Sustaining Your Pipes and Your Planet: Calcium Nitrate Dosing for Odor and Corrosion Control Reduces Methane in Collection Systems

Presenter: Danielle Arney, Xylem
New Sustainability Challenges

- Aging infrastructure
- Urbanization, population growth
- Climate change
- Water scarcity
- Fiscal constraints
- Regulatory

Historic stewardship of an Essential Resource

EXAMPLES OF SUSTAINABILITY GOALS WITH RELATED OBJECTIVES

<table>
<thead>
<tr>
<th>Goals</th>
<th>Examples of Possible Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Public Health</strong> - protect and improve</td>
<td>• Limit flooding in combined sewer system areas</td>
</tr>
<tr>
<td>human health and safety</td>
<td>• Reduce human contact with hazardous compounds or contaminants</td>
</tr>
<tr>
<td></td>
<td>• Reduce solids and floatables</td>
</tr>
<tr>
<td></td>
<td>• Improve receiving water quality*</td>
</tr>
<tr>
<td></td>
<td>• Achieve water quality at or below allowable contaminant limits*</td>
</tr>
<tr>
<td><strong>Value of Water &amp; Water Services</strong></td>
<td>• Improve public understanding of water services</td>
</tr>
<tr>
<td><strong>Promotion</strong> - demonstrate water service</td>
<td>• Increase public support for utility rates and investment needs</td>
</tr>
<tr>
<td>benefits to community</td>
<td></td>
</tr>
<tr>
<td><strong>Ecological Improvement</strong> - augment</td>
<td>• Improve receiving water quality*</td>
</tr>
<tr>
<td>environmental conditions in the community</td>
<td>• Meet drinking water standards</td>
</tr>
<tr>
<td></td>
<td>• Protect aquatic and terrestrial habitat</td>
</tr>
<tr>
<td></td>
<td>• Improve riparian corridor conditions</td>
</tr>
<tr>
<td></td>
<td>• Reduce greenhouse gas emissions*</td>
</tr>
<tr>
<td></td>
<td>• Improve ambient air conditions</td>
</tr>
<tr>
<td></td>
<td>• Increase greenspace</td>
</tr>
<tr>
<td><strong>Regulatory Performance</strong> - comply with</td>
<td>• Meet/exceed capture targets (e.g., CSO)</td>
</tr>
<tr>
<td>permit requirements and other</td>
<td>• Meet/exceed treatment targets</td>
</tr>
<tr>
<td>performance requirements</td>
<td>• Meet/exceed water quality based permit limits</td>
</tr>
<tr>
<td></td>
<td>• Achieve water quality at or below allowable contaminant limits*</td>
</tr>
<tr>
<td><strong>Water Resource Reliability</strong> - ensure</td>
<td>• Enhance reuse</td>
</tr>
<tr>
<td>that water availability is consistent with</td>
<td>• Encourage recharge</td>
</tr>
<tr>
<td>current and future customer needs</td>
<td>• Improve environmental flows</td>
</tr>
<tr>
<td></td>
<td>• Increase water use efficiency</td>
</tr>
<tr>
<td></td>
<td>• Improve source water protections</td>
</tr>
<tr>
<td><strong>System Resiliency and Asset Protection</strong></td>
<td>• Increase flexibility to adapt to changing conditions (e.g., water resource availability)</td>
</tr>
<tr>
<td>- minimize repair cost and prevent/protect</td>
<td>• Improve operational resilience</td>
</tr>
<tr>
<td>against damage to public infrastructure and</td>
<td>• Improve resistance to storm surges</td>
</tr>
<tr>
<td>private property</td>
<td>• Reduce flooding events</td>
</tr>
<tr>
<td></td>
<td>• Reduce basement backups</td>
</tr>
</tbody>
</table>
Global Commitment to a Sustainable Future

Sustainable Development Goals (SDGs) Nov 2015
- Protect environment and people
- Goal 6 - Safe drinking water and sanitation for all
- End goal 2030

The Paris Agreement Dec 2015
- Limit global warming to 1.5°C compared to pre-industrial levels
- Legally binding treaty

Global Methane Pledge Nov 2021
- Agreement to reduce global methane levels by 30%
- End goal 2030

193 countries
196 countries
122 countries

Adapted with permission from Mapping Water’s Carbon Footprint. GWI. Nov 2022. Home - Global Water Intelligence
Drive to Net Zero Emissions in the Water Industry

Global water utilities emit the same volume of GHGs as the world’s shipping industry

Net Zero Commitment
Decarbonization, greenhouse gas emissions reduction

Global Economic Forum: How the water sector can lead the way to net zero

Adapted with permission from Mapping Water’s Carbon Footprint. GWI. Nov 2022.
Global Warming Potentials

A relative measure of how much heat greenhouse gases trap in the atmosphere (CO$_2$e)

Overview of US Greenhouse Gas Emissions by Volume in 2021

<table>
<thead>
<tr>
<th>Gas</th>
<th>Top 3 Emission Sources</th>
</tr>
</thead>
</table>
| Carbon Dioxide     | • Transportation  
                          • Electricity  
                          • Industry |
| Methane            | • Natural gas/petroleum systems  
                          • Enteric fermentation  
                          • Landfills |
| Nitrous Oxide      | • Agricultural soil management  
                          • Wastewater treatment  
                          • Stationary combustion |
| Fluorinated Gases  | • Substitution for ozone-depleting substances  
                          • Electronics industry  
                          • Electrical transmission/distribution |

The Methane Problem in Collection Systems

Adapted from Overview of Greenhouse Gases. EPA. Last Updated April 13, 2023.

IPCC Guidelines underestimate the impact of sewer methane

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Previous Research

- Methane formation in sewer systems (Guisasola et al., 2007)
  - Lab tests and field data — Gold Coast, AUS
  - Sampled headspace of sewage containers mixed overnight
  - Retention time correlation
  - Super-saturation of methane

- Effects of nitrite concentration and exposure time on sulfide and methane production in sewer systems (Jiang et al., 2010)
  - Lab tests and field trial — Gold Coast, AUS
  - Toxic effect of nitrite on methane production
  - Inhibition = nitrite + exposure time

- Sector-wide GHG Emissions with Normalized Process and Effluent N₂O, Sewer CH₄, and Methanol CO₂ (Willis et al., 2020)
  - Theoretical analysis based on flow rates and emissions factors
  - Sewer methane 45.3% of Scope-1 emissions

The growing body of knowledge around sewer methane is beginning to set a scope to the problem, but is biased towards lab/theoretical
Theoretical Reactions

Methane generation from collection systems is an overlooked contributor to nationwide greenhouse gas emissions but can be mitigated with nitrate dosing.

Untreated Anaerobic (Sulfate) BOD Reduction (Methanol basis):

\[ \text{SO}_4^{2-} + 4\text{CH}_3\text{OH} \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O} + 2\text{CH}_4 + 2\text{CO}_2 \]

Anoxic Denitrification (Methanol basis):

\[ 6\text{NO}_3^- + 5\text{CH}_3\text{OH} \rightarrow 5\text{CO}_2 + 3\text{N}_2 + 7\text{H}_2\text{O} + 6\text{OH}^- \]

Biochemical Oxidation with Nitrates:

\[ 8\text{NO}_3^- + 5\text{H}_2\text{S} \rightarrow 5\text{SO}_4^{2-} + 4\text{N}_2 + 4\text{H}_2\text{O} + 2\text{H}^+ \]

Denitrification Process:

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]


Theoretical maximum of 88,598 MT/yr CO$_2$e prevented through dosing nitrate for odor control (current Evoqua customers)
Initial Case Study
Manatee County, Florida

Actual methane measurements in collection systems
Site Details and Experimentation

N4B
30 gpd Bioxide®

Greenbrook 2
41 gpd Bioxide®

Lakewood Ranch Riverwalk

Pope Road Master

Tara 20
166 gpd Alkagen®

- Continuous Datalogger
- Gastec Tubes
- Monitoring Data
- Tedlar Bags

- H₂S
- Dissolved Sulfide
- Chemical Dose
- Flow and Retention
- CO₂ (%)
Results Summary

24% average reduction of methane emissions during nitrate treatment

Methane Levels at N4B/N1B - Nitrate Dosing

Methane Levels at Greenbook 2/Riverwalk - Nitrate Dosing
Overview

**GOALS**
- Demonstrate actual change in methane emissions as a result of chemical dosing
- Identify baseline for typical methane levels within collection systems

**LIMITATIONS**
- Methane sensor
- Nitrous oxide measurements
- Time
- Current chemical dosing regimen

**NEXT STEPS**
- Larger data sets, including nitrous oxide and untreated data
- More robust testing equipment
Case Study
Southwest Florida Utility

Actual methane monitoring in collection systems
Site Details

- Recently constructed
- No permanent odor control onsite
- Relatively high untreated hydrogen sulfide levels
- No other FM contributors (direct nitrate correlation)
Experimentation

Dataloggers
- Continuous $\text{H}_2\text{S}$ (ppm)
- $\text{CO}_2$, $\text{CH}_4$ (ppm)

Monitoring Data
- Flow and Retention
- Chemical Dose

Grab Sampling
- Dissolved Sulfides (mg/L)
- Wastewater pH & Temp
- Nitrates (mg/L)
- $\text{N}_2\text{O}$, $\text{CH}_4$, $\text{CO}_2$ (ppm)

Tedlar Bag Sampling Apparatus
- Tubing
- Vacuum Chamber
- Wet Well
- Flux Chamber
Tedlar Bag Results - Methane

<table>
<thead>
<tr>
<th></th>
<th>Parkridge LS</th>
<th>Sienna Apartments LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg CH₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>untreated</td>
<td>66 ppm</td>
<td>297 ppm</td>
</tr>
<tr>
<td>treated</td>
<td>23 ppm</td>
<td>40 ppm</td>
</tr>
</tbody>
</table>

During nitrate treatment:
- Parkridge LS 66%
- Sienna Apartments LS 87%
### Tedlar Bag Results – Carbon Dioxide

<table>
<thead>
<tr>
<th></th>
<th>Parkridge LS</th>
<th>Sienna Apartments LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg CO₂</td>
<td>untreated</td>
<td>treated</td>
</tr>
<tr>
<td></td>
<td>563 ppm</td>
<td>481 ppm</td>
</tr>
<tr>
<td></td>
<td>1758 ppm</td>
<td>678 ppm</td>
</tr>
</tbody>
</table>

**During nitrate treatment:**

- Parkridge LS: **15%**
- Sienna Apartments LS: **61%**
# Tedlar Bag Results – Nitrous Oxide

<table>
<thead>
<tr>
<th>Date</th>
<th>Treated?</th>
<th>Parkridge LS</th>
<th>Sienna Apartments LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/17/2023</td>
<td>N</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>2/2/2023</td>
<td>N</td>
<td>0.2%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>2/8/2023</td>
<td>N</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>2/12/2023</td>
<td>N</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>2/14/2023</td>
<td>Y</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>2/20/2023</td>
<td>Y</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>2/27/2023</td>
<td>N</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>3/13/2023</td>
<td>Y</td>
<td>&lt; 5 ppm</td>
<td>7.4 ppm</td>
</tr>
<tr>
<td>3/14/2023</td>
<td>Y</td>
<td>&lt; 5 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>3/15/2023</td>
<td>Y</td>
<td>5.1 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>3/20/2023</td>
<td>N</td>
<td>&lt; 5 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>3/21/2023</td>
<td>N</td>
<td>&lt; 5 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>3/22/2023</td>
<td>N</td>
<td>-</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>3/23/2023</td>
<td>N</td>
<td>-</td>
<td>&lt; 5 ppm</td>
</tr>
</tbody>
</table>

*Only three results were above the detection limit.*
On average, a 107% increase in methane levels and a 21% increase in carbon dioxide levels was observed during nitrate treatment.
On average, a 13% decrease in methane levels and a 10% increase in carbon dioxide levels was observed during nitrate treatment.
Limitations & Future Steps

Test Equipment → Identify Robust Multi-sensor

Time → Data Validation

Environment Suitability
Long-term Datalogging
Sensitivity
H₂S, CH₄, CO₂, N₂O
Multiple Studies
Various Conditions
Other Chemicals

Quantifying End-to-End Impact of Bioxide®
Summary

- Sewer methane does contribute to water utility emissions
- Current odor control programs utilizing nitrate experience mitigation of methane emissions based on test data
Recognition of Contributors

Nick Wagner

Dave Hunniford
Vaughan Harshman

Quinn Moss
Eric Hansen
Calvin Horst
David Morano
Quintin Richards
Questions?