Pharmaceuticals and Personal Care Products (PPCPs), Hormones, and Alkylphenol Ethoxylates (APEs) in the North Shore Channel of the Chicago River

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Todd Nettesheim, Elizabeth Murphy, Great Lakes National Program Office, USEPA, Chicago, IL
Lawrence Zintek, Chicago Regional Laboratory, USEPA, Chicago, IL
Clifford P. Rice, Nuria Lozano, Agricultural Research Service, USDA, Beltsville, MD
Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN
James M. Lazorchak, Angela L. Batt, Marc A. Mills, USEPA ORD, Cincinnati, OH
Larry B. Barber, James L. Gray, USGS, Boulder, CO
David Lordi, Sam Dennison, Tom Minarik, Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL
Acknowledgements

● Other collaborators
  ◆ USGS National Water Quality Laboratory in Golden, CO
  ◆ U.S. EPA Office of Water – John Wathen and Leanne Stahl
  ◆ 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 who helped to collect fish and effluent samples
Things I plan to talk about...

- Objectives of study
- Study location
- Study design
- Preliminary results
Objectives of Study

● Supplemental study to EPA’s National Fish Tissue Study

● The four main objectives of the supplemental study are to:
  ■ Determine if there is reproductive impairment to resident fish;
  ■ Estimate effluent and stream concentrations of PPCPs, APEs, hormones, and general chemistry
  ■ Estimate whole fish concentrations of PPCPs, APEs, and hormones; and
  ■ Document seasonal differences in concentrations of these compounds in effluent, stream, and fish.

● Strengthen collaborative ventures
Things I plan to talk about...

- Objectives of study
- Study location
**North Side WRP**
- 333 MGD
- Serves 1.3 million people
- Secondary treatment
- Sludge pumped to another WRP

**North Shore Channel**
- Man-made (early 1900s)
- Effluent dominated
- Recreational fishery
Things I plan to talk about...

- Objectives of study
- Study location
- Study design
Study Design – Objective 1

- **Determine reproductive impairment**
  - Analyze fish blood for vitellogenin (vtg)
  - Perform mRNA analyses for vtg in livers
  - Examine livers for abnormalities
  - Examine fish gonads for imposex and abnormalities (histopathology)
  - Examine fish brains for abnormalities

- **Large mouth bass and common carp**
  - Sexually mature fish

- **Local reference sites analyzed for control**
  - Lake Michigan and Braidwood cooling pond

- **Collaborative partners**
  - St. Cloud State University
  - ORD Cincinnati
Study Design – Objective 2

- Estimate effluent and stream concentrations of PPCPs and Hormones
  - **USGS Boulder and Golden, CO, Labs** – Conduct weekly analysis of stream and effluent samples using OWC 1433 (75 organic waste water contaminants including some personal care products); Pharma 9003 (34 prescription and non-prescription drugs); and hormones method (20 natural and synthetic sex hormones)
  - **EPA ORD NERL** – Conduct weekly analysis of stream and effluent samples for 56 pharmaceuticals and metabolites using SPE and UPLC/MS/MS (Sprng only)
  - **EPA ORD NRMRL** – Conduct weekly analysis of stream and effluent samples for 8 hormones using SPE and GC/MS (Spring only)
Study Design – Objective 2 (cont.)

- Estimate effluent and stream concentrations of APEs and general chemistry
  - EPA Central Regional Laboratory (CRL) – Analyze of 2-3 effluent samples per week and weekly stream samples for long chain APEOs (NP3-18EO and OP2-12EO) and NP1EC and NP2EC using direct injection LC/MS; and NP, NP1EO, NP2EO, OP, and BPA using CLLE and GC/MS.

- MWRD – Analyze 2-3 effluent samples per week and a stream sample for general chemical parameters (e.g. N-NH3, BOD, SS, etc.)
Objective 3

- Estimate whole fish concentrations of PPCPs, APEs, and hormones (sexually mature fish)
  - **USDA** - Conduct analyses on whole fish homogenates and fillet tissue for alkylphenols and alkylphenol ethoxylates (NP, NP1-4EO, OP, OP1-4EO).
    - 6 large mouth bass from NSC and 3 large mouth bass from reference site
    - 3 fillet composite samples from National Fish Tissue study
    - 3 small mouth bass from national reference location (New Mexico)
  - **USGS** - Conduct analysis of whole fish homogenates using OWC 1433 (75 organic waste water contaminants including some personal care products) and hormones method (20 natural and synthetic sex hormones)
    - 3 large mouth bass from NSC and 3 large mouth bass from reference site
  - **Clarkson University** - Conduct analysis of whole fish homogenates for PCBs, OC pesticides, BFRs, Hg, and dioxins.
    - 6 large mouth bass from NSC and 3 large mouth bass from reference site
Study Design – Objective 4

- Document seasonal differences in concentrations of these compounds in effluent, stream, and fish.
  - Fall 2006 campaign
    - Effluent and stream samples collected from September to October
    - 24 large mouth bass collected for National Fish Tissue study
    - 12 large mouth bass collected for this study
    - 9 large mouth bass collected from local reference site (Lk Michigan)
  - Spring 2007 campaign
    - Effluent & stream samples collected from February to April
    - 24 large mouth bass collected for National Fish Tissue study
    - 9 large mouth bass & 14 common carp collected for this study
    - 12 large mouth bass, 13 carp and 2 catfish from Braidwood
Things I plan to talk about...

- Objectives of study
- Study location
- Study design
- Preliminary results
**Summary of fish sex and occurrence of vitellogenin in Fall 2006**

<table>
<thead>
<tr>
<th>Collection</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</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>
</tbody>
</table>
### Estrogenic Effects on Fish
(values mean ± standard error) Spring 2007

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Largemouth Bass</th>
<th>Common Carp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Effluent Male</td>
<td>Effluent Male</td>
</tr>
<tr>
<td>Sample size</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>Weight (g)</td>
<td>1050 ± 1110</td>
<td>3176 ± 466</td>
</tr>
<tr>
<td>VTG (µg/mL)</td>
<td>3.3 ± 1.8</td>
<td>0.08 ± 0.05</td>
</tr>
</tbody>
</table>
NPEs in Large Mouth Bass

Concentration, ng/l

NP, NP1EO, NP2EO, NP3EO, NP4EO

* Below MDL
Percent Compound Detected
Fall 2006 & Spring 2007 Collections

- NP2EC
- NP1EC
- BPA
- OP
- NP3EO
- NP2EO
- NP1EO
- NP

Percent detected
Stream
Effluent
APEs Concentrations versus Temperature
Fall 2006 & Spring 2007 Collections

$R^2 = 0.8403$

$R^2 = 0.4942$

$R^2 = 0.7681$

Temperature (F)

Concentration (ng/L)

NP
NP1EO
NP2EO
Linear (NP)
Linear (NP2EO)
Linear (NP1EO)
APEs in Northside WRP Effluent and Downstream Channel
Fall 2006 & Spring 2007 Collections

Concentration (ng/L)

NP NP1EO NP2EO NP3EO OP BPA

Effluent Stream
Bioconcentration Factor (BCF) for NPEs

- BCF = Concentration in fish / Concentration in water
  - NP = 130-230
  - NP1EO = 450-630
  - NP2EO = 200-480
  - NP3EO = 40-60

- These values agree quite well with the values published by Mitchelmore and Rice 2006.
  - NP = 280
  - NP1EO = 1713
  - NP2EO = 693
Pharmaceuticals in Effluent and Stream Samples

- atenolol
- clonidine
- oxycodone
- amphetamine
- hydrocodone
- triamterene
- enalaprilat
- metoprolol
- lisinopril
- enalapril
- trametrendil
- hydrocodone
- amphetamine
- oxycodone
- clonidine
- atenolol

% detect
Pharmaceuticals in Effluent and Stream Samples (for those with eyesight worse than 20/10)

Pharmaceuticals present at high ppt to ppb
- Lisinopril
- Valsartan
- Hydrochlorothiazide
- Ibuprofen-2-hydroxy
- Gemfibrozil

Pharmaceuticals present at mid ppt
- Atenolol
- Metoprol
- Diltiazem
- Ciprofloxacin
- Trimethoprim
- Carbamazepine
- Furosemide
- ibuprofen

Pharmaceuticals not detected
- Clonidine
- Oxycodone
- Propoxyphene
- Amitriptyline-10-OH
- Alprazolam
- Liothyronine
- Levothyroxine
- Acetaminophen
- Prednisone, Prednisolone, Betamethasone, Methylprednisolone
- Norethindrone
- Testosterone
- Fluocinonide
- Fluticasone
- Progesterone
- Simvastatin
- Theophylline
- Warfarin
- Glipizide
- Hydrocortisone
- glyburide
Summary and Next Steps

- Collaboration is **KEY**!
- Estrogenic effects present
  - What is the significance?
- Fish tissue concentrations vary along with effluent and stream concentrations
  - Similar BCFs in fall and spring
- Wastewater effluent is a soup of 1000s of compounds
- Much more data to come
  - Hormones is effluent, stream and fish
  - PPCPs in effluent, stream and fish
Thank You!

Todd Nettesheim
U.S. EPA GLNPO
(312) 353-9153
nettesheim.todd@epa.gov