Utilizing Toxchem Wastewater Emissions Modeling to Generate Emission Reduction Credits

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Overview

• Wastewater Emissions Modeling Basics
• Two Modeling Programs: Water9 & Toxchem
• Applications of modeling
• Case Study on ERC Generation in Houston Area
Processes in a Typical Industrial Wastewater Treatment Plant

Physical Separation
- API Separators, Dissolved Air Floatation, Primary Clarifiers, etc.

Biodegradation
- Activated Sludge Units, SBRs, Secondary Clarifiers, etc.

Sorption
- Contaminants leaving system in sludge/solid phase

Volatilization
- Any interface between aqueous VOCs & atmosphere
Factors Impacting WWTP Emissions

• Ambient/Facility-wide conditions
  • Ambient Temperature
  • Elevation (i.e. Ambient Air Pressure)
  • Local Wind Speed

• Characteristics of Wastewater being treated
  • WW Temperature
  • Flow Rate(s)
  • Non-aqueous phase material (i.e. Oil/Grease, Suspended Solids)
  • Chemical Composition
Factors Impacting WWTP Emissions (cont.)

- Chemical Properties
  - Gas/liquid Partitioning (i.e. Henry’s Law Coefficient)
  - Solubility Product ($K_{sp}$)
  - Molecular Weight
  - Density
  - Liquid/solid & liquid/liquid Partitioning ($K_p$ & $K_{ow}$)
  - Biodegradability
Factors Impacting WWTP Emissions (cont.)

- Process Unit Properties
  - Dimensions (Open Surface Area, Liquid Depth)
  - Covered vs. Open Process
  - Ventilation/Aeration rates
  - Drop heights
  - Bioactivity (MLSS, SRT, etc.)
  - Mixing Power (mechanical aeration)
  - Sludge/Oil removal
Two Primary WWTP Modeling Programs:

Water9

Toxchem
## Comparison of the Models—History

<table>
<thead>
<tr>
<th>Water9</th>
<th>Toxchem</th>
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</thead>
<tbody>
<tr>
<td>• Developed by EPA/RTI in early 1990s initially</td>
<td>• Developed by Hydromantis in late-90s</td>
</tr>
<tr>
<td>• First practical wastewater emissions tool</td>
<td>• Developed partially in response to “warts” in Water9</td>
</tr>
<tr>
<td>• Support and documentation lacking since 2007</td>
<td>• Hydromantis continues to update, support, and provide documentation</td>
</tr>
<tr>
<td>• Most commonly used modeling tool in industry (free!)</td>
<td>• Up-and-coming tool for industry (requires license fee)</td>
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### Comparison of the Models—Operation/Use

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<tr>
<td>• Simplistic/sparse design</td>
<td>• User-Friendly/detailed design</td>
</tr>
<tr>
<td>• Possible to only model wastewater flows</td>
<td>• Forces modeler to account for wastewater, air, sludge, oil flows</td>
</tr>
<tr>
<td>• Errors not caught until model is running (crashes common)</td>
<td>• Built in checks &amp; balances for data/connection errors prior to running model</td>
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## Comparison of the Models—Calculations

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<td>• Volatilization: Raoult’s Law</td>
<td>• Volatilization: Mackay-Yuen</td>
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<td>• Static Equilibrium assumption</td>
<td>• Dynamic Equilibrium model</td>
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<tr>
<td>• Only considers gas phase resistance to volatilization</td>
<td>• Uses two-film theory in gas-liquid mass transfer</td>
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<tr>
<td>• Often ignores pollutants in sludge/oil phase</td>
<td>• Accounts for pollutant transport in all phases</td>
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<td>• Calculation methodology and chemical properties not documented</td>
<td>• Full documentation; Hydromantis can be contacted for questions</td>
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<tr>
<td>• Unclear which unit properties are relevant</td>
<td>• Sensitivity Analysis tool shows most impactfulful properties</td>
</tr>
<tr>
<td>• Generally a conservative model!</td>
<td>• Gives more accurate results!</td>
</tr>
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Comparison of the Models—Example 1

Mid-sized Refinery
(~2.5 MGD WW influent)
Example 1—Key Unit Comparisons

API Separators in Water9 (Modeled as “Covered Separator”)

- Simplistic diagramming
- Fate of skimmed oil, sludge unclear
- Modeled Pre-control VOC emissions: 1.77 & 1.34 tpy

API Separators in Toxchem (Modeled as “API Separator”)

- More complicated connections
- Clear Oil, Sludge, and Air emission streams
- Modeled Pre-control VOC emissions: 0.14 & 0.19 tpy

Primary difference: impact of partitioning to Oil/Grease phase
Example 1—Key Unit Comparisons

Activated Sludge Units in Water9

- Simplistic diagramming
- Modeled VOC emissions: 0.85 & 2.81 tpy
- Modeled NH$_3$ emissions: 0.16 & 0.34 tpy

Activated Sludge Units in Toxchem

- More lines to connect
- Modeled VOC emissions: 0.70 & 2.58 tpy
- Modeled NH$_3$ emissions: $2.68 \times 10^{-5}$ & $6.15 \times 10^{-5}$ tpy

Primary difference: impact of biodegradation factors & reaction rates
Comparison of the Models—Example 2

Large Refinery
(~10.1 MGD WW influent)
Comparison of the Models—Example 2

W9 VOC emissions: 154.9 tpy (~90 min)

TC VOC emissions: 88.3 tpy (~60 sec)

Decreased run time leads to more flexibility on modeling different scenarios!!!
Toxchem-Specific Features: Sensitivity Analysis Tool

Allows for quick determination of effect of varying a single parameter on overall or unit-specific emissions

• Can be used to determine optimal settings across a range of operating parameters
• Useful in understanding parameters with largest impact on emissions
• Provides graphical representations of impact on contaminant fate
Sensitivity analysis is a valuable tool; discrete changes to emissions can occur from simple changes in wastewater pH, temperature, and oil & grease fraction. The sensitivity analysis allows for quick and effective iterations of the model.
Toxchem-Specific Features: Back Solver Tool

Allows for upstream calculation of flows & concentrations via iterative methods to a specified accuracy (default 0.01%)

- Water9 only allows inlet-forward calculation
- Sometimes richer data set available at points other than WWTP inlet
- Determination of allowable influent range based on outlet specifications/limits
- Can be used in determining upstream collection system emissions (drains, catchments, manholes, lift stations, etc. ---- much more accurate than AP-42 emission factors) --- often able to achieve 5X reduction or more in drain emissions vs. AP 42
Case Study: VOC ERC Generation in Houston-Galveston-Brazoria area

Chemical Facility in HGB ozone non-attainment area

• Existing Water9 model, Sage had updated and run model for client
• Conversion to Toxchem
  • More accurate, potentially lower modeled emissions
  • Pointed study on specific fixes to WWTP for reduced VOC emissions-- Much easier in Toxchem:
    • Sensitivity analysis tool
    • Much shorter run time (~30 seconds vs ~35-40 minutes per iteration)
Case Study on ERC Generation (cont.)

Moderately Large Chemical Facility (~4-4.5 MGD)
Case Study on ERC Generation (cont.)

Initial Conversion:

• Water9 VOC emissions: 44.1 tpy
• Toxchem VOC emissions: 28.9 tpy

Important: All vessels initially uncovered

• Modeling goals:
  • Assess impact of covering process units
  • Perhaps guide in targeted roof installation
    • Two vessels contributed 17.5 of Toxchem-modeled 28.9 tpy VOC emissions
    • Objective was to generate ERC’s from covering of vessels
Case Study on ERC Generation (cont.)

Modeled Results:

- Installing roofs on all vessels (21 in total): 6.68 tpy
- Installing on two of 21 vessels with most impact: 13.2 tpy

In either case, VOC reductions are available --- either used for permit VOC offsets, or for ERC’s

Bottom line…..Toxchem is a powerful wastewater emission modeling tool that allows tremendous iterative model capability……Toxchem can and does reduce modeled VOC emissions ----- how those emission reductions are used is up to the facility --- but can certainly can be used to support ERC’s
Conclusions

Toxchem is rapidly becoming the go-to modeling software for WWTP emissions

• More accurately modeled (and almost always lower) VOC emissions
• High degree of flexibility—can model many scenarios much faster
• Continues to be developed and improved to reflect a larger array of potential WWTP process units and layouts
• Water9 truly pales in comparison and doesn’t allow the model flexibility necessary for many permitting efforts
Thank you!

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