Trace Organic Microconstituents
Bringing Antimicrobials and Nano-particles into Focus

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National Pretreatment / Pollution Prevention Workshop
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Presentation Outline

• Trace Organic Microconstituent Overview
• Water Quality Trends
• Treatment Effectiveness
• Yes, Microconstituents are Present in Our Lives
• Health Concerns
• Sustainable Implementation
• What Can We Do? What Can You Do?
Magnitude of Microconstituent Chemicals

American Chemical Society - Chemical Abstract Service

- Organic and inorganic compounds: 44,142,652
- Commercially available: 30,240,845
- Inventoried or regulated: 247,755
- New: 10,000 Synthetic Organic Chemical / year

http://www.cas.org/cgi-bin/cas/regreport.pl

- Additional considerations:
  - Reactions and interactions that occur between chemicals
  - Matrix effects of compounds combined

http://mail.chemicosystems.com/myweb/Chemicals.jpg
Trace Organic Microconstituents

- Pharmaceuticals
  - Antibiotics
  - Anti-inflammatories
  - Antidepressants
  - X-ray contrast media
  - Contraceptives
  - Steroids
- Personal Care Product
  - Antibacterial Soap
  - Hair Care
  - Cosmetics
  - Cleaning Products
  - Flame retardants
- Household Chemicals
- Industrial Chemicals
- Agricultural
  - Pesticides
  - Herbicides
- Disinfection byproducts
- Synthetic and Naturally occurring hormones
- Metals
Understanding Concentration

- One \textit{ppb} is \(1/1,000,000,000 = 0.000000001\):
  - 1 ppb of one year is 1/32 of a second, or one in 32 years
  - 1 cent in $10 million
  - 1 sheet of toilet paper in a roll stretching from NY to London

One \textit{ppm} is \(1/1,000,000 = 0.000001\):

- Half a person in Alaskan population
- One car in bumper-to-bumper traffic from Cleveland to San Francisco
- Four drops of ink in one 55-gallon barrel of water (mixed thoroughly) would produce an ink concentration of 1 ppm
Water Quality Trends from USGS Studies

• Untreated Drinking Water Sources
  – 25 ground and 49 surface in 25 states and Puerto Rico
  – More common in surface than groundwater
  – 60% of the 36 pharmaceuticals only slightly above detection limits

• Ground Water
  – 47 wellheads in 18 states tested for 65 chemicals
  – 35% of sites had detectable
  – 87% of the 137 detections were less than 1µg/L
Compounds in the Environment
USGS Research Results

• Five most frequently detected chemicals - surface water
  – cholesterol (59%, natural sterol)
  – metolachlor (53%, herbicide)
  – cotinine (51%, nicotine metabolite)
  – β-sitosterol (37%, natural plant sterol)
  – 1,7-dimethylxanthine (27%, caffeine metabolite)
• Five most frequently detected chemicals - ground water
  – tetrachloroethylene (24%, solvent)
  – carbamazepine (20%, pharmaceutical)
  – bisphenol-A (20%, plasticizer)
  – 1,7-dimethylxanthine (16%, caffeine metabolite)
  – tri (2-chloroethyl) phosphate (12%, fire retardant).

http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6V78-4SBRTJ2-3&_user=628632&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000033138&_version=1&_urlVersion=0&_userid=628632&md5=c2226e5db8d79a45313ee77d7be8e799
Ubiquitous Compounds
From WateReuse Research

• Pharmaceuticals
  – DEET
  – Caffeine
  – Triclosan
  – Bisphenol A
• Human Steroids
  – Cholesterol
  – Coprostanol
• Nutrients
  – N & P
• Volatile Organics
  – Chloroform
• Semi Volatile Organic
  – Dichloroacetic Acid
  – THAs
  – Dibromoacetic Acid
  – Trichloroacetic Acid
• Microbiologicals
  – Coliphage, general
  – Fecal Coliforms
• Synthetic Organics
  – Atrazine
  – Diethylatrazine
Fate and Transport

• Understanding needed for the dynamics and persistence within our environment

• Mechanisms for transformations and removal
  – Chemical reactions
  – Adsorption
  – Biodegradation
  – Physical separation
  – Volatilization
Treatment Methods

• Activated Sludge
  – Biodegradation and removal of organics

• Membrane – Micro, Ultra, Nano, and RO
  – Physical separation and adsorption

• Membrane Bioreactors
  – Combination Activated Sludge and Membranes

• Disinfection – UV, Chlorine, Ozone

• Advanced Oxidation
  – Ozone with $\text{H}_2\text{O}_2$
  – Chemical breakdown with oxidation

• Multiple Barrier Mechanisms Needed
Treatment Plant Removal Efficiency
UNC Charlotte – MWH Research

% Removal

- 4-Methylphenol
- Bis Phenol A (BPA)
- Caffeine by GCMS LLE
- DEET
- Phenol
- Triclosan
- Tris (2-butoxyethyl) phosphate
<table>
<thead>
<tr>
<th>Occurrence</th>
<th>Treatment</th>
<th>Bin T1</th>
<th>Bin T2</th>
<th>Bin T3</th>
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<tbody>
<tr>
<td>Bin O1</td>
<td>Infrequent</td>
<td>Good</td>
<td>Moderate</td>
<td>Poor</td>
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<tr>
<td></td>
<td></td>
<td>Removal</td>
<td>Removal</td>
<td>Removal</td>
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<tr>
<td>Bin O2</td>
<td>Intermediate</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Bin O3</td>
<td>Frequent</td>
<td></td>
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</tr>
</tbody>
</table>

- **Bin O1 Infrequent**
  - Caffeine
  - Ibuprofen
  - Oxybenzone

- **Bin O2 Intermediate**
  - Chloroxylenol
  - Methylparaben
  - Benzyl salicylate
  - 3-phenylpropionate

- **Bin O3 Frequent**
  - Butylbenzylphthalate
  - Octylmethoxycinnamate

- **SRT_{80} ≤ 5 Days**
## Removaal Rates for Biological Degradation, Soil Adsorption, and Model

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Biological Dissolved Organic Carbons</th>
<th>Aquifer Storage and Recovery</th>
<th>Field Sites (Golf Course and WWTF Infiltration Pond)</th>
<th>QSAR Modeling</th>
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<tbody>
<tr>
<td>Hydrocodone</td>
<td>M</td>
<td>R</td>
<td>ND</td>
<td>NP</td>
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<td>Trimethoprim</td>
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<td>R</td>
<td>M</td>
<td>M</td>
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<td>Acetaminophen</td>
<td>R</td>
<td>R</td>
<td>AMB</td>
<td>R</td>
</tr>
<tr>
<td>Caffeine</td>
<td>R</td>
<td>R</td>
<td>AMB</td>
<td>NP</td>
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<tr>
<td>Erythromycin-H2O</td>
<td>S</td>
<td>AMB</td>
<td>S</td>
<td>S</td>
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<tr>
<td>Sulfamethoxazole</td>
<td>S</td>
<td>S</td>
<td>AMB</td>
<td>M</td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>S</td>
<td>R</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Dilantin</td>
<td>S</td>
<td>M</td>
<td>M</td>
<td>R</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>S</td>
<td>M</td>
<td>M</td>
<td>M</td>
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<tr>
<td>DEET</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>R</td>
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<td>Atrazine</td>
<td>S</td>
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<td>M</td>
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<td>Diazepam</td>
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<td>ND</td>
<td>R</td>
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<td>Estriol</td>
<td>M</td>
<td>R</td>
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<td>ND</td>
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<tr>
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<td>R</td>
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<td>Testosterone</td>
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<td>AMB</td>
<td>R</td>
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<td>Triclosan</td>
<td>AMB</td>
<td>AMB</td>
<td>M</td>
<td>S</td>
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<tr>
<td>Gemfibrozil</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
</tbody>
</table>

**KEY:**
- **R** = Rapid degraded/adsorbed
- **M** = Moderately degraded/adsorbed
- **S** = Slowly degraded/adsorbed
- **ND** = Non Detected
- **AMB** = Ambiguous
- **NP** = Not Predicted
Ultraviolet/Hydrogen Peroxide Oxidation – AWWARF Report

(UV Dose = 372 mJ/cm², H₂O₂ Dose = 5 mg/L)

Percent Removal

- Analgesics
- Antimicrobials
- Pesticides
- Psychoactive
- Steroids
- Other
Treatment Effectiveness for Removal from AWWARF Report

Excellent
- PAC (e.g. Cary)
- GAC (e.g. NRWASA)
- Nanofiltration & Reverse Osmosis (e.g. Dare County)
- Ozone (e.g. Wilmington)
- Ozone/H₂O₂
- UV/H₂O₂

Moderate
- Chlorine
- Ultrafiltration*
- UV (439 mJ/cm²)

Ineffective
- Coag/Floc
- Microfiltration
- MIEX
- Chloramines
- UV (40 mJ/cm²)
Trace Organics Are Present

“This concentration is roughly equivalent to 1/2 of an inch in the distance between the earth and the moon...”

(Excerpt from Shane Snyder testimony to Congress)
Significance as A Health Concern

- Widespread Usage
- Continually Released
- Potential for Health Effects
  - Toxicological
    - Wildlife - Aquatic Life
    - Human Health
- Detectable does not mean harmful to humans.
- Trace substances detected at very low levels in source waters.
- Higher concentrations through medicines, food, beverage and other sources.
Mechanisms of Endocrine Disruptors

Red Normal / Yellow Mimics / Yellow Blocks

www.wwfcanada.org/satellite/hormone-disrupters/science/frameset.html
Personal Risk and Choices

EEq Comparison ("Worst" WWTP)

Mug of Beer (6 ng/L, 500 mL) ≈ 1.4 L Wastewater (4.6 ng/L)
Sustainable Implementation

• Determine health risks to justify advanced treatment needs
• Design treatment strategies to a new criteria:
  – Minimize energy requirements
  – Lower carbon footprints
  – Use resources wisely
  – Decrease environmental impacts
• Set up a matrix to judge the sustainability of design
## Air Quality Impacts Magnified

- **WWTF Energy Demand**
  - WWTF with Activated Sludge: 166 kWh/Day
  - Reverse Osmosis and Electro-deionization: 7,777 kWh/Day
  - High Efficiency Reverse Osmosis: 5,068 kWh/Day

<table>
<thead>
<tr>
<th>Impacts</th>
<th>Emission Factor*</th>
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</thead>
<tbody>
<tr>
<td>CO₂ (lbs/day)</td>
<td>1.46</td>
</tr>
<tr>
<td>NOₓ (lbs/day)</td>
<td>0.0017</td>
</tr>
<tr>
<td>VOC (g/day)</td>
<td>0.025</td>
</tr>
<tr>
<td>PM (g/day)</td>
<td>0.061</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WWTF</th>
<th>RO/EDI</th>
<th>HERO</th>
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<tbody>
<tr>
<td>243</td>
<td>0.28</td>
<td>13</td>
</tr>
<tr>
<td>11355</td>
<td>194</td>
<td>127</td>
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<tr>
<td>5068</td>
<td>474</td>
<td>309</td>
</tr>
</tbody>
</table>

*Charlotte Area*
What’s To Be Done?

Environmental Management

- Water\textsubscript{2}Water
- Science Based Decisions
- Source Reduction – Individual Level /Industrial
- On-going Treatment Reduction at the Focus Point (WWTF)
- Site Specific Treatment and Remediation
- Implement Strategies Balanced with Sustainable Practices
- Long-Term and Large Scale Monitoring
- Regulations for Reduction
- Determination of Health Effects
- Limiting Exposure of Vulnerable Populations
You are one in a million making a difference in a part per billion!
The struggle to save the global environment is in one way much more difficult than the struggle to vanquish Hitler, for this time the war is with ourselves. We are the enemy, just as we have only ourselves as allies.

~Al Gore
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References


• Current Literature Status: There are 7,094 literature articles noted with EPA http://www.epa.gov/ppcp/citations.pdf
Website Resources

• US Department of Health and Human Services – Household Database:
  http://hpd.nlm.nih.gov/cgi-bin/household/list?tbl=TblChemicals&alpha=A

• AWWA – Endocrine Disruptors:
  http://www.awwa.org/Resources/topicspecific.cfm?ItemNumber=3647&navItemNumber=32969