Attenuation of Trace Organic Chemicals (TOrCs) by Advanced Treatment Technologies (ATTs) in Water Reuse

Tarun Anumol & Shane Snyder
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Chemical & Environmental Engineering
Water Reuse: Yuck Factor

Water Reuse: Acceptance

“For billions of years, earth has been reusing water over and over again.”

Better to drink my own piss rather than someone else’s
Water Reuse

Courtesy: NY Times

PPCPs in Water

Since the pharmacy is closed, the doctor said you should take three glasses of water.
Identification of Estrogenic Chemicals in STW Effluent. 1. Chemical Fractionation and In Vitro Biological Screening

Why do we care?

Wastewater Effluent
Managed Aquifer Recharge
Nanofiltration
Ozone/UV-H₂O₂

Typical Water Reuse Treatment Train

Potable Water To Distribution

Biological Activated Carbon

Are pharmaceuticals potent environmental pollutants? Part I: Environmental risk assessments of selected active pharmaceutical ingredients

Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change?

Christian G. Daughton1 and Thomas A. Termeer2
**Ozone: FLU & UV_{254} Removal**

- WW Effluent
- Ozone 1.5 mg/L
- Ozone 3.0 mg/L
- Ozone 4.5 mg/L
- Ozone 6 mg/L

**Ozone: Treatment Efficacy**

- Removal (%)
- Ozone
- Atenolol
- Trimethoprim
- Primidone
- Meprobamate
- DEET
- TCEP
- Triclosan
Ozone: Treatment Efficacy

Ozone

Removal (%)

O3:TOC-0.19
O3:TOC-0.39
O3:TOC-0.59
O3:TOC-0.77

Atenolol
Trimethoprim
Primidone
Meprobamate
DEET
TCEP
Triclosan
Ozone: Treatment Efficacy

- Arylazide
- Trimethoprim
- Primaquine
- Mefloquine
- DES
- TCEP
- Triazines

Ozone Dose: 0.19, 0.39, 0.59, 0.77
Removal (%)

Ozone:

N-nitrosodimethylamine
Lifetime Cancer Risk: 0.7 ng/L

H₃C \text{N} \text{N}_\text{O} \text{CH}_3

NDMA Concentration (ng/L)

- WW effluent

Ozone Dose
Ozone: Achilles Heel

N-nitrosodimethylamine

Lifetime Cancer Risk: 0.7 ng/L

Achilles Heel

H₂C-N-N₃O
CH₃

UV Advanced Oxidation Processes

UV/H₂O₂
**Toxicity**

Formation and removal of genotoxic activity during UV/H₂O₂–GAC treatment of drinking water

Bromate Formation during Ozonation of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions

Urs von Gunten* and Jürg Holgée

N-nitrosodimethylamine (NDMA) formation during ozonation of dimethylamine-containing waters

**Managed Aquifer Recharge (MAR)**

Trace Organic Compounds (TOrCs)

<table>
<thead>
<tr>
<th>Sample (Conc. in ng/L)</th>
<th>NDMA formation</th>
<th>After MAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1260</td>
<td>BLO</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>6210</td>
<td>BLO</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>1090</td>
<td>BLO</td>
</tr>
<tr>
<td>Propylene</td>
<td>811</td>
<td>BLO</td>
</tr>
<tr>
<td>Phenol</td>
<td>135</td>
<td>BLO</td>
</tr>
<tr>
<td>Mecropilbromine</td>
<td>692</td>
<td>BLO</td>
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<tr>
<td>Ethylenedihydramine</td>
<td>173</td>
<td>BLO</td>
</tr>
<tr>
<td>Ditiazem</td>
<td>310</td>
<td>BLO</td>
</tr>
<tr>
<td>Carbovaspin</td>
<td>310</td>
<td>BLO</td>
</tr>
<tr>
<td>DEET</td>
<td>48</td>
<td>BLO</td>
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<tr>
<td>Biphensol A</td>
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<td>BLO</td>
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<tr>
<td>Naproxcam</td>
<td>500</td>
<td>BLO</td>
</tr>
<tr>
<td>PEG 800</td>
<td>811</td>
<td>BLO</td>
</tr>
<tr>
<td>PEG 800</td>
<td>48</td>
<td>BLO</td>
</tr>
<tr>
<td>ICPP</td>
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<td>BLO</td>
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<td>Ipirprofen</td>
<td>170</td>
<td>BLO</td>
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<tr>
<td>Benfluorid</td>
<td>48</td>
<td>BLO</td>
</tr>
<tr>
<td>PEG 800</td>
<td>48</td>
<td>BLO</td>
</tr>
</tbody>
</table>

**NDMA Concentration (ng/L)**

* WW effluent

Ozone Dose

Post MAR Water
**Granular activated carbon (GAC)**

- Transformation products

**Bulk Organic Parameters (BOPs)**

- Total (Dissolved) Organic Carbon
- Total Color
- Fluorescence Spectroscopy
- Ultra-Violet Absorbance
Background: BOPs as Surrogates

Monitoring emerging chlorination by-products in drinking water using UV-absorbance and fluorescence indexes

Development of surrogate correlation models to predict trace organic contaminant oxidation and microbial inactivation during ozonation

Evaluation of UV/H₂O₂ treatment for the oxidation of pharmaceuticals in wastewater

Experiments

Rapid small-scale column testing (RSSCT)
**UV$_{254}$ v TOrC (5-95% breakthrough)**

**PFOA**

- **Slope:** 1.57
- **Y-intercept:** -1
- **$R^2$:** 0.83

**Gemfibrozil**

- **Slope:** 2.23
- **Y-intercept:** 10
- **$R^2$:** 0.81
**Triclocarban**

Reduction in UV254 Absorbance (%)

Contaminant Removal (%)

Slope: 0.19
Y-intercept: 86
R²: 0.16

Molecular properties calculated with ChemAxon

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
<th>Charge (pH=6.5)</th>
<th>Log D_m (pH=6.5)</th>
<th>Slope</th>
<th>Y-Intercept</th>
<th>R²</th>
<th>N_UV</th>
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<tbody>
<tr>
<td>Atenolol</td>
<td>9.7</td>
<td>+</td>
<td>-2.0</td>
<td>2.07</td>
<td>22</td>
<td>0.68</td>
<td>39</td>
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<tr>
<td>PFPA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.57</td>
<td>-1</td>
<td>0.83</td>
<td>53</td>
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<tr>
<td>Sulfamethoxazole</td>
<td>7.5</td>
<td>92% neutral, 8% -</td>
<td>0.5</td>
<td>1.85</td>
<td>-4</td>
<td>0.85</td>
<td>49</td>
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<tr>
<td>Meprobamate</td>
<td>15</td>
<td>Neutral</td>
<td>0.9</td>
<td>1.81</td>
<td>2</td>
<td>0.90</td>
<td>42</td>
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<tr>
<td>Primidone</td>
<td>11.6</td>
<td>Neutral</td>
<td>1.0</td>
<td>1.94</td>
<td>-1</td>
<td>0.79</td>
<td>55</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>1.9</td>
<td>Negative</td>
<td>1.9</td>
<td>2.23</td>
<td>10</td>
<td>0.81</td>
<td>55</td>
</tr>
<tr>
<td>Trimeprazine</td>
<td>7.1</td>
<td>20% Neutral, 80% +</td>
<td>1.1</td>
<td>2.38</td>
<td>24</td>
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<td>36</td>
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<tr>
<td>Diltiazem</td>
<td>8.0</td>
<td>97% +, 3% Neutral</td>
<td>1.1</td>
<td>1.29</td>
<td>50</td>
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<td>+</td>
<td>3.2</td>
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<td>72</td>
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<td>49</td>
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<tr>
<td>PFOA</td>
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<td>-</td>
<td>3.2</td>
<td>0.19</td>
<td>86</td>
<td>0.16</td>
<td>38</td>
</tr>
</tbody>
</table>

Carbon: Norit DARCO 12x40; Water Qualities: Four
Figure 1: EEMs at different bed volumes (BV) for WWTP 2 secondary effluent treated with Norit Hydro DARCO 12x40 carbon.

TOC: 6.3 mg/L
TF: 32,000

TF v TOC (5-95% breakthrough)

Slope: 1.2
Y-intercept: -21
R²: 0.83
TF v TOc (5-95% breakthrough)

Gemfibrozil

- Slope: 1.26
- Y-intercept: 3
- $R^2$: 0.84

Triclocarban

- Slope: 0.15
- Y-intercept: 76
- $R^2$: 0.29
TF v TOrC Correlation

Carbon: Norit DARCO 12x40; Water Quality: Four

Table 3. Summary of regression parameters for total fluorescence for Batch 1 experiments

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
<th>Charge (pH=6.5)</th>
<th>Log D_{so} (pH=6.5)</th>
<th>Slope</th>
<th>y-Intercept</th>
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<td>9.7</td>
<td>+</td>
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<td>1.59</td>
<td>13</td>
<td>0.89</td>
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<td>PFOA</td>
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<td>-</td>
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<td>1.20</td>
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<td>0.83</td>
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<td>-11</td>
<td>0.77</td>
<td>50</td>
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<tr>
<td>Meprobamate</td>
<td>15</td>
<td>Neutral</td>
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<td>Neutral</td>
<td>1.0</td>
<td>1.16</td>
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<td>0.79</td>
<td>54</td>
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<td>Gemfibrozil</td>
<td>4.4</td>
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<td>1.9</td>
<td>1.23</td>
<td>3</td>
<td>0.84</td>
<td>58</td>
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<tr>
<td>Diphenhydramine</td>
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<td>PFOS</td>
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<td>Triclocarban</td>
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</tr>
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Real-time Monitoring

On-line sensor system
Questions

QUESTIONS ANSWERED HERE EVEN THE SILLY ONES