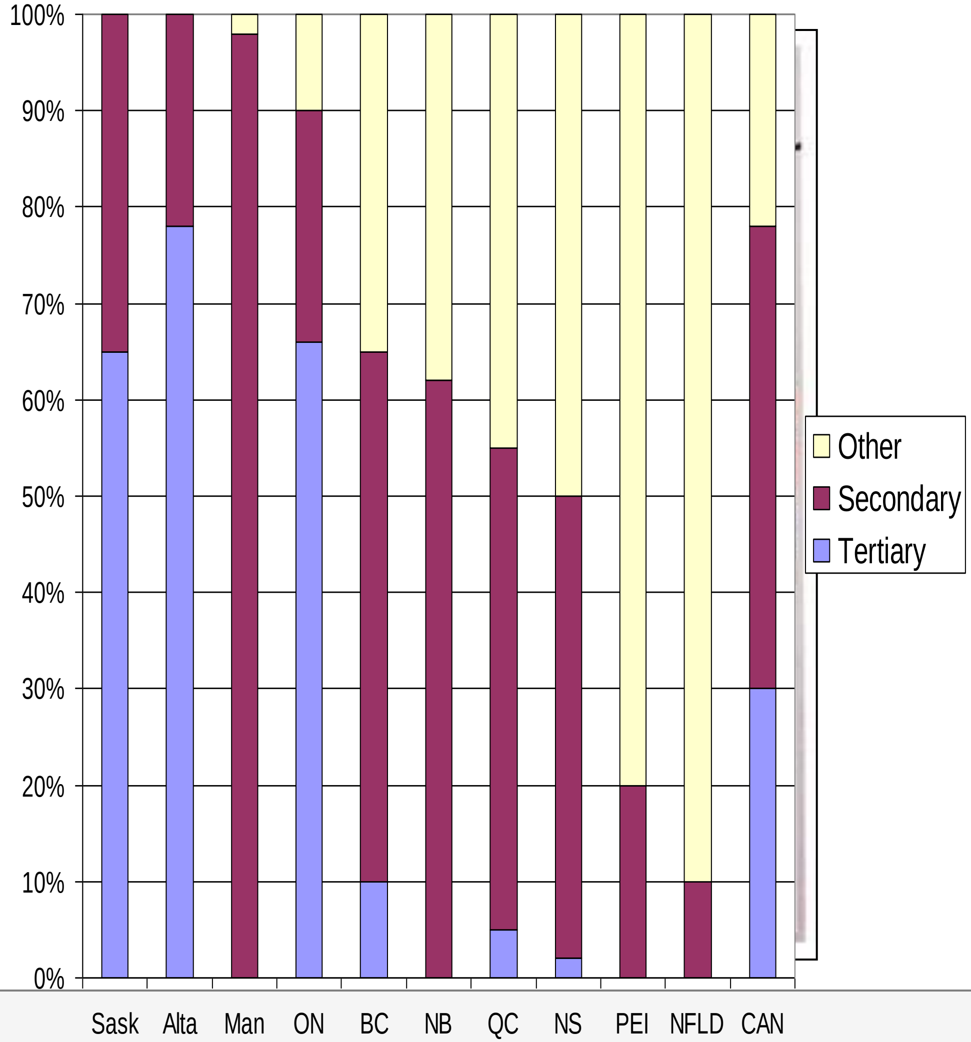
Wastewater Treatment in Canada

<u>**The Good, the Bad and the Ugly:**</u>

- **Treatment technologies vary from primary to secondary (activated sludge most common) to tertiary; lagoons in small municipalities**
- **Nutrient removal not always required**
  - **Many WWTPs are out of compliance for ammonia discharges (>100 ppb)**
  - **Nitrates are typically unregulated**
- **Disinfection systems:**
  - **Chlorination > UV > ozone**
  - **Often seasonal disinfection**



FOCUS OF PRESENTATION:

- Microcontaminants studied in Canada
- Predicting concentrations in wastewater
- Degree of treatment (1^{o}, 2^{o}, 3^{o}), HRT, SRT
- Seasonal variations
- Nitrification and redox conditions
- Treatment lagoons
- Removals by disinfection

Microcontaminants studied in Canada

Pharmaceuticals

- Studied:
  - Analgesics
  - Anti-inflammatories
  - Lipid regulators
  - Beta-blockers
  - Anti-depressants
  - Anti-epileptics
  - Antibiotics
  - Illicit drugs
  - Synthetic hormones
- Not well studied:
  - Antacids and ulcer drugs
  - Anti-asthmatics
  - Anti-anxiety drugs
  - Anti-histamines
  - Anti-neoplastics
  - X-ray contrast agents

Personal care & industrial products:

- Studied:
  - Synthetic musks
  - Antibacterials
  - Alkylphenols
  - Bisphenol A
  - Perfluorinated compounds
  - PBDEs
- Not well studied:
  - UV-stabilizers and plastic additives
  - Fragrances
  - Parabens
  - Dandruff control agents
  - Alternative brominated flame retardants
  - Nanomaterials

PECs in untreated wastewater

Data on pharmaceuticals are available (for a price) from IMS Health:

<u>Example:</u>

Venlafaxine dispensed in 2007	= 22,186 kg
Excretion in urine (% of dose):	
Venlafaxine	= 5%
O-Desmethyl venlafaxine	= 9.8%
$PEC_{WWTP\ in}$:	
Venlafaxine	= 1.69 ug/L
O-desmethyl venlafaxine	= 9.83 ug/L
$MEC_{WWTP\ in}$ =	
Venlafaxine	= 1.12 ug/L
O-desmethylvenlafaxine	= 2.60 ug/L

Data on imports of commercial products are compiled by Environment Canada:

<u>Example:</u>

Triclosan imports into Canada in 2004 = 54,287 kg

$PEC_{WWTP\ in}$	= 2.3 ug/L
$MEC_{WWTP\ in}$	= 1.2 – 4.4 ug/L

from A. Alder, EAWAG

Need <u>more</u> data to predict effluent concentrations !

PECWWTPout = Predicted concentration in the treated WWTP effluent [ng L-1]

PECWWTPin = Predicted concentration in the raw sewage [ng L-1]

Conjcleavage = Concentration of conjugated compounds in the WWTP influent that can be retransformed into the original active pharmaceutical ingredient during treatment (e.g. by cleavage) [ng L-1]

Kd = Primary or secondary solids partition coefficient at ambient pH (can be assumed equal for primary and secondary sludge in most cases; see below) [L g SS-1]

SP = Specific primary or secondary sludge production per amount of wastewater treated, including primary and secondary sludge [g SS L-1]

kbiol = degradation rate constant [L g SS-1 d-1]

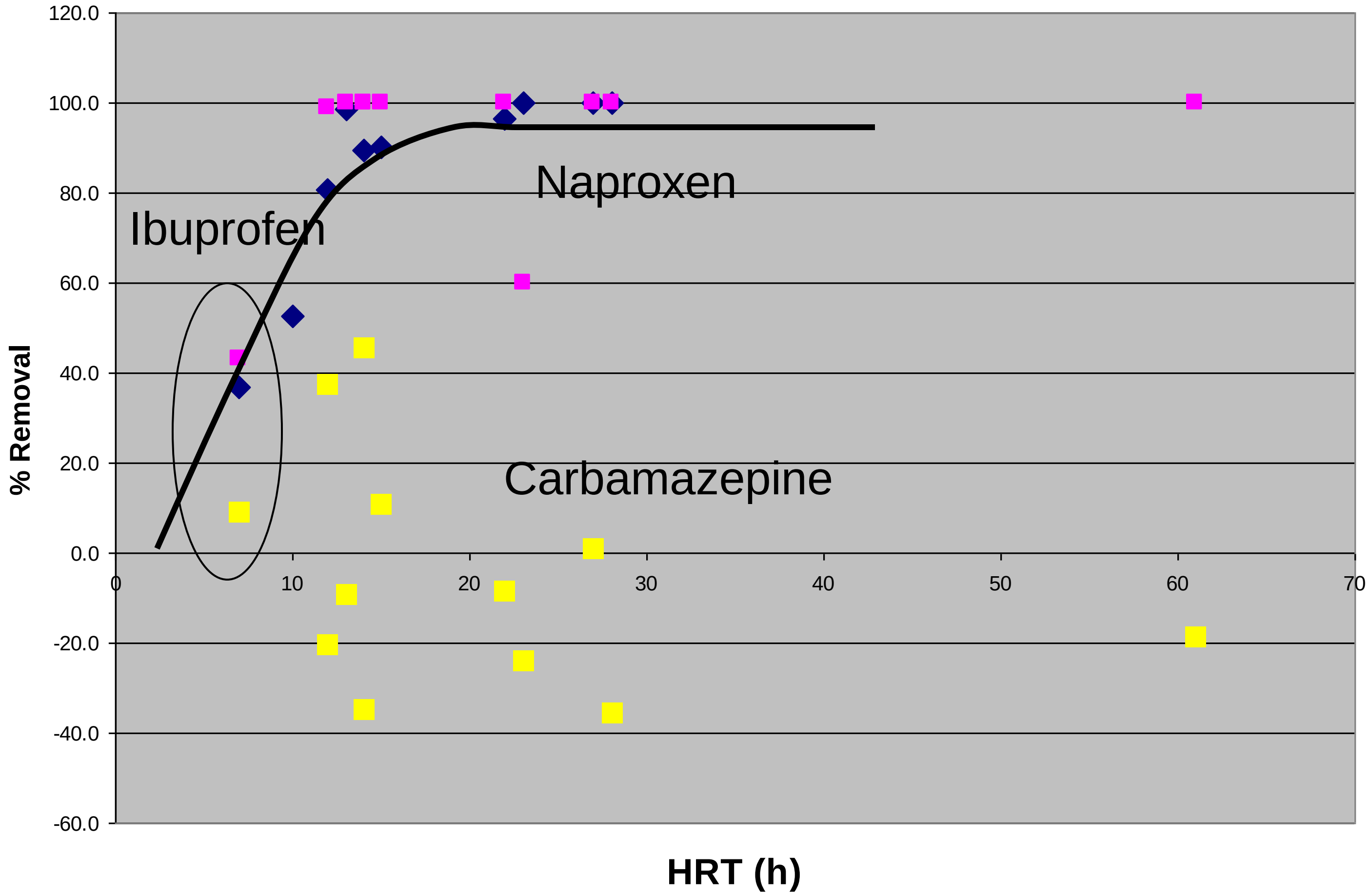
XSS = suspended solids concentration in the reactor [g SS L-1]

Θ = hydraulic retention time of the wastewater in the biological reactor [d]

KH = Henry Law coefficient (dimensionless gas water partitioning coefficient) [-]

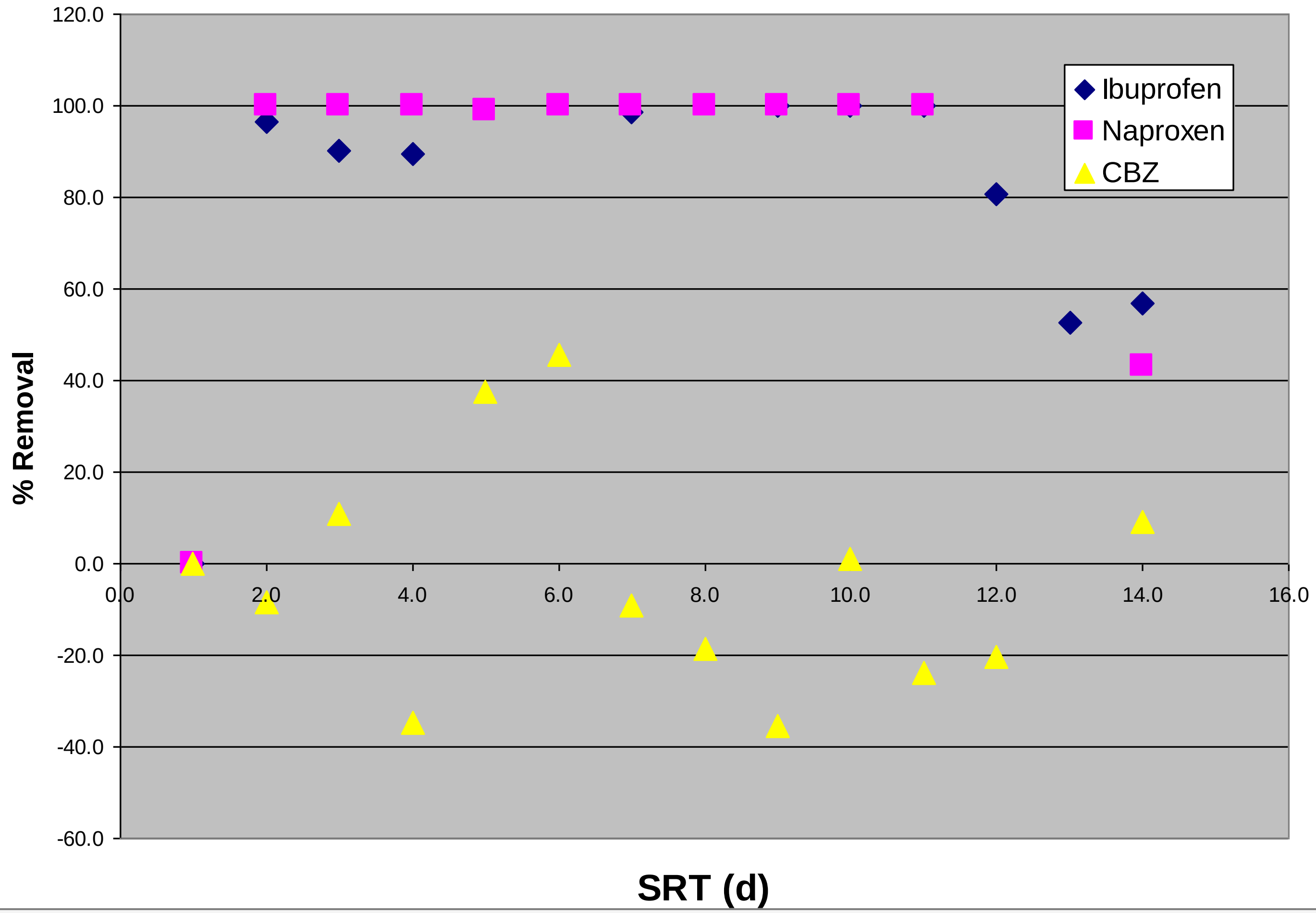
Qair= specific air consumption for aeration [m3air m-3wastewater]

Sewage Treatment and Microcontaminant Removal - HRT



Data from 14 WWTPs (Metcalfe et al. 2003)

Sewage Treatment and Microcontaminant Removal - SRT



Data from 14 WWTPs (Metcalfe et al., 2003)

WWTPs in Region of Waterloo, ON (discharge to Grand River watershed)
D. Andrews, P. Huck, S. Peldszus, C. Metcalfe

Project Objectives

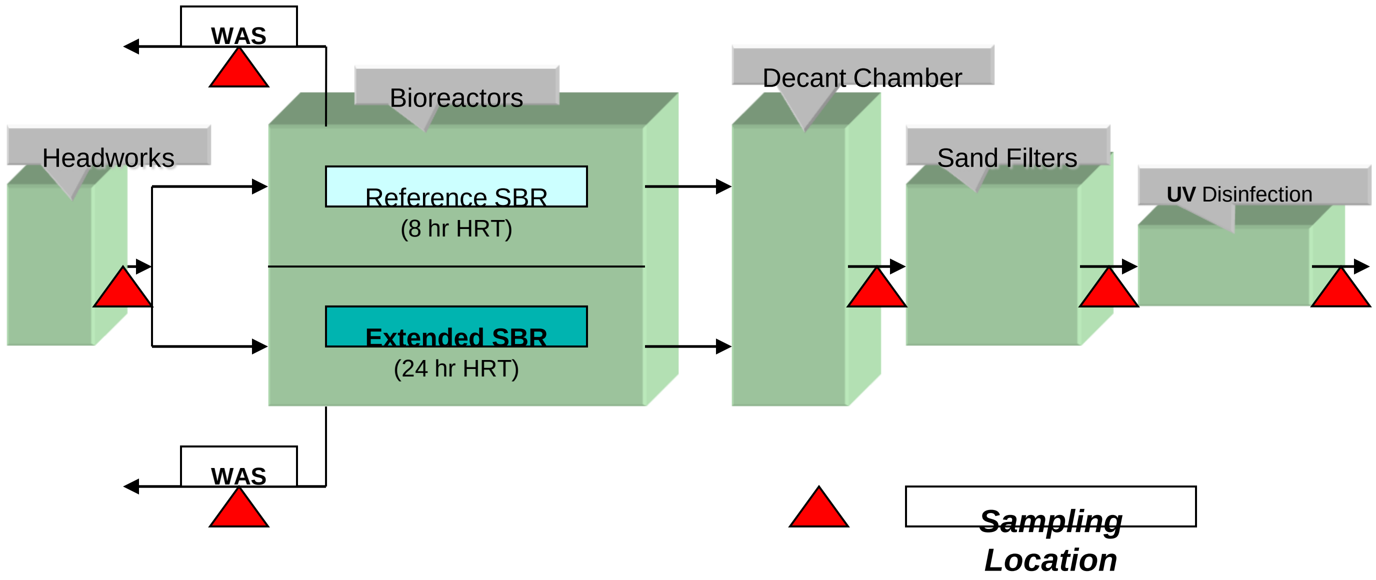
- Identify the impact of HRT, SRT and redox conditions on the removal of a selected PPCPs
- Assess different treatment processes for capacity to remove PPCPs at full scale
- Evaluate the impact of season on PPCP removal
- Sampled 4 WWTPs (2005-08)

Area = 6,965 km2
Population = 925,000
Water availability = 7,025 m^3/capita/yr
23 WWTPs

HRT Investigation

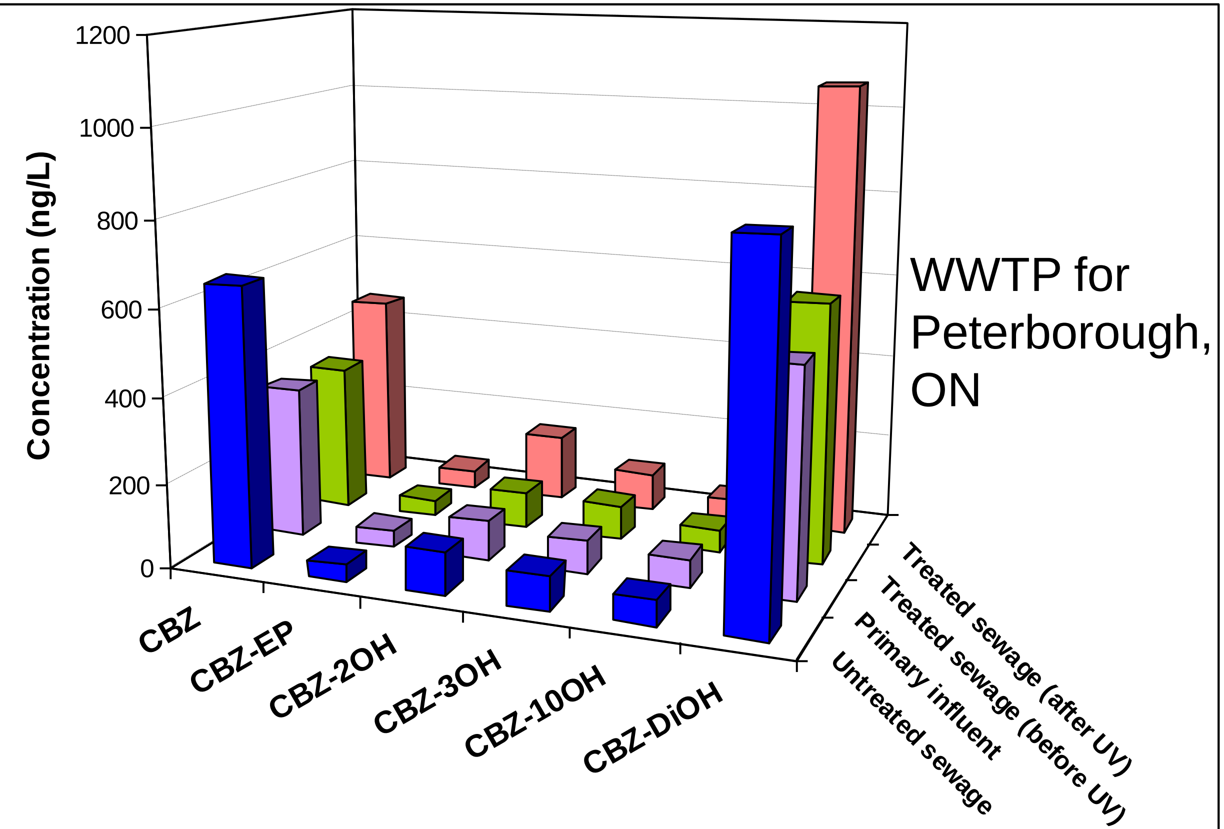
WWTP 1

- Sequencing batch reactor with filtration and UV disinfection
- Two bioreactors in parallel operation
  - 8 hours HRT
  - 24 hours HRT



Conclusions: 1) High HRT increased removals for some PPCPs, but not others 2) Treatment in summer increased removals for some PPCPs

Fate of carbamazepine and metabolites

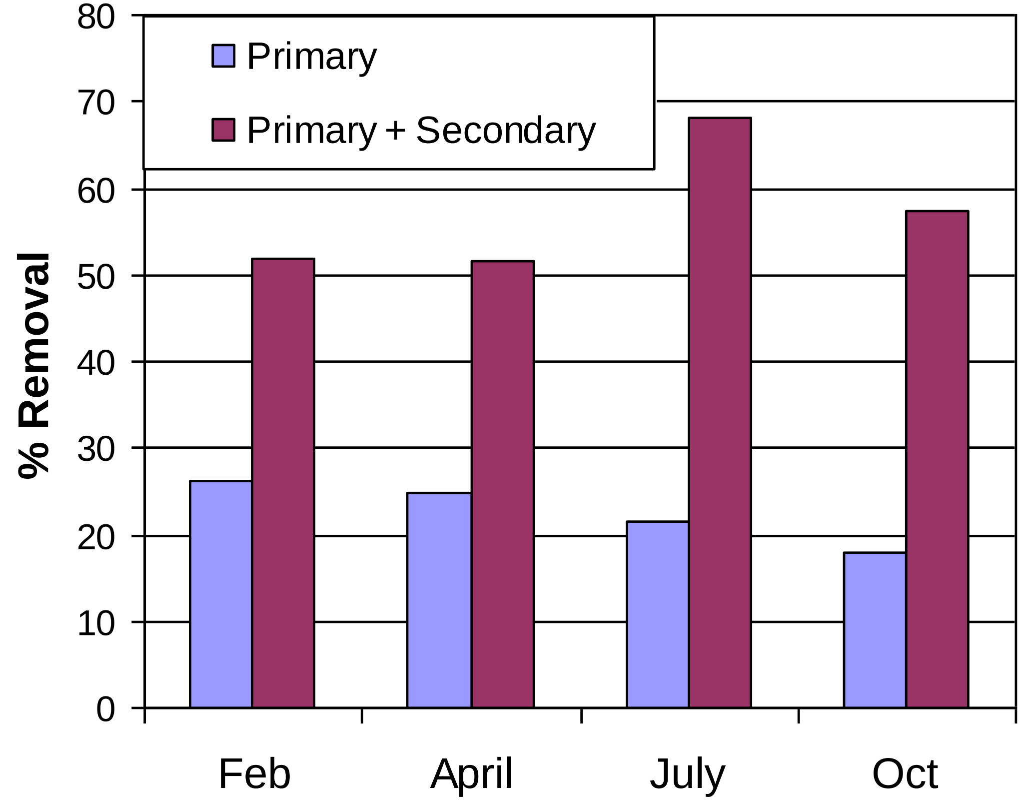


Mean daily inputs = 78.9 g; Mean daily outputs = 91.2 g

Have to consider metabolites, including conjugates

Miao, Yang and Metcalfe (2005)

Effect of season on removal of synthetic musks



Average removals of synthetic musks in WWTP for Peterborough, ON

Yang and Metcalfe (2005)

Effect of season on removal of synthetic musks

Percent removal of synthetic musks

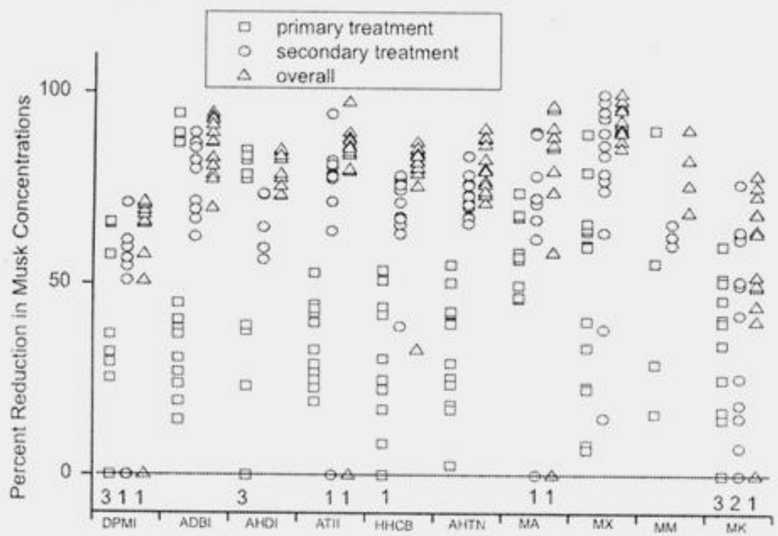


Fig. 4. Percent removal of musks from liquid phase, warm sampling periods. Numbers above each analyte indicate the number of "zero" removal values.

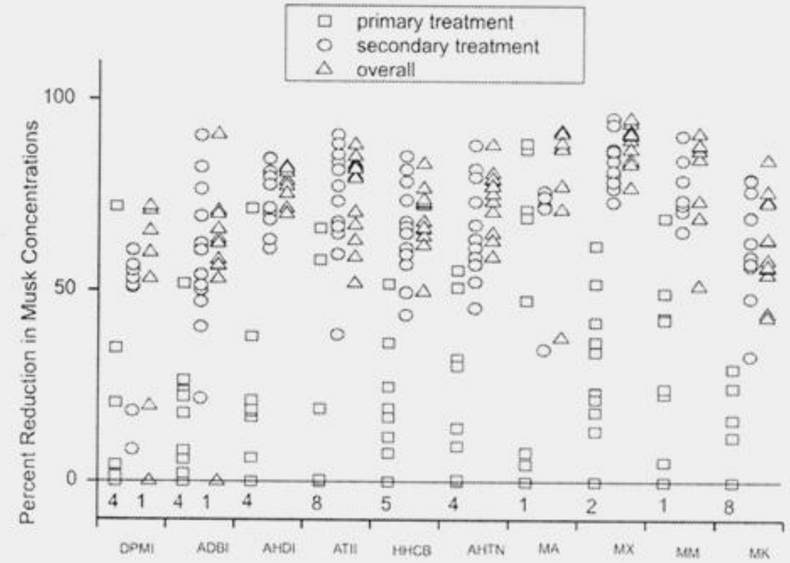


Fig. 5. Percent removal of musks from liquid phase, cold sampling periods. Numbers above each analyte indicate the number of "zero" removal values.

Mean temp = 22^{o}C

Mean temp = 15^{o}C

Study at Burlington, ON WWTP by Smyth et al. (2007)

SRT Investigation

WWTP 2

- Conventional activated sludge with filtration and UV disinfection
- Design capacity – 56,800 m^3 per day
- Two treatment trains in parallel operation
  - 5 day SRT
  - 10 day SRT

Conclusion: SRT did not affect removals of PPCPs.

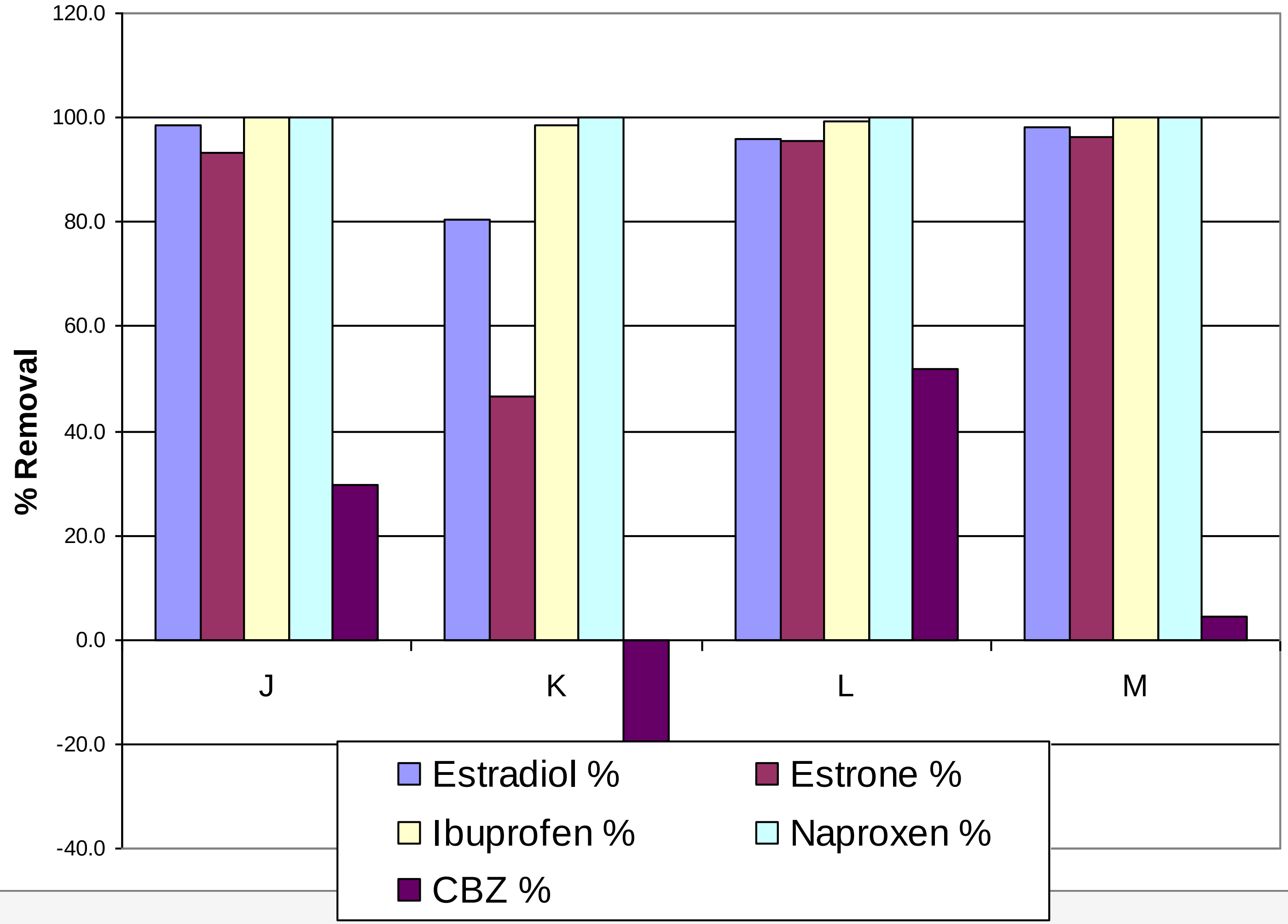
Redox investigation

WWTP 3

- Biological nutrient removal (BNR) with filtration and UV disinfection
- Two bioreactors in parallel operation:
  - anaerobic/anoxic/aerobic (removal of P and N)
  - anoxic/aerobic (removal of N)

Conclusion: Redox conditions affected removals of some PPCPs.

Sewage lagoons



4 lagoons in Ontario:
HRTs >150 h;
Flows = 400 to 2,400 m^3/d;
Pops = 1,600 to 6,500 people

Pharmaceutical data presented in Metcalfe et al. (2003)

Conclusions

- Carbamazepine, some beta-blockers and some antibiotics are poorly removed in WWTPs
  - Must consider fate of metabolites in WWTPs
- Other PPCPs are effectively removed (>90%) by conventional wastewater treatment processes
- However, poor removals in WWTPs with HRTs <15 h
- SRTs do not affect rates of removal
- Redox conditions selected for BNR may affect removals of some PPCPs.
- Season has impact on removals of some PPCPs
- Lagoon systems for small municipalities are just as, or more effective for removal of PPCPs and estrogens

Removals by disinfection processes

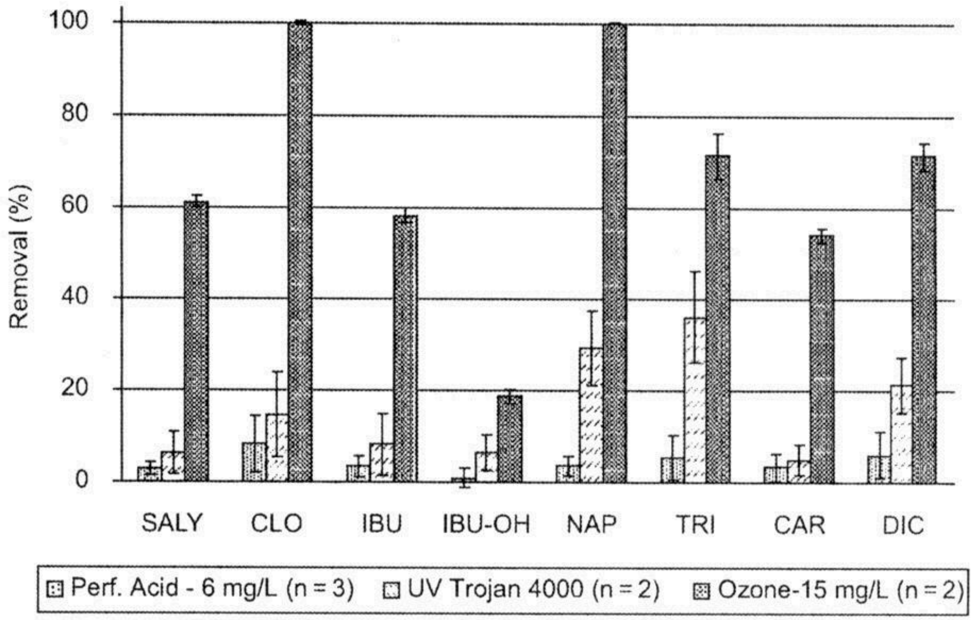


FIGURE 1. Reduction of pharmaceuticals in primary-treated wastewater by different disinfection processes. SALY: salicylic acid; CLO: clofibric acid; IBU: ibuprofen; IBU-OH: 2-hydroxy-ibuprofen; NAP: naproxen; TRI: triclosan; CAR: carbamazepine; DIC: diclofenac.

"Performic acid" = formic acid (55%), H_2O_2 (35%), sulfuric acid (10%)

UV at fluence = 25 mJ per cm^2, MPL

Ozonation = 15 mg/L

Montreal WWTP – pilot scale study by Gagnon et al. (2008)

UV irradiation experiments– Carlson, Stefan and Metcalfe (in prep)

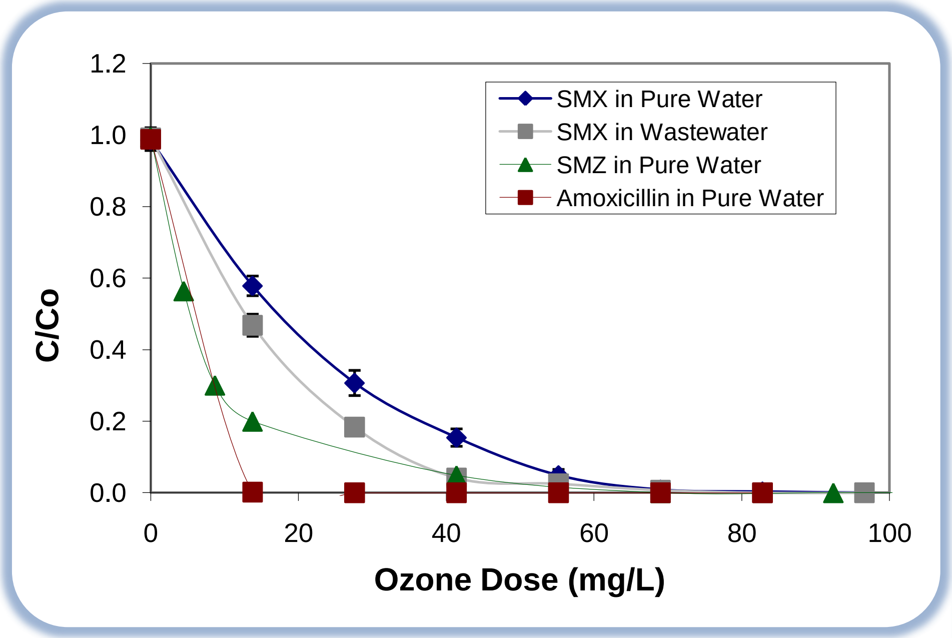
LP

Compound	Fluence Rate Constant x 10^4 cm^2 mJ^{-1}	Percentage Removal at 40 mJ/cm^2	Percentage Removal at 500 mJ/cm^2	Percentage Removal at 2000 mJ/cm^2
Sulphamethoxazole	27.1 ± 2.8	(10.1 ± 1.2) %	(73 ± 4) %	(99 ± 1) %
Sulphachloropyridazine	3.8 ± 0.8	(1.5 ± 0.3) %	(17 ± 3) %	(52 ± 7) %
Nonylphenol	5.1 ± 1.8	(2.0 ± 0.9) %	(22 ± 9) %	(60 ± 17) %
Acetaminophen	1.7 ± 0.9	(0.7 ± 0.3) %	(8.1 ± 3.4) %	(28 ± 10) %
Triclosan	27.6 ± 5.4	(10.4 ± 0.1) %	(75 ± 1) %	(99 ± 1) %

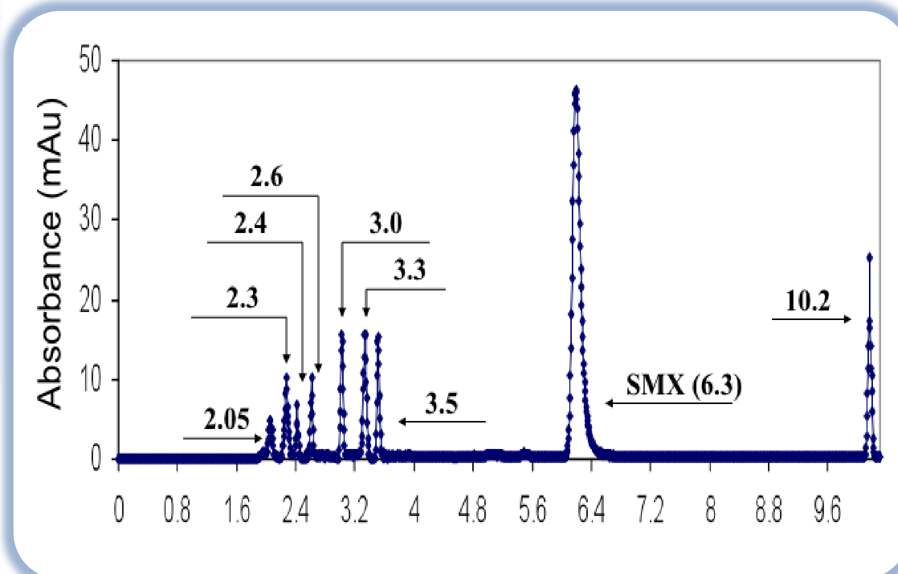
MP

Compound	Fluence Rate Constant x 10^4 cm^2 mJ^{-1}	Percentage Removal at 40 mJ/cm^2	Percentage Removal at 500 mJ/cm^2	Percentage Removal at 2000 mJ/cm^2
Sulphamethoxazole	28.1 ± 2.0	(15.9 ± 9.1) %	(83 ± 13) %	(99.7 ± 0.3) %
Sulphachloropyridazine	8.6 ± 1.3	(3.4 ± 1.0) %	(35 ± 8) %	(81 ± 9) %
Atenolol	4.5 ± 0.6	(1.8 ± 0.4) %	(20 ± 4) %	(59 ± 8) %
Carbamazepine	1.7 ± 0.6	(0.7 ± 0.4) %	(7.9 ± 4.2) %	(27 ± 13) %
Caffeine	1.4 ± 0.7	(0.5 ± 0.2) %	(6.6 ± 2.1) %	(24 ± 7) %
Trimethoprim	1.4 ± 1.5	(0.6 ± 0.2) %	(6.7 ± 2.1) %	(24 ± 7) %
Bisphenol A	2.6 ± 1.7	(1.0 ± 0.2) %	(12 ± 3) %	(40 ± 7) %
Estradiol	5.0 ± 3.4	(2.0 ± 0.1) %	(22 ± 1) %	(63 ± 1) %
Estrone	9.7 ± 4.1	(3.8 ± 1.0) %	(38 ± 8) %	(85 ± 7) %
Ethinylestradiol	3.6 ± 1.4	(1.4 ± 0.2) %	(17 ± 2) %	(52 ± 4) %
Nonylphenol	5.4 ± 1.4	(2.1 ± 0.2) %	(24 ± 2) %	(66 ± 4) %
Acetaminophen	4.7 ± 0.7	(1.9 ± 1.6) %	(20 ± 15) %	(54 ± 27) %
Gemfibrozil	3.3 ± 0.9	(1.3 ± 0.8) %	(15 ± 9) %	(45 ± 24) %
Ibuprofen	7.9 ± 0.7	(3.1 ± 0.1) %	(32.7 ± 0.4) %	(80 ± 1) %
Triclosan	16 ± 16	(6.3 ± 4.6) %	(52 ± 28) %	(89 ± 14) %

Ozonation: Fate of pharmaceuticals



Ozone dose of 55 mg/L

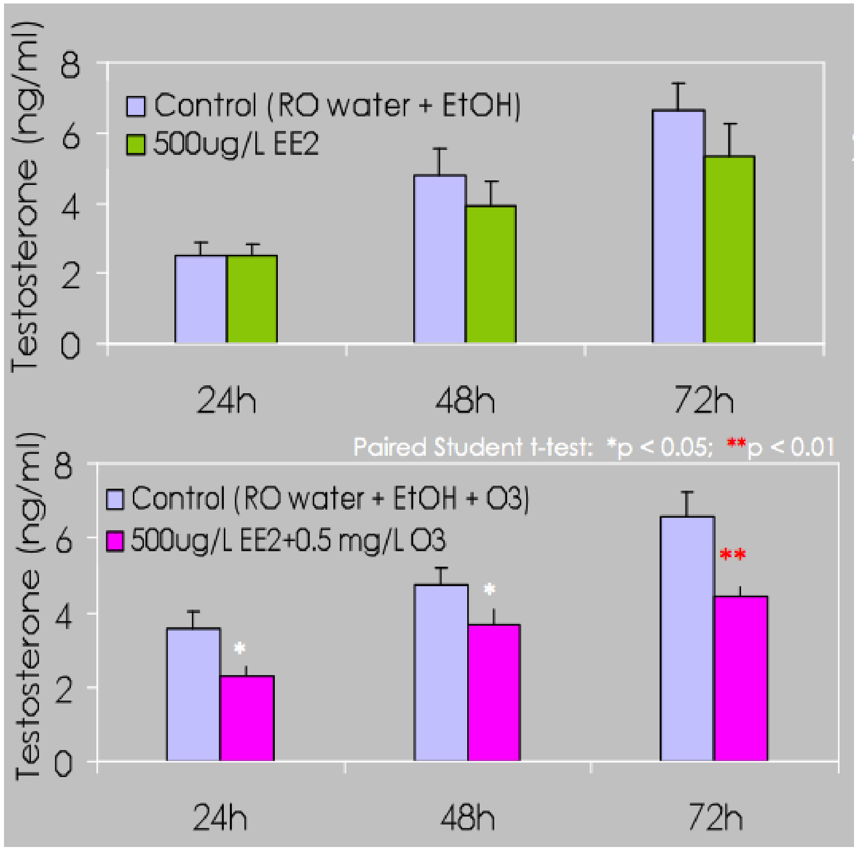


Many transformation products
Low mineralization

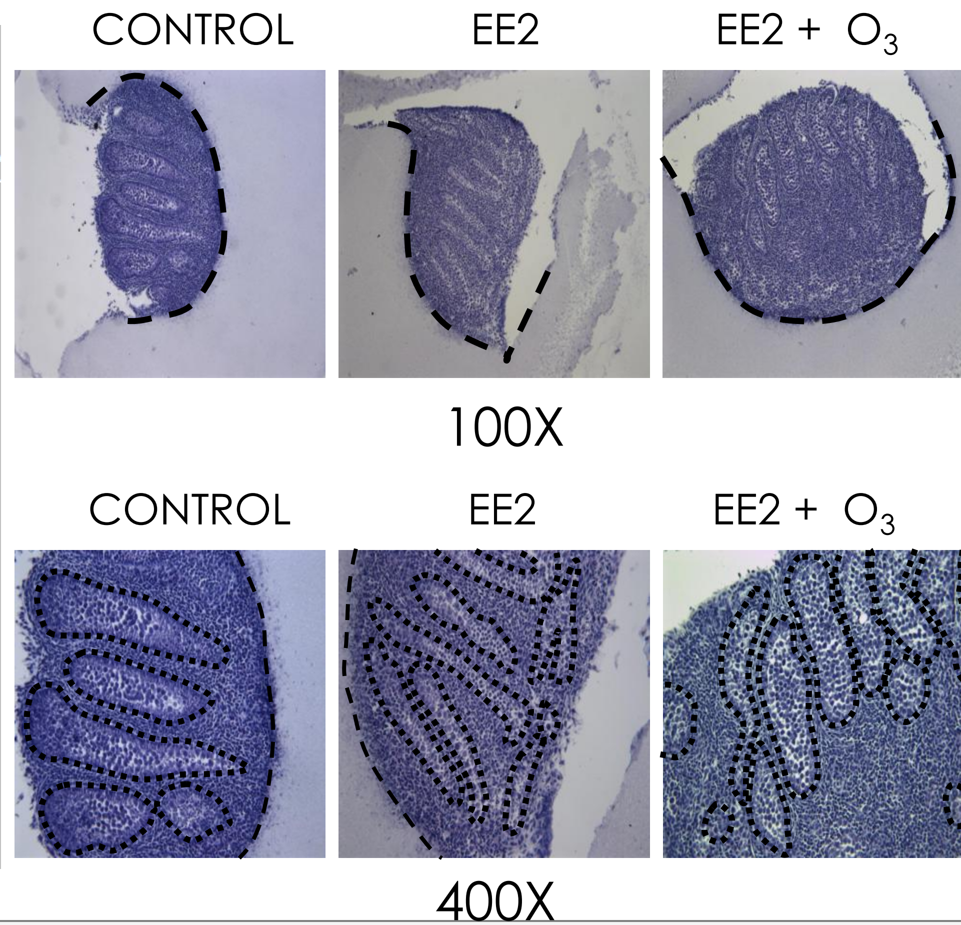
RODAYAN, A., KHAN, S., DANYLO, F., Yargeau et al., unpublished
(data not published)

Effect of EE2 & its O_3 biproducts on rat fetal testis development

Testosterone production



Testicular development



Yargeau et al., unpublished

Conclusions

- UV irradiation is not likely to remove PPCPs from wastewater at the fluences used for disinfection (i.e. <40 mJ/cm^2)
- Disinfection with ozone may have an added benefit of removing PPCPs and other microcontaminants from the wastewater
- However, ozonation may lead to the formation of harmful disinfection biproducts
- Studies are needed in Canada to evaluate the biproducts formed from microcontaminants as a result of disinfection using chlorine or chlorine dioxide (see Lee and Von Gunten, 2009).

Research in Canada on wastewater

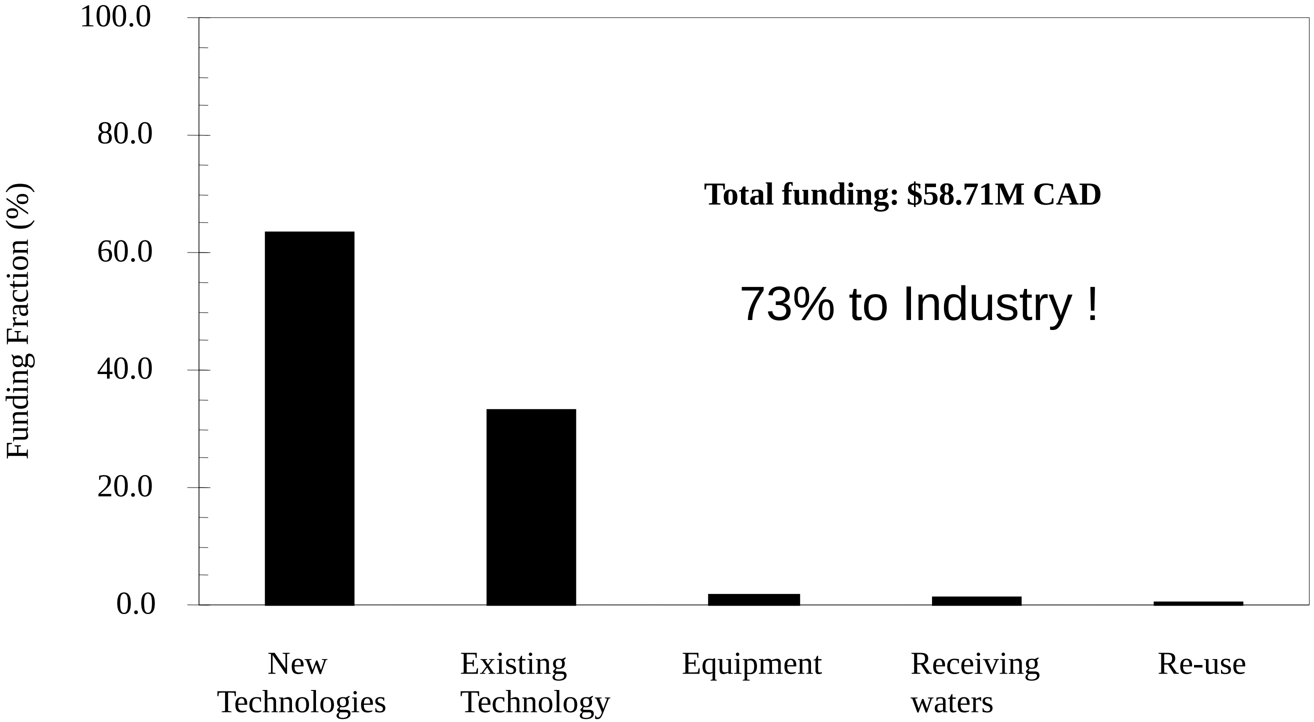


Figure 1: Overview of funded municipal wastewater research conducted in Canada, 1998-2005

Source: Report to CCEM by Gagnon and Metcalfe (2007)

Research in Canada on wastewater

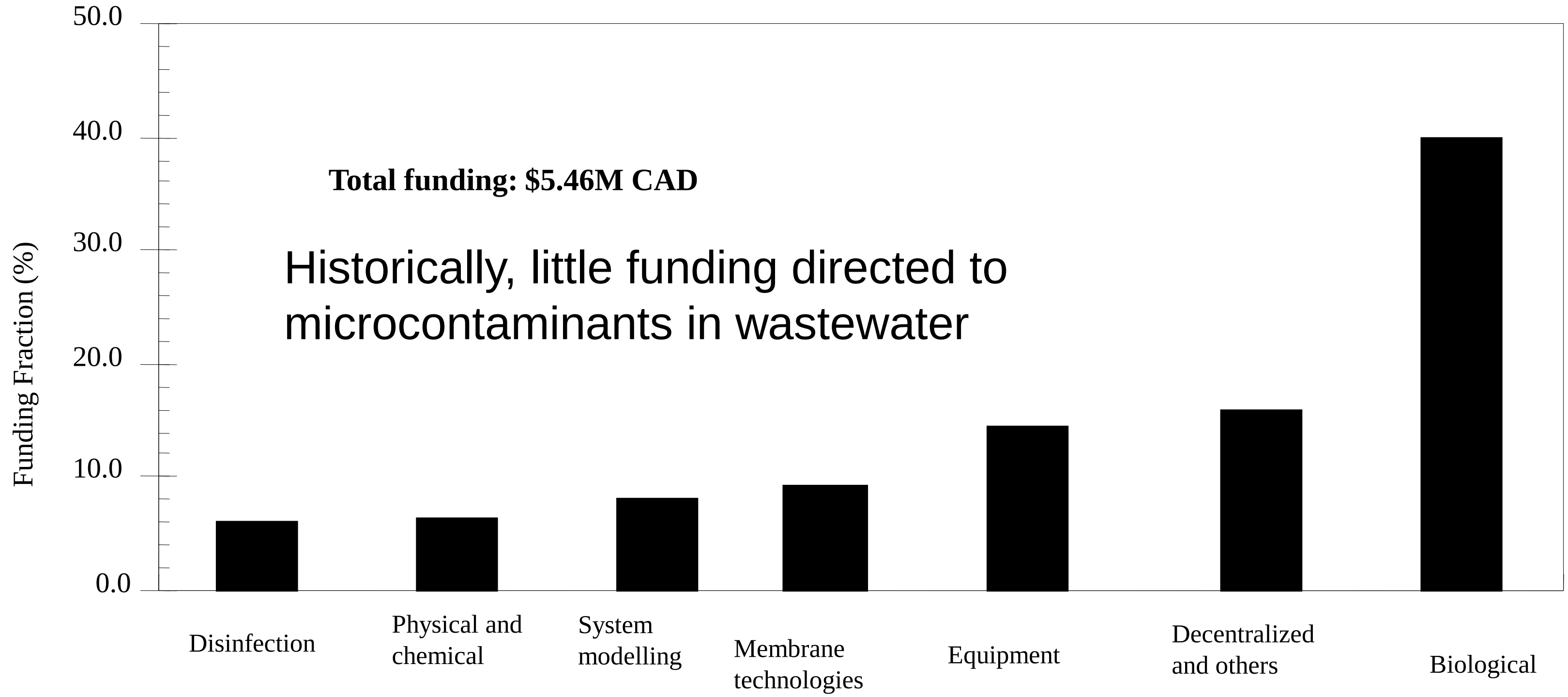


Figure 2: Overview of funded municipal wastewater research conducted by academic and research institutions in Canada, 1998-2005

Source: Report to CCME by Gagnon and Metcalfe (2007)

Research in the EU on wastewater

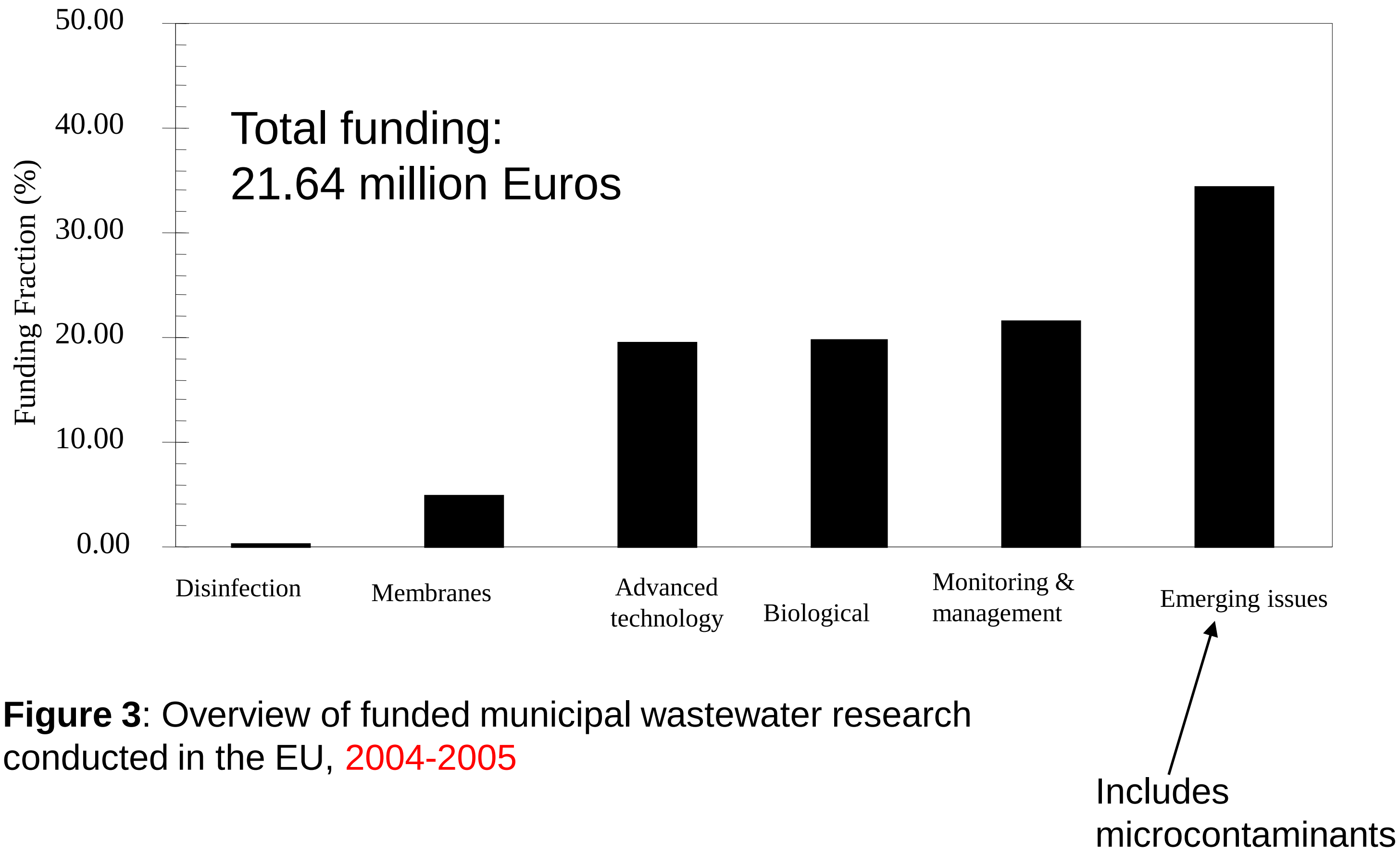


Figure 3: Overview of funded municipal wastewater research conducted in the EU, 2004-2005

Source: Report to CCME by Gagnon and Metcalfe (2007)

Conclusions

- As a result of the report to the CCME and other reports and workshops, there is more support in Canada for research on microcontaminants in wastewater, biosolids, surface waters and drinking water.
- EXAMPLES:
  - CCME funded contract to evaluate microcontaminants in biosolids (Hydromantis); 2009-2010
  - Municipal consortium funded (through CWN) research on microcontaminant removals in WWTPs (Parker and colleagues) and biological impacts downstream of WWTPs (Metcalfe and colleagues); 2010-2013
  - Health Canada contract to survey drinking water for microcontaminants (Servos and colleagues); 2009-2010