High-Resolution Monitoring of Pharmaceuticals and Personal Care Products in Lake Michigan and Comparison to Microbial Indicators

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Pharmaceuticals and Personal Care Products (PPCPs)

- Antibiotics, antimicrobials, detergents, anti-fungals, blood pressure medications, diabetic drugs, etc.
- Comprise thousands of chemical substances \(^1\)
- Primary source is waste water effluent and raw sewage.
- PPCPs are found in natural waters around the world\(^2,3,4\)

\(^1\)U.S. EPA, 2010. Pharmaceuticals and Personal Care Products


Triclocarban Co-Occurrence with Spikes in *E. coli* at Three Beaches in 2012
Objectives

• Characterize the suite of PPCPs that occur in water at a popular municipal beach on Lake Michigan.
• Describe any temporal co-occurrence of PPCPs.
• Determine if any PPCPs correlate with *E. coli*
• Identify environmental drivers of total PPCP intensity.
• Examine interannual variation in PPCP dynamics.
Water Quality Monitoring for Wisconsin Beaches
Milwaukee, WI beaches on Lake Michigan

- Bradford Beach
- McKinley Beach
- South Shore Beach
Bradford Beach – Milwaukee, WI
Milwaukee Beach Monitoring Program

- Sampled 6 days/week during 2013 and 2014 beach season, June-August (PPCPs analyzed approximately three times per week)
- Daily *E. coli* levels quantified by Colilert-18 assay and predicted by Nowcast modeling
- Suite of associated environmental variables collected
  - Weather
  - Chlorophyll
  - Turbidity
  - Nutrients
  - Waves
  - Current
  - Inflows
  - pH
  - Organic Carbon
- Surveyed Bradford Beach on Lake Michigan for the presence of more than 70 PPCPs
  - 97 sample dates x 74 compounds x 2 target ions = more than 14,000 data points!
Detecting PPCPs with LC-MS/MS

- Lyophilize 20mL of water sample
- Resuspend in Methanol with 10% Acetic Acid
- Sonicate
- Dry down until $N_2$ gas
- Resuspend in 50% Methanol
- Analyze with LC-MS/MS
Some of the PPCPs Targeted in This Study

<table>
<thead>
<tr>
<th>Antibiotics</th>
<th>Antibiotics</th>
<th>Antifungal</th>
<th>Cardiovascular Medications</th>
<th>Depression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ampicillin</td>
<td>PenicillinG</td>
<td>Thiabendazole</td>
<td>Simvastatin (Cholesterol)</td>
<td>(Prozac)</td>
</tr>
<tr>
<td>Azithromycin</td>
<td>PenicillinV</td>
<td>Miconazole</td>
<td>Lysinopril (Blood Pressure)</td>
<td>(Prozac)</td>
</tr>
<tr>
<td>Carbadox</td>
<td>Roxithromycin</td>
<td></td>
<td>Digoxin (Heart Failure)</td>
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</tr>
<tr>
<td>Cefotaxime</td>
<td>Sarafloxacin</td>
<td></td>
<td>Diltiazem (Blood Pressure)</td>
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<tr>
<td>Ciprofloxin</td>
<td>Sulfachloropyridazine</td>
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<td></td>
<td></td>
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<tr>
<td>Clarithromycin</td>
<td>Sulfadiazone</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Clindamycin</td>
<td>Sulfadimethoxine</td>
<td></td>
<td></td>
<td>(Non-prescribed)</td>
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<tr>
<td>Cloxacillin</td>
<td>Sulfamerazine</td>
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<tr>
<td>Enrofloxacin</td>
<td>Sulfamethazine</td>
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<tr>
<td>Erythromycin</td>
<td>Sulfamethizole</td>
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<tr>
<td>Flumequine</td>
<td>Sulfanilamide</td>
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<tr>
<td>Lomefloxacin</td>
<td>Sulfathiazole</td>
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</tr>
<tr>
<td>Norfloxacin</td>
<td>Thiabendazole</td>
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</tr>
<tr>
<td>Ofloxacin</td>
<td>Trimethoprim</td>
<td></td>
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</tr>
<tr>
<td>Oxacillin</td>
<td>Tylosin</td>
<td></td>
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</tr>
<tr>
<td>Oxolinic acid</td>
<td>Virginiamycin</td>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Triclosan</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Triclocarban</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Caffeine</td>
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<tr>
<td></td>
<td></td>
<td>Paraxanthine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Digoxigenin</td>
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<td></td>
<td></td>
<td>Fluoxetine (Prozac)</td>
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<tr>
<td></td>
<td></td>
<td>Diphenhydramine</td>
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<tr>
<td></td>
<td></td>
<td>(Benadryl)</td>
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<tr>
<td></td>
<td></td>
<td>Codeine</td>
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<tr>
<td></td>
<td></td>
<td>Acetaminophen</td>
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<thead>
<tr>
<th>Diabetes</th>
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<tbody>
<tr>
<td></td>
<td>Metformin</td>
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</tbody>
</table>
Most Frequently Detected PPCPs
2013 Frequent Detects

- Caffeine
- Paraxanthine
- Metformin
- Simvastatin
- Triclocarban
- Triclosan
2014 Frequent Detects
Total PPCPs Significantly Correlate with *E. coli* in 2013

But no individual PPCP was significantly correlated

No correlation in 2014
Environmental Drivers of PPCPs Compared to *E. coli* in 2013

### Correlates of Total PPCPs

<table>
<thead>
<tr>
<th>Correlate</th>
<th>R</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind Speed</td>
<td>-0.414</td>
<td>0.006</td>
</tr>
<tr>
<td>Wind Direction</td>
<td>-0.338</td>
<td>0.028</td>
</tr>
<tr>
<td>Cloud Cover</td>
<td>-0.346</td>
<td>0.025</td>
</tr>
<tr>
<td>River Inflow (48H)</td>
<td>-0.273</td>
<td>0.08</td>
</tr>
</tbody>
</table>

### Correlates of *E. coli*

<table>
<thead>
<tr>
<th>Correlate</th>
<th>Cor</th>
<th>Prob</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind Direction</td>
<td>-0.394</td>
<td>0.010</td>
</tr>
<tr>
<td>Chlorophyll</td>
<td>0.399</td>
<td>0.009</td>
</tr>
<tr>
<td>Air Temp</td>
<td>-0.387</td>
<td>0.011</td>
</tr>
<tr>
<td>Wave Height</td>
<td>0.436</td>
<td>0.004</td>
</tr>
<tr>
<td>Precip. (48 hr)</td>
<td>0.353</td>
<td>0.022</td>
</tr>
</tbody>
</table>

### 2013 PPCP Model

\[
\log(\text{Total PPCPs}) = 3.316 - 0.337 \log(\text{Wind Speed}) \\
+ 0.154 \log(\text{Wind Dir}) \\
- 0.624 \sqrt{\text{Cloud Cover}} \\
- 0.615 \log(\text{Inflow 48Hr})
\]
Next Steps

• Further develop models of individual PPCPs and total PPCP abundance across years.

• Examine causes of interannual variation in PPCP occurrence

• Major question: What factors control concentration and frequency of PPCP occurrence at beaches?
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