An Exploration of Emerging Contaminants in the Chicago Waterways: Ongoing Collaborative Research between EPA and the Metropolitan Water Reclamation District

MWRD Research & Development Seminar
Friday, May 30, 2008

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Acknowledgments

● Other collaborators
  ♦ Tetra Tech – Blaine Snyder and Jennifer Pitt
  ♦ Baylor University
  ♦ Clarkson University, SUNY-Oswego, SUNY-Fredonia
  ♦ Illinois DNR – Rob Miller and Jim Langbein
  ♦ Exelon Corp – John Petro

● Captains of the MWRD PC-1 boat

● MWRD R&D Laboratory staff

● Countless others at MWRD and GLNPO who helped to collect fish and effluent samples
Outline of talk

• Background on emerging chemicals of concern
• Collaborative studies
  - Distribution of Chemical Contaminants within a Large Wastewater Treatment Plant and in Downstream Surface Waters (*Calumet*)
  - Pharmaceuticals and Personal Care Products (PPCPs), Hormones, and Alkylphenol Ethoxylates (APEs) in the North Shore Channel of the Chicago River (*NSC*)
• Conclusions and next steps
An AP Investigation: Pharmaceuticals found in Drinking Water - Headlines

• Pharmaceuticals found in drinking water, affecting wildlife and maybe humans
• Pharmaceuticals found in drinking water of 24 major metro areas, 34 say no testing
• Fish, wildlife affected by drug contamination in water
• No standards to handle pharmaceuticals in water
• Tests of Philadelphia's drinking water reveal 56 drugs
• And many more…

http://hosted.ap.org/specials/interactives/pharma
water_site/index.html
Personal Care Products

Bath additives, shampoos, skin care products, hair sprays, oral hygiene, soaps, detergents

Fragrances

Preservatives

Disinfectants/Antiseptics

Sunscreen Agents

Daughton and Ternes (1999)
What are APEs?

APE = Alkylphenol Ethoxylates (APEs)

- Nonyl & Octyl Phenol Ethoxylates
- High Production Volume Chemical
  - ~ 391.5 million lbs/year NPEs and 77 million lbs/yr OPEs used in North America (U.S. & Canada) in 2003
- Uses - Detergents, wetting agents, dispersants, emulsifiers, solubilizers and foaming agents
- Industrial applications - Pulp and paper, textiles, coatings, agricultural pesticides, lube oils and fuels, metals and plastics
- Chief concern is NP based compounds.
  - OP is also toxic, and more potent ED but only = 10 – 15% of APEs used
Why are PPCPs (including APEs) of concern?

- Produced and used in large volumes
- May be “pseudo-persistent”
  - Chronic exposure
- May have biological effects
  - Therapeutic design
  - Non-target organisms
- May be endocrine disruptors
  - alterations to sexual differentiation
    - Boulder Creek
    - Potomac River
  - reproduction and growth impairments
  - behavioral effects
- Little known about environmental persistence, fate
Distribution Study at the Calumet WRP
Objective of Distribution Study

- Fate of toxic substances throughout a WWTP
  - Solid and hydraulic cycles
- Degree of treatment effectiveness across treatment processes
- 3 sampling events
  - Approximately 11 aqueous and 11 sludge samples per event
  - Between 140 and 300 analytes per sample
  - Over 12,000 data points!
- Strengthen collaborative ventures
Aerated Grit → 1º Settling → Aeration Tanks → 2º Settling → Final Effluent

Raw Influent → 1º Settling

Primary sludge to WAS + Primary Sludge Concentration Tanks

Centrate recycle → 5W

Secondary Digesters

Lagoons

Drying beds

Final Disposal

Calumet
Most action occurs in the aeration tanks!

Nonylphenol Ethoxylates in the Calumet WRP

Concentration (ng/l)

Primary Influent  Primary Effluent  Mixed Liquor  Final Effluent

NP  NP1EO  NP2EO  NP3EO  NP4EO  NP5EO  NP6EO  NP7EO  NP8EO  NP9EO  NP10EO  NP11EO  NP12EO  NP13EO  NP14EO  NP15EO  NP16EO
Nonylphenol Carboxylates in the Calumet WRP
Total NP0-16EO Concentrations (dissolved + particulate) in grab sewer samples (May 2005)
Aeration Tanks are also effective at removing PBTs - due to partitioning

PBDEs in Sludge at CWRP

Increasingly concentrated
Almost 2x increase

Conc (µg/kg dry wt)

1S 2S 3S 4S 11S 5S 10S 6S

BDE-47 BDE-99 BDE-100 BDE-153 BDE-154 BDE-209
Nonylphenol and its Ethoxylates in the Cal-Sag Channel
Downstream Persistence in the Cal-Sag

Concentration (ng/l)

28 km downstream

outfall

Triclosan

Calumet

Bisphenol A
Estrogens in Cal-Sag (August 2005)

km downstream of outfall

concentration, ng/L

-1.5  0  2  10  15.5  22  28

17α-Estradiol  17β-Estradiol  Estrone  17α-Ethinyl estradiol  Estriol
Summary of Calumet Distribution Study

- Sampling is a HUGE challenge
- Low-level analysis in complex matrices is also a HUGE challenge
- Removal mechanisms can be degradation, partitioning, and/or others
  - Consider the by-products and additives!
- Many compounds persist well downstream of outfall
  - What is the significance?
NSC Study Objectives

- Supplemental study to EPA’s National Fish Tissue Study
- Strengthen collaborative ventures
- The main objectives of the supplemental study are to:
  - Determine if there is reproductive impairment to resident fish;
  - Estimate whole fish concentrations of PPCPs, APEs, and hormones; and
  - Document seasonal differences in concentrations of these compounds in effluent, stream, and fish.
  - Identify any correlations between common wastewater treatment plant parameters and APEs/hormones in effluent
Collection Location and Time

NCS Pilot Study

Lake Michigan 9/2006
Braidwood Cooling Pond 3/2007

Nat. Pilot Study

AZ Nov-06
NM Nov-06
FL Oct-06
PA Aug-06
IL Sep-06
TX Oct-06

Study Location
Reference Site
NSC Study Design

- Whole fish collected, processed, and stored from NSC and reference sites in the fall and spring.
- Effluent & Stream samples collected on same day.
  - MWRD (Northside WRP effluent; 2-3/week)
  - U.S. EPA (NSC stream; 1/week)
- Study changes from Fall to Spring
  - St. Cloud State collected additional species to add statistical power
  - Analysis of livers for mRNA vitellogenin - a better indicator of recent exposure to endocrine disruptors
  - Different reference site used
### Chemicals of Concern in Fish

#### EPA Pilot Study
- NP
- m-toluamide
- musk xylene
- octocrylene
- celestolide
- OP
- tonalide
- tricolsan
- 4-methylbenzylidene camphor
- 1,7-dimethylxanthine
- acetaminophen
- atenolol
- caffeine
- cimetidine
- codeine
- carbamazepine
- diltiazem
- diphenylhydramine
- erythromycin
- fluoxetine
- gemfibrozil
- ibuprofen
- lincomycin
- metoprolol
- micronazole
- norfluoxetine
- propranolol
- sertraline
- sulfamethoxazole
- thiabendazole
- trimethoprim
- tylosin
- warfarin
- galaxolide

#### NSC Supp. Study
- NP
- NP1EO
- NP2EO
- NP3EO
- NP4EO
- OP
- OP1EO
- OP2EO
- OP3EO
- OP4EO
- Diethylstilbestrol
- 17α-Estradiol
- 17β-Estradiol
- Estrone
- Mestranol
- Equilenin
- Equilin
- 17β-Ethynyl estradiol
- Estriol
- cis-Androsterone
- Epitestosterone
- Androstenedione
- Dihydrotestosterone
- Testosterone
- 11-Ketotestosterone
- 19-Norethindrone
- Progesterone
- 3β-Coprostanol
- Cholesterol
- and ~75 OWCs
- and PCBs, PBDEs, Hg, organochlorine pesticides
Water analyzed by a variety of labs

- USGS (CO) (75 organic wastewater contaminants, 34 pharmaceuticals, and 20 hormones)
- MWRD (General chemical parameters of plant effluent)
- U.S. EPA, ORD – NERL (56 pharmaceuticals and metabolites in 2007)
- U.S. EPA, ORD – NRMRL (8 hormones in 2007)
- U.S. EPA, Chicago Regional Laboratory (APEs)
# Estrogenic Effects on Fish
## Fall 2006

<table>
<thead>
<tr>
<th></th>
<th>North Shore Channel</th>
<th>Outer Chicago Harbor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immature fish (w/ VTG)</td>
<td>4 (0%)</td>
<td>0 (0%)</td>
</tr>
<tr>
<td>Male fish (w/ VTG)</td>
<td>5 (60%)</td>
<td>4 (0%)</td>
</tr>
<tr>
<td>Female fish (w/ VTG)</td>
<td>3 (100%)</td>
<td>5 (100%)</td>
</tr>
<tr>
<td><strong>Total Fish</strong></td>
<td><strong>12</strong></td>
<td><strong>9</strong></td>
</tr>
</tbody>
</table>

( ) = % fish expressing VTG

*Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN*
<table>
<thead>
<tr>
<th></th>
<th>North Shore Channel</th>
<th>Braidwood Cooling Pond</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Large Mouth Bass</td>
<td>Common Carp</td>
</tr>
<tr>
<td>Male fish (w/ VTG)</td>
<td>1 (3.3)</td>
<td>9 (38±17)</td>
</tr>
<tr>
<td>Female fish (W/VTG)</td>
<td>8 (7±1.8)</td>
<td>5 (38900±9334)</td>
</tr>
<tr>
<td>Total Fish</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Large Mouth Bass</td>
<td>Common Carp</td>
</tr>
<tr>
<td></td>
<td>8 (0.08±05)</td>
<td>11 (29±12)</td>
</tr>
<tr>
<td></td>
<td>4 (9.3±5.1)</td>
<td>2 (48350±31950)</td>
</tr>
</tbody>
</table>

\((\mu g/mL)\) VTG expressed ± standard error

*Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN*
Estrogenic Effects on Fish  
Spring 2007

- High plasma [VTG] in most female fish, as to be expected.
- NSC and Braidwood male LMB cannot be compared for VTG analysis.
- Male carp did not exhibit clear trends.
- [VTG] comparable in several males at both sites.
- No gross abnormalities of testes or livers
- No intersex or other severe pathological conditions were found at either site.
- NSC fish exhibited greater amounts of fatty tissue in the liver than Braidwood site.
- Males at the cooling pond site were generally in an earlier spermatogenic stage than males at the NSC site.
**Histopathology - Liver**

**Fall**
- No clear pattern between males and females or b/w VTG males and those without VTG
- 76% of mature fish displayed brown inclusions
- 25% NSC (2 of 8) & 11% LM (1 of 9) contained cysts in livers consistent with parasite infection

**Spring**

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**NSC LMB**

**Pollutant exposure**

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**Braidwood LMB**

**Healthy**

*Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN*
Fall

• No observable trends between study sites
• All female LMB contained all stages of oogenesis in ovaries
• All male LMB exhibited all stages of spermatogenesis
• Greater abundance of connective tissue in testis of male LMB from NSC
• No ovate testis observed in any fish

Spring

NSC Carp

Typical Carp Testis Healthy

Braidwood LMB

LMB testis, recently spawned

*Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN*
APEs in NSC Large Mouth Bass

Fall 2006

Spring 2007

Concentration (ng/g)

NP NP1EO NP2EO NP3EO NP4EO NP NP1EO NP2EO NP3EO NP4EO

*Clifford P. Rice, Nuria Lozano, Agricultural Research Service, USDA, Beltsville, MD
VTG vs. NP in Large Mouth Bass

**Female Fish in NSC**

![Graph showing the relationship between VTG (ug/mL) and NP (ng/g) for female fish in NSC. The equation is y = -0.014x + 8.0903, with R² = 0.572.]

**Male Fish in Ref. Site and NSC**

![Graph showing the relationship between VTG (ug/mL) and NP (ng/g) for male fish in the Ref. Site and NSC. The equation is y = 0.0159x - 0.2559, with R² = 0.8975.]

**Correlation Coefficient**

- Female Fish in NSC: -0.3964
- Male Fish in Ref. Site and NSC: 0.9474

*Clifford P. Rice, Nuria Lozano, Agricultural Research Service, USDA, Beltsville, MD & Lawrence Zintek, Chicago Regional Laboratory, USEPA, Chicago, IL*
Percent of APEs Detected

Analyzed for:
BPA, NP, NP1EO-NP18EO, NP1EC, NP2EC, OP, OP2EO-OP12EO

<table>
<thead>
<tr>
<th>Analyte</th>
<th>% Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>75.61%</td>
</tr>
<tr>
<td>NP1EO</td>
<td>86.54%</td>
</tr>
<tr>
<td>NP2EO</td>
<td>69.23%</td>
</tr>
<tr>
<td>NP3EO</td>
<td>50.00%</td>
</tr>
<tr>
<td>NP</td>
<td>76.92%</td>
</tr>
<tr>
<td>OP</td>
<td>53.85%</td>
</tr>
<tr>
<td>NP1EC</td>
<td>50.00%</td>
</tr>
<tr>
<td>NP2EC</td>
<td>73.08%</td>
</tr>
</tbody>
</table>
Attenuation

Effluent Sample
Stream Sample
Seasonality of Observed NPE Concentrations

- Conc. ↑ as temps. ↓
- NP levels below toxicity based criteria for aquatic life
Seasonality of NPEC Concentrations

Concentration (ng/L)

Date

Effluent Temperature (C)

Spring

Fall

Effluent Temperature (C)

Concentration (ng/L)

0 5,000 10,000 15,000 20,000 25,000 30,000 35,000 40,000 45,000 50,000

0 5 10 15 20 25

09/14/06 09/20/06 09/26/06 10/04/06 10/10/06 10/16/06 10/24/06 03/02/07 03/12/07 03/20/07 03/28/07 04/05/07 04/13/07 04/23/07

0

NP1EC NP2EC Temperature
### Correlation with Temperature

The graph shows the correlation between Concentration (ng/L) and Temperature (°C) for three different compounds: NP1EO, NP2EO, and NP.

- **NP1EO**:
  - Linear equation: $y = mx + b$
  - Correlation coefficient: $R^2 = 0.705$

- **NP2EO**:
  - Linear equation: $y = mx + b$
  - Correlation coefficient: $R^2 = 0.3863$

- **NP**:
  - Linear equation: $y = mx + b$
  - Correlation coefficient: $R^2 = 0.7511$

The graph includes points for each concentration level (10,000, 12,000, 6,000, 8,000, 7.5, 9.5, 11.5, 13.5, 15.5, 17.5, 19.5, 21.5) and temperature range (7.5 to 21.5 °C). The data points for each compound are indicated by different markers (NP1EO: pink squares, NP2EO: yellow diamonds, NP: blue triangles).
# Pharmaceuticals Present at...

<table>
<thead>
<tr>
<th>High ppt to ppb levels (&lt; 500 ng/L)</th>
<th>Low ppt levels (&lt;100 ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>lisinopril</td>
<td>amphetamine</td>
</tr>
<tr>
<td>valsartan</td>
<td>hydrocodone</td>
</tr>
<tr>
<td>hydrochlorothiazide</td>
<td>triamterene</td>
</tr>
<tr>
<td>ibuprofen-2-hydroxy</td>
<td>enaliprilat</td>
</tr>
<tr>
<td>gemfibrozil</td>
<td>enalipril</td>
</tr>
<tr>
<td></td>
<td>propanolol</td>
</tr>
<tr>
<td></td>
<td>diltiazem-desmethyl</td>
</tr>
<tr>
<td></td>
<td>verapamil</td>
</tr>
<tr>
<td></td>
<td>norverapamil</td>
</tr>
<tr>
<td></td>
<td>amlodipine</td>
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<tr>
<td></td>
<td>sulfamethoxazole</td>
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<tr>
<td></td>
<td>promethazine</td>
</tr>
<tr>
<td></td>
<td>paroxetine</td>
</tr>
<tr>
<td></td>
<td>amitriptyline</td>
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<tr>
<td></td>
<td>benztropine</td>
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<tr>
<td></td>
<td>norfluoxetine</td>
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<tr>
<td></td>
<td>fluoxetine</td>
</tr>
<tr>
<td></td>
<td>sertraline-desmethyl</td>
</tr>
<tr>
<td></td>
<td>sertraline</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mid ppt levels (100 - 500 ng/L)</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>atenolol</td>
<td></td>
</tr>
<tr>
<td>metoprolol</td>
<td></td>
</tr>
<tr>
<td>diltiazem</td>
<td></td>
</tr>
<tr>
<td>furosemide</td>
<td></td>
</tr>
<tr>
<td>ciprofloxacin</td>
<td></td>
</tr>
<tr>
<td>carbamazepine</td>
<td></td>
</tr>
<tr>
<td>trimethoprim</td>
<td></td>
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<tr>
<td>ibuprofen</td>
<td></td>
</tr>
</tbody>
</table>
## Pharmaceutical Chemicals Detected in EPA Pilot Study & Fillet and Liver Tissue from NSC

<table>
<thead>
<tr>
<th>Detected Chemicals &amp; Method Detection Limits (MDLs)</th>
<th>Use</th>
<th>National Composites with Detection (N=30)</th>
<th>Detections in NSC (N=6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fillet</td>
<td>Liver</td>
</tr>
<tr>
<td>Carbamazepine (1.86 ppb)</td>
<td>Anti-seizure</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Diltiazem (0.26ppb)</td>
<td>Anti-hypertension</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>Diphenylidyramine (0.26ppb)</td>
<td>Antihistimine</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>Fluoxetine (12.41ppb)</td>
<td>Antidepressant</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Gemfibrozil (24.82ppb)</td>
<td>Antilipemic</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Norfluoxetine (15.31ppb)</td>
<td>Fluoxetine metabolite</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>Sertaline (17.29ppb)</td>
<td>Antidepressant</td>
<td>12</td>
<td>23</td>
</tr>
</tbody>
</table>

*Leanne Stahl, Office of Water, USEPA, Washington DC, USA*
Levels of E1 and E2 in stream >> levels in effluent

Additional explanations:
- Conversion of E2 to E1 in environment
- Stream redox conditions
- Sediment resuspension source
- Combined Sewer Overflows (CSOs)

* - below reporting limit of 2 ng/L
Correlation Between Hormones and Ammonia

- E2 and NH3
- TEST and NH3
- E1 and NH3
- Linear (E1 and NH3)
- Linear (TEST and NH3)
- Linear (E2 and NH3)

R² = 0.3473

R² = 0.3098

R² = 0.6283
Some male fish do have measurable levels of VTG, but no intersex or other severe pathological conditions at either site.

- Loose correlation between APEs concentration and VTG levels in fish.

Significance of sampling timing and duration

- Observed concentrations in fish and effluent correlated with effluent temperature and other wastewater treatment parameters

Analytical capabilities and reporting limits a work in progress

- Many compounds often below MDLs or RLs

Effluent (and therefore streams) contain a wide mixture of compounds

- Persistent exposure to aquatic life

Other possible sources

Emerging concern that we’ve just begun to investigate
Next Steps

- Collaboration is **KEY**!
- Publication on various pieces of the project
  - Estrogenic effects
  - Seasonality of fish tissue and effluent concentrations
- Much more data to come
  - Hormones in fish
  - PPCPs fish
    - National Pilot Study
    - Fall and Spring fish samples
  - Legacy contaminants (that are suspected EDs) in fish
  - Pharms, OWCs, and extended hormone list in effluent and stream
Questions?

Thank You!
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