Efficacy of Selected Organic Microconstituents as Markers for Nitrogen and Phosphorus Loading from Reclaimed Water Plants in Florida

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I. Project Overview - Goals

To understand the relative nutrient load contributions from stormwater runoff and reclaimed water irrigation

Identify source specific conservative markers that demonstrate volumetric load contributions

Translate volumetric load contributions to nutrient loads from source concentrations and fate and transport behavior
I. Project Overview: Approach

- Establish Nutrient/Marker Concentrations in Reclaimed Water
- Marker Occurrence in other Sources and Transport Fate
- Positive and Negative Site Control Studies
I. Project Overview: Key Findings

**Nutrient and Marker Concentrations in Reclaimed Water**
- Florida reuse facility effluent 50th percentile TN is 6 mg/L
- Florida reuse facility effluent 50th percentile TP is close to 1 mg/L
- Sucralose (Splenda®) is the best conservative marker of reclaimed water loading

**Marker Occurrence in other Sources and Transport Fate**
- Sucralose also found in septic samples
- Gd anomaly and carbamazepine are two other good reclaimed water markers that occur infrequently in septic, so ratios of markers might work in distinguishing reuse and septic inputs
- Transport fate of these markers differ, but sucralose is most recalcitrant to all fate processes

**Positive and Negative Site Control Studies**
- Sucralose, Gd anomaly, and carbamazepine are detectable in golf course runoff irrigating with reclaimed water
- These same markers are absent from golf course runoff irrigating with groundwater
- These same markers are absent in stormwater ponds & present in reclaimed water irrigation collection ponds
II. Detailed Approach & Findings

**Nutrient and Marker Concentrations in Reclaimed Water**
- Characterize Florida reuse facility effluent quality (50 plant survey)
- Identify universe of potential markers and develop marker short-list
- Conduct follow-up survey of 8 representative facilities, expanded to include analysis of markers

**Marker Occurrence in other Sources and Transport Fate**
- Assess marker presence and concentrations in reuse effluent and other sources
- Determine marker presence/absence in selected waterways
- Evaluate environmental fate and transport of markers through bench-scale studies

**Positive and Negative Site Control Studies**
- Assess marker and nutrient differences at sites irrigating with reclaimed water and groundwater
- Assess capability to distinguish reuse from stormwater and septic waste
Critical Marker Characteristics

- Detectability:
  \[
  \frac{\text{Source concentration}}{\text{Analytical PQL}} > \text{Environmental Dilution Factor}
  \]

- Source Specificity:
  - Presence/Absence
  - Precision

- Environmental Fate during Transport:
  - Conservative
  - Mimic Nutrient Fate Behavior
Short-list of Markers

<table>
<thead>
<tr>
<th>Marker</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atenolol</td>
<td>Beta blocker</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>Mood stabilizer</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>NMR imaging compound</td>
</tr>
<tr>
<td>Galaxolide (HHCB)</td>
<td>Synthetic musk fragrance</td>
</tr>
<tr>
<td>Iohexal</td>
<td>X-ray contrast media</td>
</tr>
<tr>
<td>Sucralose</td>
<td>Sugar substitute (Splenda®)</td>
</tr>
<tr>
<td>Stable C,N,O Isotopes</td>
<td>Naturally present</td>
</tr>
</tbody>
</table>
II. Detailed Approach and Findings

Survey Nutrient and Marker Concentrations in Reclaimed Water

- Characterize Florida reuse facility effluent quality (50 plant survey)
- Identify universe of potential markers and develop marker short-list
- Conduct follow-up survey of 8 representative facilities, expanded to include analysis of markers

Marker Occurrence and Fate in the Environment

- Assess marker presence and concentrations in reuse effluent and other sources
- Determine marker presence/absence in selected waterways
- Evaluate environmental fate and transport of markers through bench-scale studies

Positive and Negative Site Control Studies

- Assess marker and nutrient differences at sites irrigating with reclaimed water and groundwater
- Assess capability to distinguish reuse from stormwater and septic waste
### Detectability: Marker Presence in US Waterways with & without WW Discharges

<table>
<thead>
<tr>
<th>Compound (MRL, ng/L)</th>
<th>Wastewater Effluent Mean (ng/L)</th>
<th>Waterway with WW Discharges (% Detects)</th>
<th>Waterway without WW Discharges (% Non-detects)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucralose (100)</td>
<td>27,000</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbamazepine (5)</td>
<td>416</td>
<td>36</td>
<td>100</td>
</tr>
<tr>
<td>Atenolol (5)</td>
<td>1,310</td>
<td>45</td>
<td>92</td>
</tr>
<tr>
<td>Iohexal (10)</td>
<td>4,780</td>
<td>45</td>
<td>100</td>
</tr>
</tbody>
</table>

Source Specificity: Sucralose Presence in Reclaimed Effluent
**8 Florida Septic System Marker Levels**

<table>
<thead>
<tr>
<th>Sucralose (ng/L)</th>
<th>Carbamazepine (ng/L)</th>
<th>Gadolinium Anomaly* (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>69,000</td>
<td>&lt;5</td>
<td>0</td>
</tr>
<tr>
<td>40,000</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>80,000</td>
<td>&lt;5</td>
<td>0</td>
</tr>
<tr>
<td>42,000</td>
<td>&lt;5</td>
<td>3</td>
</tr>
<tr>
<td>24,000</td>
<td>55</td>
<td>1</td>
</tr>
<tr>
<td>40,000</td>
<td>&lt;5</td>
<td>1</td>
</tr>
<tr>
<td>12,000</td>
<td>&lt;5</td>
<td>1</td>
</tr>
<tr>
<td>12,000</td>
<td>&lt;5</td>
<td>2</td>
</tr>
</tbody>
</table>

*Ranged from 17 to 139 in 12 water reuse effluent samples*
Presence of Sucralose in Loxahatchee Canals (Dry Season)
## Fate Behavior Suggested from Experiments

<table>
<thead>
<tr>
<th>Compound</th>
<th>Adsorption</th>
<th>Biodegradation</th>
<th>Photodegradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atenolol</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Galaxolide</td>
<td>Yes</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Iohexal</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Sucralose</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
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Survey Nutrient and Marker Concentrations in Reclaimed Water

- Characterize Florida reuse facility effluent quality (50 plant survey)
- Identify universe of potential markers and develop marker short-list
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Marker Occurrence and Fate in the Environment

- Assess marker presence and concentrations in reuse effluent and other sources
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Positive and Negative Site Control Studies

- Assess marker and nutrient differences at golf courses irrigating with reclaimed water and groundwater
- Assess capability to distinguish reuse effluent from stormwater and septic infiltration
## Marker Values at PBC Golf Courses Irrigating with Reclaimed Effluent & Groundwater

<table>
<thead>
<tr>
<th>Marker</th>
<th>Rainfall</th>
<th>Reclaimed Effluent Source</th>
<th>Ground Water Source</th>
<th>Reclaimed Effluent Runoff</th>
<th>Ground Water Runoff</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}C_{\text{o/oo}}$</td>
<td>-22.76</td>
<td>-31.19</td>
<td>-24.05</td>
<td>-20.28</td>
<td>-19.93</td>
</tr>
<tr>
<td>Sucralose (ng/L)</td>
<td>&lt;100</td>
<td>14,000</td>
<td>&lt;100</td>
<td><strong>1,100</strong></td>
<td>&lt;100</td>
</tr>
<tr>
<td>Carbamazepine (ng/L)</td>
<td>&lt;5</td>
<td>160</td>
<td>&lt;5</td>
<td>33</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Atenolol (ng/L)</td>
<td>&lt;5</td>
<td>290</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Iohexal (ng/L)</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Galaxolide (ng/L)</td>
<td>&lt;5</td>
<td>3,800</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Gd Anomaly (ng/L)</td>
<td>1.1</td>
<td>68</td>
<td>2</td>
<td><strong>29</strong></td>
<td>3.5</td>
</tr>
</tbody>
</table>
### Distinguishing Reuse from Stormwater

<table>
<thead>
<tr>
<th>Site Type</th>
<th>Sucralose (ng/L)</th>
<th>Carbamazepine (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW Retention Pond (n=3)</td>
<td>ND*</td>
<td>ND</td>
</tr>
<tr>
<td>Irrigation Collection Pond (n=3)</td>
<td>3300-5500</td>
<td>5.3 – 7.8</td>
</tr>
</tbody>
</table>

*One detect @ 150 ng/L
Gd/Sucralose Ratio Analysis

The graph shows the Gd/Sucralose ratio analysis with different zones for unreliable and reliable data. The x-axis represents Sucralose in ng/L, while the y-axis represents Gd/Sucralose (x1000). The data points are categorized into various sources:

- **Reuse Effluent**
- **Septic Tank**
- **Pond (Stormwater Runoff)**
- **Lake Marden**
- **Pond (Reuse Irrigation)**
- **Palm Beach Reuse Fertigation**
- **Reuse Fertigation Runoff**
- **Septic Influenced Canal**

The graph distinguishes between a reliable zone and an unreliable zone, with data points falling within these zones indicating the ratio analysis results for different sources.
III. Future Work – Assessment of Nutrient Impaired Water Bodies

• Conduct survey of representative statewide nutrient impaired water bodies to assess wastewater loading impacts by:
  – Analyzing for presence of sucralose
  – Analyzing additional markers as sucralose ratios in order to identify presence of septic loading
  – Interpret data findings as approximate relative percentages of wastewater and septic source loading
  – Translate each source load to a worst-case nutrient load estimate

• Establish links between water quality models and proven markers
Proposed Monitoring Scheme for Assessment of Impaired Water Bodies

1. Does impaired waterbody contain sucralose?
   - NO: Wastewater load < 1%; Investigate alternative watershed inputs
   - YES: Does watershed contain septic systems?
     - NO: (a) Estimate maximum wastewater fractional load contribution to waterbody from ratio of sucralose concentration in waterbody to reclaimed effluent concentration; (b) Multiply this fraction by maximum observed reclaimed effluent nutrient concentrations to estimate maximum possible nutrient mass loading from wastewater.
     - YES: Measure gadolinium anomaly and carbamazepine concentrations. If detected, use ratios with sucralose to estimate fractional input load from municipal wastewater. Fractional load estimate for septic dependent upon site specific evaporation and precipitation data and fate and transport studies for these compounds.

To refine assessment of wastewater load's contribution to nutrient impairment, additional site specific fate and transport modeling is required.
Potential Utility Applications

• Assess zone of impact of reclaimed effluent recharge to groundwater
• Identify septic intrusion to canals
• Estimate reclaimed effluent percentage loading to waterbodies
Acknowledgments

• WateReuse Research Foundation
  – City of North Port
  – City of Orlando
  – City of Pompano Beach
  – Florida Department of Environmental Protection
  – Hillsborough County
  – JEA
  – Loxahatchee River District
  – Miami-Dade Water and Sewer Department
  – Orange County Utilities Department
  – Palm Beach County
  – South Florida Water Management District
  – Southwest Florida Water Management District
  – St Johns River Water Management District
Sucralose Presence in Waterways With and Without Municipal Point Source Discharges

Concentration, ng/L

Wastewater Effluent  Impacted Source  Clean Source
Carbamazepine Presence in Water bodies With and Without Municipal Point Source Discharges

![Box plot showing concentration of Carbamazepine in water bodies with and without municipal point source discharges.](image-url)
Correlation of Sucralose and TP in Loxahatchee Canals
### Hillsborough County Sampling

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Units</th>
<th>Woodberry</th>
<th>Calusa</th>
<th>Van Dyke</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nutrients</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂-N</td>
<td>mg/L</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>NO₃ –N</td>
<td>mg/L</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>mg/L</td>
<td>0.61</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>TKN</td>
<td>mg/L</td>
<td>2.9</td>
<td>0.74</td>
<td>0.84</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>mg/L</td>
<td>0.051</td>
<td>0.088</td>
<td>ND</td>
</tr>
<tr>
<td>TP</td>
<td>mg/L</td>
<td>0.26</td>
<td>0.1</td>
<td>0.027</td>
</tr>
<tr>
<td><strong>Markers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atenolol</td>
<td>ng/L</td>
<td>29</td>
<td>21</td>
<td>14</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>ng/L</td>
<td>5.3</td>
<td>7.8</td>
<td>5.3</td>
</tr>
<tr>
<td>Iohexol</td>
<td>ng/L</td>
<td>ND</td>
<td>28</td>
<td>ND</td>
</tr>
<tr>
<td>Sucralose</td>
<td>ng/L</td>
<td>3300</td>
<td>4400</td>
<td>5500</td>
</tr>
<tr>
<td>Galaxolide</td>
<td>ng/L</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Gd Anomaly</td>
<td>ng/L</td>
<td>2</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>
Potential Sources of Nutrient Loading to Waterways

- **Wastewater:** Municipal Discharge, Reuse, OWTS (Septic)
- **Stormwater:** Paved Surface, Animal Waste, Vegetation, Detergents, Fertilizer
- **Atmospheric Deposition:** Falling particles, Gas absorption, Rain

Receiving Water Body
Presence of Sucralose in Loxahatchee Canals (Wet Season)

Nitrogen

Note: All sites had TN concentrations below reference level (i.e. <2 mg/L)
I. Project Overview - Next Steps

• Sucralose should be used to identify reclaimed water/septic in nutrient impaired water bodies
  – **NO** sucralose, **NO** reclaimed influence


  – Sucralose can provide a conservative estimate of nutrient contribution into a waterbody
Location of 50 Reuse Facilities Surveyed
Location of Eight Plant Follow-Up Survey
Nutrients in 50 Plant Survey and 8 Plant Follow-up Survey
Performance Based Treatment Systems (PBTS)

Wakulla County Septic Tank Study

Phase II Report on Performance Based Treatment Systems

FDEP AGREEMENT NO: WM926

The Florida State University
Department of Earth, Ocean and Atmospheric Science

December 7, 2010
Prepared by

Harmon Harden¹, Jeffrey Chanton², Richard Hicks³ and Edgar Wade⁴

Legend
- Phase II Study Site
- Spring
- Karst Plain Area

Tallahassee Region

HOOT (suspended nitrifiers)

FAST – 3 Tanks (fixed nitrifiers)

FAST – Dual Chamber (fixed nitrifiers)
Nitrogen and Oxygen Stable Isotope Composition of Nitrate Sources

www/geo.sunysb.edu/reports/bleifuss/figures/fig5.html
Golf Course Irrigation Runoff with and without use of Reclaimed Water

- Atmospheric Nitrates
- Denitrification
- Nitrate Fertilizer
- Nitrification
- NH4 Fertilizer
- Septic Animal Wastes

- Reuse Effluent
- PBTS
- Rainfall
- Runoff Phairway Reuse
- Runoff Potable Source

\[ \delta O_{18} \]

\[ \delta N_{15} \]
Stable Isotopes as Possible Markers

- $\delta^{15}$N signature has been used to discern wastewater input
- $\delta^{13}$C might also be an indicator of wastewater nitrogen sources

- $\delta$ notation denotes ratio of ratios multiplied by 1000

$$\delta X = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000$$

where:
- $X$ is the element (C or N), and
- $R$ is the ratio of the heavy and light isotopes in the sample and the standard ($C^{13}/C^{12}$ or $^{15}N/^{14}N$)
Conventional Septic Systems

Loxahatchee Region

- Manhole cover removed
- Bottle inverted through scum
- Wastewater sample collected
Septic Effluent Nutrient Performance

• PBTS EFFLUENT RESULTS:
  - $T_{N\text{mean}} = 30 \text{ mg/L (prior study)}$
  - $T_{N\text{mean}} = 22 \text{ mg/L (this study) (5.2 to 31 mg/L range)}$
  - $T_{P\text{mean}} = 7.7 \text{ mg/L (this study) (5.1 to 9.6 mg/L range)}$

• CONVENTIONAL EFFLUENT RESULTS:
  - $T_{N\text{mean}} = 92 \text{ mg/L (32 to 130 mg/L range)}$
  - $T_{P\text{mean}} = 11.6 \text{ mg/L (5.3 to 15 mg/L range)}$

• Marker consistently >100 times MRL:
  - Sucralose
  - Ratio of markers might distinguish septic from reuse