Managing Wastewater Treatment Plant Impacts on Air Emissions

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Outline

- Introduction
- Drivers & Standards
- Wastewater Fugitive Emissions Estimates
- Emissions Examples
  - Methanol
  - Hydrogen Sulfide
- Questions
Drivers

- Methanol
  - Hard-pipe option for MACT I compliance
    - 92% or > lb/ton of treatment
  - Clean Condensate Alternative for MACT II compliance
    - < X Lb/ton of emissions
  - Reporting

- Hydrogen Sulfide
  - Reporting

- Other Air Toxics
  - Ambient impact of wastewater fugitives
    - No real standard, maximum impact level
  - Reporting
Introduction

- Fugitive emissions from wastewater treatment sources
  - Complex chemistry and biochemistry
  - Large wastewater systems
  - Load, operation and ambient conditions are variable
- As direct measurements are unfeasible, emissions must be estimated from empirical models
  - Emissions estimates can be tailored to be very site-specific
Wastewater Treatment Plant Emissions

Turbulent Zone around Surface Aerators

Illustration by Thibodeaux
(Figure reproduced from Thibodeaux 1996, page 174)
Introduction – “Generic” Estimates

- Default estimation approach is emissions fraction based

- NCASI SARA Handbook presents emissions, effluent and removal fractions for many chemicals for a “typical” PC/ASB/AST
  - Most “air toxics”: Result of WATER9 Models
  - For methanol and H₂S: Result of field test data
Introduction – Site-Specific Estimates

- Two Types of Estimation Approaches
  - Mechanistic Modeling
    - Simulation of the behavior of a chemical in a wastewater treatment process unit or set of units along multiple fate pathways
    - NOCEPM, WATER9, H2SSIM
  - Pond Profile Based Modeling
    - Characterization of chemical emissions based upon direct measurements of in-basin concentrations and concurrent operational information
    - Appendix C Approach
Introduction – Mechanistic Modeling

- Mass-balance model that incorporates multiple pathways to simulate the site-specific behavior and fate of a chemical

- Requires WWTP characterization and declaration of biorate for each chemical

- Software Tools:
  - WATER9 & H2SSIM
Appendix C calculation procedures
- Empirical model that combines chemical concentration profile with site-specific mass transfer estimates
- Results in a “snapshot”
- Requires chemical concentrations throughout WWTP, basin characterization
- Avoids the need for information on the biological destruction rate (Can be used to calculate)
Methanol Issues

- Hard-pipe
  - Lower demonstrated treatment

- CCA
  - Higher emissions

- Issues are more often **not** related to treatment system performance
  - Methanol analysis
  - Calculation errors or changes
  - Collection issues

- Treatment issues may not be seen in monitoring of traditional effluent parameters

- May be localized to the primary hard-pipe treatment zone
ASB - Methanol Example – Baseline

\[
E_{\text{emissions}} = K_{L,1} A_1 C_1 + K_{L,2} A_2 C_2 + K_{L,3} A_3 C_3 = 63.4 \text{ g/s}
\]

\[
F_{\text{bio}} = \frac{(\text{Influent} - \text{Effluent} - \text{Emissions})}{\text{Influent}} = 0.954 = 95.4\%
\]

- **Zone 1**
  - Influent: \( C = 29.0 \text{ mg/L} \)
  - \( C_1 = 9.1 \text{ mg/L} \)

- **Zone 2**
  - \( C_2 = 2.0 \text{ mg/L} \)

- **Zone 3**
  - \( C_3 = < 0.5 \text{ mg/L} \)
  - Effluent: \( C = < 0.5 \text{ mg/L} \)
ASB - Methanol Example – Higher MeOH Concentration

Emissions = \( K_{L,1} A_1 C_1 + K_{L,2} A_2 C_2 + K_{L,3} A_3 C_3 \) = 139.4 g/s

\[ F_{bio} = \frac{(\text{Influent} - \text{Effluent} - \text{Emissions})}{\text{Influent}} = 0.899 = 89.9\% \]
Hydrogen Sulfide Issues

- Higher Emissions due to
  - Treatment system performance issues
  - Increase with lower pH
    - Emissions as “Free” $\text{H}_2\text{S}$
  - Some systems can have sulfide generation due to anaerobic activity
Sulfur Transformations in a Treatment Pond

Intermediate Sulfur forms:

- $\text{HS}^-$
- $\text{SO}_4^{2-}$

- Bacterial reduction
- $\text{CH}_3\text{COO}^-$, e.g.

- $\text{H}_2\text{S}$ gas

- Metal sulfides: Zn, Fe, Cu...

- Bacterial & chemical oxidation

- $K_H$, $pK=7$

- $K_{sp}$

- Anaerobic bacterial reduction

Chemical reactions:

- $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- \\ pK=7$

- $\text{H}_2\text{S} + \text{HS}^- \rightleftharpoons \text{SO}_4^{2-}$
### $\text{H}_2\text{S}$ Emissions – Baseline emissions

<table>
<thead>
<tr>
<th>Sample Point (SP)</th>
<th>Sulfide (ppb)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP 1</td>
<td>300</td>
<td>7.2</td>
</tr>
<tr>
<td>SP 2</td>
<td>300</td>
<td>7.2</td>
</tr>
<tr>
<td>SP 3</td>
<td>250</td>
<td>7.3</td>
</tr>
<tr>
<td>SP 4</td>
<td>100</td>
<td>7.4</td>
</tr>
<tr>
<td>SP 5</td>
<td>50</td>
<td>7.5</td>
</tr>
<tr>
<td>SP 6</td>
<td>&lt;30</td>
<td>7.5</td>
</tr>
<tr>
<td>SP 7</td>
<td>&lt;30</td>
<td>7.5</td>
</tr>
<tr>
<td>Effluent</td>
<td>&lt; 30 ppb</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Estimated Emission Rate = 0.143 g/s
### H$_2$S Emissions – Lower pH

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<tbody>
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<tr>
<td>SP 2</td>
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<td>6.8</td>
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<tr>
<td>SP 6</td>
<td>&lt;30 ppb</td>
<td>7.3</td>
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<tr>
<td>SP 7</td>
<td>&lt;30 ppb</td>
<td>7.5</td>
</tr>
<tr>
<td>Effluent</td>
<td>&lt; 30 ppb</td>
<td>7.5</td>
</tr>
</tbody>
</table>

**Estimated Emission Rate** = 0.247 g/s
## H$_2$S Emissions – Sulfide Generation

<table>
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<th>Sulfide</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP 1</td>
<td>300 ppb</td>
<td>7.2</td>
</tr>
<tr>
<td>SP 2</td>
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<tr>
<td>SP 6</td>
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<tr>
<td>SP 7</td>
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<tr>
<td>Effluent</td>
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</tbody>
</table>

Estimated Emission Rate = 0.220 g/s
Summary
Best strategy to maintain emission levels

- Methanol
  - Maintain good treatment

- Hydrogen Sulfide
  - Maintain good treatment
  - Avoid low pH spikes
  - Avoid anaerobic conditions, especially in front of the system
Questions and contact information

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