Investigating Treatment Effects on Targeted Endocrine Disrupting Compounds and Pharmaceuticals in Drinking Water

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Partners: EarthTech & 13 Utilities
EDCs and PPCPs

Why study these?
- Direct impacts on ecological health
  - Well documented: feminization of fish, etc.
- Direct impacts on human health
  - Maybe not? Sub therapeutic doses
- Indicators & promoters of antibiotic resistance
- Precursors to more Hazardous DBPs
- Tracers of wastewater contamination
- Public perception
  - Becoming a very sensitive issue
Antibiotic Resistance

- One of the most critical human health challenges of the 21st century (WHO report)
  - >1,000,000 Americans infected each year
  - 14,000 deaths annually
- Cause: antibiotics are everywhere
  - Up to 95% of antibiotics in US are excreted in an unaltered state
  - Over prescription in humans
  - Heavy use in agriculture
- Result: Antibiotic resistant genes (ARGs) are ubiquitous in the aquatic environment
  - e.g., Pruden et al., 2006 [ES&T]
UMass Research Study

- Purpose
- Process
- Any utility can participate
- Outputs
- Schedule
Scope

- Task 1: literature update
- Task 2: Raw Water Occurrence Survey
  - Anonymous: Double Blind design
- Task 3: Site-specific Removal
  - On spiked raw water
    - 3a: Existing treatment
    - 3b: Oxidation: $O_3$, HOCl, NH$_2$Cl
- Task 4: $O_3$/Biofiltration
  - Lab pilot (next slide)
### Selected Compounds

<table>
<thead>
<tr>
<th>EDC</th>
<th>PhAC</th>
<th>WW associated</th>
</tr>
</thead>
<tbody>
<tr>
<td>17(\beta)-estradiol</td>
<td>Atorvastatin or Gemfibrozil</td>
<td>Nitroso-dimethylamine</td>
</tr>
<tr>
<td>Estriol</td>
<td>Naproxen</td>
<td></td>
</tr>
<tr>
<td>Estrone</td>
<td>Sulfamethoxazole</td>
<td></td>
</tr>
<tr>
<td>17(\alpha)-ethinylestradiol</td>
<td>Trimethoprim</td>
<td></td>
</tr>
<tr>
<td>Perchlorate</td>
<td>Atenolol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ranitidine</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Primidone?</td>
<td></td>
</tr>
</tbody>
</table>
Precursors to NDMA??

- NDMA (nitrosodimethylamine) is a very potent probable human carcinogen
- Formation of NDMA from chloramination of dimethylamine (DMA)
  - Not enough DMA to account for anything much
- NDMA formation is much higher in municipal WW than in pristine natural waters
- Major precursor is not natural???
The Unnatural Precursor?

- **Ranitidine (Zantac)**
  - 63% conversion to NDMA
    - Schmidt et al., 2006 [WQTC]
  - Introduced in 1981, largest selling prescription drug by 1988
    - Stomach ulcers and esophageal reflux
  - Mean concentration of 3000 ng/L estimated for raw municipal WW (national average)
    - Sedlak 2005 AWWARF report
  - 450 ng/L formation in raw WW expected
  - Unknowns: how much does this persist in treatment and in the environment?
WW Tracers

- WW contributions: use “conservative” PPCP tracers
  - Primidone
  - Others? Carbamazepine, caffeine, etc.
- Raw vs Treated WW: use PPCPs with unique structural geometry
  - Two “sterioisotopes exist of many pharmaceuticals
  - In some cases only one of the two forms is removed in wastewater treatment
  - Ratio of the two forms tells you if the PPCP came from treated or untreated WW contributions
    - Propranolol example: Fono & Sedlak, 2005 [ES&T]
Experimental Design: Lab Pilot

- Ozone/biofiltration with controls
  - No-\(O_3\)
  - No bio
Pilot Operation

- One year duration
  - 3 months initial acclimation
  - 9 months testing
- Target 10 min EBCT
- Spike raw water with PPCPs
- Run until stable removals under varying conditions
  - Ozone doses
  - Temperatures
  - Others: EBCT, backwash?
Raw Water

Objective
- 1 year supply for pilot; stable & consistent
- Representative of WW impacted river
- Containing organic & inorganic matrix

Blackstone River
- Location: Downstream of the Upper Blackstone WPAD wastewater treatment outfall

Sample treatment
- 1,100 liters collected
- Rotary evaporated to 11,000 mL.
- Brought to dryness in a freeze dryer
- Homogenized and stored in a freezer
Lab Analysis

- Conventional parameters
  - DOC, etc.
- PPCP Analysis
  - LC/MS
    - HPLC or UPLC with triple quadrupole MS; isotope dilution
  - Parent Compound & Daughter Products
- Estrogenic Activity
  - Cell-based reporter assay
    - stably-transfected MCF-7 cell line which produces luciferase
  - Measuring changes in gene expression in the Japanese medaka fish and the fathead minnow
# Utility Participation

<table>
<thead>
<tr>
<th>Participation Level</th>
<th>Contribution</th>
<th>Source Water</th>
<th>After Oxidation (O₃, Cl₂, NH₂Cl)</th>
<th>Bench-scale treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>$12,000</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Silver</td>
<td>$6,000</td>
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<td>X</td>
</tr>
<tr>
<td>Bronze</td>
<td>$3,000</td>
<td>X</td>
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</tbody>
</table>
Cooperative Effort

- State regulators/University/Private
- Focus on emerging contaminants is challenging
Regulatory challenges

- Solicit PWS participation
  - PWS reporting requirements under CCR
- Incentives for water suppliers
  - Sample anonymity
  - New sampling category
- Senior management support
  - Make the case to senior management
Risk Communication

Challenges
- Describing the current state of occurrence
  - Is my water safe?
- What if a chemical is detected without health guidance

Solutions
- PPCP workgroup
- Prepare outreach strategy
  - Mission statement
  - Website
  - Identify and work with stakeholders
PIE Risk Reduction Strategy

MassDEP will:
- aggressively pursue the issues of pharmaceuticals in the environment,
- develop a framework to rank and prioritize PPCPs for further regulations and,
- Commit to sharing information with all interested parties especially the public

- Pollution Prevention a major component
Summary

- Multi-component project
  - Analytical chemistry
  - Toxicity
  - Treatment
- Collaborative
- Encourage PWS participation
- Contacts
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