Fate of low molecular weight dissolved organic matters in reclaimed water treatment systems

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November 26, 2015 RECWET Symposium

Reclaimed Water in Urban Region

Tachikawa-city, Tokyo

Parking Area on a Highway

Dissolved Organic Matter (DOM) in Reclaimed Water

Problems/concerns related to DOM in reclaimed water

- Membrane fouling
- EOPs
- Formation of Disinfection byproducts (DBPs)
- Microbial regrowth & biofilm
- Pathogen
- Fate of DBPs

Guideline of Reclaimed Water Quality

Ministry of Land, Infrastructure, Transport, and Tourism, 2005

<table>
<thead>
<tr>
<th></th>
<th>Toilet Flushing</th>
<th>Water Sprinkling</th>
<th>Landscape Irrigation</th>
<th>Recreational Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (degree)</td>
<td>&lt;2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>5.8-8.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance &amp; Odor</td>
<td></td>
<td>pleasant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color (degree)</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>E. coli (CFU/100mL)</td>
<td>ND</td>
<td>ND</td>
<td>(T. coli, 1000)</td>
<td>ND</td>
</tr>
<tr>
<td>Residual chlorine (mg/L)</td>
<td>Free: 0.1&lt; or Combined: 0.4&lt;</td>
<td>Free: 0.1&lt; or Combined: 0.4&lt; (Optional)</td>
<td>Free: 0.1&lt; or Combined: 0.4&lt; (Optional)</td>
<td></td>
</tr>
</tbody>
</table>

To expand reclaimed water application, more comprehensive water quality information is necessary.
Objectives

- Characterize DOM in Reclaimed Water
  - DBPs and their precursors

- Evaluate BOM removal/production in Reclaimed Water Treatment Processes
  - ozonation, activated carbon, sand filtration, chlorination

- Identify the BOM molecules and the fate in the processes

Sampling at Water Reclamation Plant

- Receiving secondary effluent (Activated sludge process) from municipal wastewater treatment plant
- Average reclaimed water production: 800 m³/d

- Secondary effluent
- Sampling Point
  - Biofiltration
    - Removal of remaining biodegradable organic matters

- Ozonation
  - Removal of color and odor
  - 4.5 g O₃/m³ water

- Chlorination
  - Disinfection
  - NaOCl (6 mg/L as Cl₂) to achieve 1 mg/L of total chlorine

Orbitrap Mass Spectrometer

- High Resolving Power: ~ 100,000
  - Resolution in complex samples

- Mass accuracy: < 2 ppm
  - Enables molecular formula identification

- Ionization: Electron Spray Ionization (ESI)
  - Soft ionization results in producing molecule-related ions [M+H]⁺, [M-H]⁻

“Exactive” (Thermo Scientific)

Unknown Screening Analysis of DOM

- Filtration
  - ~500mL
  - 0.7 µm + 0.45 µm Glass-fiber filter

- SPE
  - Bond Elut PPL (Varian)
  - Styrene-Divinylbenzene polymer
  - Hydrophilic ~ Hydrophobic

- Orbitrap-MS
  - Polarity: Negative ion mode
  - m/z range: 100-1,000
  - Low MW Organic matters

- Post analysis
  - Molecular formula identification (“Xcalibur”, Thermo Scientific”)
Molecular formula determination

\[ m/z = 284.1393 \]

\[ M = 284.1393 \]

\[ ^{13}C \text{ isotope peak} = M + 1.0033 \]

\[ ^{34}S \text{ isotope peak} = M + 1.9958 \]

\[ \text{Compute molecular formula within } M \pm 5 \text{ ppm} \]

\[ \text{Set mass accuracy} = 5 \text{ ppm} \]

\[ \text{Narrow down mass error down to 1.5 ppm} \]

\[ \text{Refer to } ^{13}C/^{12}C \text{ ratio, } ^{34}S \text{ Isotope peak} \]

\[ \text{Compute molecular formula within } M \pm 5 \text{ ppm} \]

\[ \text{Determination} \]

\[ C_{16}H_{18}O_2N_3 \]

Mass Spectra

- DOC recovery by PPL SPE cartridge was 55% on average
- Intense peaks – observed in m/z 100-500 (or 100-500 Da)

Cluster analysis of mass spectra

- In total, 2,078 formulae were identified
- Elemental compositions of wastewater – more complex compared to river NOM
- After chlorination, 133 chlorine-containing formulae – additionally detected
Van Krevelen Diagram of CHO formulae in Secondary Effluent

- Most of CHO formulae found in regions of lignin or tannin\(^{13-14}\) and condensed aromatic structure compounds
  - Originated from NOM

[ChemSpider Databases](https://www.chemspider.com) (contains >30,000,000 compounds)

Tracking Precursors of Chlorinated DBPs

Electrophilic substitution

- Most predominant reaction at wastewater treatment condition\(^{16}\)

\[
\begin{align*}
\text{C}_6\text{H}_6\text{O} & \xrightarrow{\text{Cl}} \text{C}_6\text{H}_5\text{OCl} \\
\text{C}_6\text{H}_6\text{O} & \xrightarrow{\text{Cl}} \text{C}_6\text{H}_5\text{OCl}_2 \\
\text{C}_6\text{H}_6\text{O} & \xrightarrow{\text{Cl}} \text{C}_6\text{H}_5\text{OCl}_3
\end{align*}
\]

- The reaction results in molecule with +1 Cl and -1 H

Putative Precursors and DBPs after Chlorination

<table>
<thead>
<tr>
<th>m/z (error in ppm)</th>
<th>Chemical formula</th>
<th>Present in</th>
<th>m/z (error in ppm)</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>161.0239 (2.95)</td>
<td>C(_4)H(_6)O(_3)</td>
<td>All processes</td>
<td>194.9857 (1.31)</td>
<td>C(_3)H(_5)O(_2)Cl</td>
</tr>
<tr>
<td>195.0660 (1.24)</td>
<td>C(_4)H(_5)O(_4)</td>
<td>All processes</td>
<td>229.0271 (0.92)</td>
<td>C(_3)H(_4)O(_3)Cl</td>
</tr>
<tr>
<td>229.0717 (0.92)</td>
<td>C(_4)H(_5)O(_6)</td>
<td>All processes</td>
<td>296.9938 (0.05)</td>
<td>C(_3)H(_6)O(_2)Cl(_2)</td>
</tr>
<tr>
<td>241.0718 (0.18)</td>
<td>C(_4)H(_5)O(_6)</td>
<td>All processes</td>
<td>308.9942 (1.23)</td>
<td>C(_3)H(_7)O(_2)Cl(_2)</td>
</tr>
<tr>
<td>179.0710 (2.05)</td>
<td>C(_4)H(_5)O(_3)</td>
<td>Raw, Bf, and Oz</td>
<td>213.0323 (0.44)</td>
<td>C(_3)H(_5)O(_3)Cl</td>
</tr>
<tr>
<td>213.0403 (0.56)</td>
<td>C(_4)H(_5)O(_6)</td>
<td>Bf, Oz, and Rm</td>
<td>280.9626 (0.34)</td>
<td>C(_3)H(_6)O(_2)Cl</td>
</tr>
<tr>
<td>207.0660 (1.17)</td>
<td>C(_4)H(_5)O(_4)</td>
<td>Oz and Rm</td>
<td>241.0275 (0.89)</td>
<td>C(_3)H(_5)O(_4)Cl</td>
</tr>
<tr>
<td>243.0512 (0.61)</td>
<td>C(_4)H(_5)O(_7)</td>
<td>Oz and Rm</td>
<td>310.9734 (1.27)</td>
<td>C(_3)H(_6)O(_2)Cl(_2)</td>
</tr>
</tbody>
</table>

- 8 DBP precursors were identified by assuming electrophilic substitution
- Putative precursors originate not only in secondary effluent but also treatment processes

\(^{13}\)Ohno et al., 2010 and \(^{14}\)Kim et al., 2006

\(^{16}\)Deborde et al., 2008
Biodegradable Organic Matter in RW

Bacterial Regrowth after chlorination
Growth of chlorine-tolerant microorganisms by using their growth substrates

To suppress the regrowth,

- Increase chlorine dose
- Reduce biodegradable organic matters (BOM)

Develop methods to characterize BOM in RW

Method developed to evaluate BOM

Extend Assimilable Organic Carbon (AOC) method

1. Isolate bacterial strains
2. Evaluate substrate spectra
3. Reclaimed Water, Process water from 7 RWTPs

R2A media 25 ºC, 7 days

Isolate morphologically different colonies (198 strains obtained)
rRNA gene sequencing

34 phylogenetically distinctive strains

Method developed to evaluate BOM (contd)

3. Growth pattern in RW

Iso-13 (Pseudomonas sp.)
Grown in all RW

Iso-59 (Nevskia sp.)
No Growth in A

Iso-52 (Riemerella sp.)
Grown only in C

Through steps 1-3, we screened 9 bacterial strains to be used for BOM evaluation

(Bhayanukul et al., 2013b)

Bacterial Growth Fingerprint (BGF)

Step1 Inoculation
Inoculate $10^3$ cells/mL of the isolates individually

Step2 Incubation, enumeration
Incubate at 20 ºC for 10 days

Step3 Max Growth
Flow Cytometer
Total cell counts by staining with SYBR® Green I

(Thayanukul et al., submitted)
Reclaimed water samples

Reclaimed water treatment facilities in domestic wastewater treatment plants near Tokyo, Japan.

Plant A
Secondary Effluent -> Sand Filtration -> Activated Carbon -> UV disinfection -> Chlorination

Plant B
Secondary Effluent -> Biological Filtration -> Ozonation -> Chlorination

Plant C
Secondary Effluent -> Sand Filtration -> Ozonation -> Chlorination

Growth of BGF strains in process water

Ex. 1 Iso-2 in Plant A Process water
2nd eff. Sand filtered

Ex. 2 Iso-3 in Plant C Process water
Ozonated Chlorinated

Mass spectrum before the growth

Mass spectrum after the growth

Which OM is used for the growth?

(Orbitrap MS analysis, m/z = 150-250)

Activated carbon removed substrate for all 11 strains

Ozonation produced substrate for all except for Iso-9

BGF successfully evaluated the BOM change in the reclaimed water treatment processes

What are the BOMs utilized by the strains?
BOM consumed by BGF strains

<table>
<thead>
<tr>
<th>MW</th>
<th>Formula</th>
<th>Isolates (Iso-1~9)</th>
<th>AOC P</th>
<th>NOX</th>
</tr>
</thead>
<tbody>
<tr>
<td>119.0363</td>
<td>C₆H₆O N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>123.0313</td>
<td>C₆H₆O N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>147.0314</td>
<td>C₆H₆O N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>165.0420</td>
<td>C₆H₆O N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>191.0578</td>
<td>C₆H₆O N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>211.9422</td>
<td>C₆H₆O S₂</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>214.0507</td>
<td>C₆H₆O₂N P</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>237.0634</td>
<td>C₆H₇O₃N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>259.1093</td>
<td>C₈H₉O₃N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>272.2775</td>
<td>C₁₀H₉O₃N</td>
<td>○ ○ ○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>282.0926</td>
<td>C₁₄H₁₈O₄S</td>
<td>○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>327.2775</td>
<td>C₁₉H₄₅O₇N</td>
<td>○ ○ ○ ○ ○ ○ ○</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

7 compounds out of 16 were not utilized by conventional AOC strains

⇒ BGF method can capture wide variety of BOM

Fate of BOM substances in the process

<table>
<thead>
<tr>
<th>C₆H₅O₂N (utilized by Iso-5)</th>
<th>C₁₀H₇NO₃ (utilized by Iso-1~9,NOX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Niacin)</td>
<td>(5-Hydroxyindolylacetic acid)</td>
</tr>
</tbody>
</table>

Remove by ozonation and activated carbon

May cause regrowth

Summary

- Ozonation substantially altered DOM composition
- Yet to be known DBP and their precursors can be found by the unknown screening analysis
- BOM removal/production in Reclaimed Water Treatment Processes can be described by Bacterial Growth Fingerprint (BGF) method
- BOM molecules were identified and the fate in the processes were illustrated

Reference