Potential of Advanced Oxidation Processes (AOP) for Simultaneous Disinfection and Polishing of Drinking Water

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Introduction

Scope of Presentation

- Potential application of advanced oxidation processes (AOP) for drinking water treatment

Specific Objectives

1. Overview of conventional treatment for disinfection and micropollutants
2. EDCs/PPCPs as emerging micropollutants
3. Potential applications of AOP in meeting conventional treatment goals for micropollutants
4. Ongoing research at Tulane University
Outline

- **Background**
  - Micropollutants - EDC/PPCPs
  - Conventional WT

- **Ongoing Research at Tulane**
  - Occurrence of EDC/PPCP in SE Louisiana
  - Advanced Oxidation Processes (AOPs)

- **Methods**

- **Preliminary Conclusions**

- **Next Steps**
Background - Contaminated Drinking Water Sources

- **Micropollutants**
  - Pesticides, fertilizers, industrial solvents
    - Toxics, carcinogens
  - Typical concentrations in Miss River Water
    - Atrazine = 1 ppb (Source: Goolsby and Pereira, USGS)
  - Seasonal characteristics (e.g., storm events)
    - Atrazine = 7 ppb
    - MCL = 3 ppb (Source: Goolsby and Pereira, USGS)
  - Emerging low-level contaminants
    - Endocrine disrupting chemicals (EDCs)
    - Pharmaceuticals and personal care products (PPCPs)
Background--EDCs

➢ Chemicals which affect the endocrine system

Background - Micropollutants

Why are low levels of EDCs a cause for concern?

Dose Response

Dose Calculation

Theoretical Concentration in Drinking Water Source

= 100 ppt (ng/L)

70 kg Adult drinks 2 L of water per day

Dose = (100 * 2)/70,000

= \textbf{0.003 ng/g}

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Vom Saal et al., 1997

http://www.safewater.org/conferences/proceedings/lawrence.htm
Background--Micropollutants

- Synergistic effect of mixture of EDCs? --> 0.003 ng/g dose?
Background – Conventional WT

Some PPCPs/EDCs are soluble and refractory-->
not removed by conventional water treatment

J. Lawrence “Drinking Water Treatment Present and Future Developments”
http://www.safewater.org/conferences/proceedings/lawrence.htm
Background – Chlorine in Conventional WT

- Chlorine does kill harmful microorganisms
  - Fecal coliform
  - E. coli
  - Enterococci

- Does not kill protozoan oocysts
  - Cryptosporidium
  - Giardia
Background--Chlorine for Conventional WT

- Chlorine combines with natural organic matter (NOM) to form disinfection byproducts (DBPs)
  - Trihalomethanes (THMs)

- Effects of Cl₂ on organic micropollutants (EDC/PPCPs)?
  - Possible formation of chlorinated metabolites
  - Need more research
Background – Conventional WT

Granular Activated Carbon (GAC)

- **May be used to remove organics**
  - Adsorbs organic chemicals
  - Dependent on solubility of chemical
    - Many drugs designed to be highly water soluble (check $K_{ow}$)

- **Can be used at water treatment plant**
  - Highly expensive
  - Must be regenerated

- **Also implemented at point of use (Brita, Pur)**
Background - AOPs

- Advanced Oxidation Processes -- generate free radicals (OH⁺, O₃⁺, OH₂⁺)

- Hydroxyl radicals indiscriminately oxidize organic matter
  - Recalcitrant organics
  - Cell walls of protozoan oocysts
  - Process combines disinfection/oxidation into one step

- May be more effective than Cl₂ and GAC
## Background - AOPs

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidizing Power (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl Radical (OH·)</td>
<td>2.6</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>2.1</td>
</tr>
<tr>
<td>Hydrogen Peroxide (H₂O₂)</td>
<td>1.8</td>
</tr>
<tr>
<td>Chlorate (ClO₄⁻)</td>
<td>1.7</td>
</tr>
<tr>
<td>Chlorite (ClO₃⁻)</td>
<td>1.7</td>
</tr>
<tr>
<td>Chlorine Dioxide (ClO₂⁻)</td>
<td>1.7</td>
</tr>
<tr>
<td>Chlorine (Cl₂/OCI⁻)</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Research at Tulane – EDC/PPCPs in Source Waters

Target Compounds and Detection Limits

<table>
<thead>
<tr>
<th>Target Compound</th>
<th>IDL [ng/L]</th>
<th>Average % Recov.</th>
<th>% RSD</th>
<th>Compl of Deriv (%)</th>
<th>MDL* [ng/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clofibric acid</td>
<td>3</td>
<td>60.8</td>
<td>12.6</td>
<td>100</td>
<td>0.6</td>
</tr>
<tr>
<td>Estrone</td>
<td>3</td>
<td>91.9</td>
<td>5.1</td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>17β-Estradiol</td>
<td>1</td>
<td>90.5</td>
<td>9.1</td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>13</td>
<td>47.1</td>
<td>26.9</td>
<td>0</td>
<td>3.5</td>
</tr>
<tr>
<td>Naproxen</td>
<td>3</td>
<td>87.9</td>
<td>2.8</td>
<td>0</td>
<td>0.4</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>45</td>
<td>N.D.</td>
<td>N.D.</td>
<td>100</td>
<td>N.D.</td>
</tr>
<tr>
<td>Bisphenol-A</td>
<td>0.6</td>
<td>99.7</td>
<td>3.5</td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>Chlorophene</td>
<td>0.6</td>
<td>71.7</td>
<td>5.9</td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>Triclosan</td>
<td>1</td>
<td>53.8</td>
<td>24</td>
<td>100</td>
<td>0.2</td>
</tr>
</tbody>
</table>
### Monitoring Lake Pontchartrain & Mississippi River

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>Lake Pontchartrain</th>
<th>Mississippi River</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>9/14/01</td>
<td>9/14/01</td>
</tr>
<tr>
<td></td>
<td>9/24/01</td>
<td>9/24/01</td>
</tr>
<tr>
<td>Target Compound</td>
<td>ng/L</td>
<td>ng/L</td>
</tr>
<tr>
<td>Naproxen</td>
<td>107</td>
<td>22</td>
</tr>
<tr>
<td>Bisphenol-A-d14*</td>
<td>13.6%</td>
<td>13.9%</td>
</tr>
<tr>
<td>Estrone-d4*</td>
<td>52.6%</td>
<td>28.9%</td>
</tr>
<tr>
<td>Acetaminophen-d4*</td>
<td>1.1%</td>
<td>1.2%</td>
</tr>
</tbody>
</table>

*indicates deuterated compound.
Research at Tulane – AOPs

Bench Scale Experiments

Comparison of four different AOPs:

1. **Peroxone**
   - $O_3 + H_2O_2 \rightarrow OH^-$

2. **Ozone plus UV**
   - $O_3 + UV \rightarrow OH^-$

3. **Hydrogen Peroxide plus UV**
   - $H_2O_2 + UV \rightarrow OH^-$

4. **Mixed Oxidants**
   - High energy vapor including $OH^-$
Research at Tulane - AOPs

- Oxygen feed gas
- Chiller (T)
- Ozone generator (P, Q)
- Ozone monitor
- Mixed oxidant generator
- Stabilization tank (T, P)
- 3-way valve
- 254 nm UV lamp
- Contact chamber
- Diffuser
- Water recirculation
- Sampling valve
Research at Tulane - AOPs

**Preliminary Conclusions**

- Mixed oxidants have a slightly greater oxidizing power than ozone alone.
- Mixed oxidants are an effective disinfectant.
- Mixed oxidants were more effective in the oxidation of micropollutants (MTBE) than ozone alone—more research needed.
Use AOPs bench scale apparatus to investigate removal of EDC and PPCP micropollutants
- Naproxyn
- 17β-Estradiol
- Bisphenol-A

Spike DI water samples
- 0 to 10 µg/L

Spike Mississippi River samples
- 10 to 100 ng/L

Isolate using SPE, derivatize using BSTFA, analyze using GC/MS
Methods - Naproxyn

- Anti-inflammatory prescription drug
- No known endocrine disrupting effects
- \( \text{Log } K_{ow} \approx 3.10 \)
Methods - 17β-Estradiol

- Hormone
- Endocrine Disruptor
- Log $K_{ow} = 3.94$
Methods - Bisphenolol-A

- Plasticizing agent
- Suspected endocrine disruptor
- $\log K_{ow} = 3.32$
Methods

Overview of Experiments

- Study each compound separately in a DI water matrix
- Determine doses of ozone, peroxide, UV light and mixed oxidants required for complete mineralization
- Compare material and power costs of AOPs to Cl$_2$ and GAC estimated values
AOPs may be a more cost effective means to disinfect and polish potable water compared to chlorine and GAC.

Data from bench scale experiments at Tulane University may be used in the design of a pilot scale AOP system for New Orleans drinking water.
## Next Steps

<table>
<thead>
<tr>
<th>Date</th>
<th>Task</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct 2002</td>
<td>Complete ongoing AOP experiments--optimization of Tulane mixed oxidant process</td>
</tr>
<tr>
<td>Dec 2002</td>
<td>Develop laboratory standards and analytical procedures for EDC/PPCP micropollutants</td>
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<tr>
<td>Mar 2003</td>
<td>Complete AOP experiments for treatment of spiked DI and Miss. R. water samples</td>
</tr>
<tr>
<td>June 2003</td>
<td>Compare results to GAC data</td>
</tr>
</tbody>
</table>
Acknowledgements

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