Development of Markers to Identify Nutrient Sources Impacting Surface Water Bodies

Webcast on WateReuse Research Foundation Tailored Collaboration Project

May 16, 2013
Participants

- South Florida Water Management District
- Southwest Florida Water Management District
- St. Johns River Water Management District
- Loxahatchee River District
- Hillsborough County
- Orange County
- Palm Beach County
- City of Orlando
- City of North Port
- City of Pompano Beach
- Florida Department of Environmental Protection
- Jacksonville Electric Authority
- Miami-Dade Water and Sewer Department


Badruzzaman, M., Oppenhiemer, J.A. and Jacangelo, J.G. “Impact of environmental conditions on the suitability of selected microconstituents as markers for identifying nutrient loading into surface waters from reclaimed water.” (submitted to Water Research).
Webcast Presentation Outline

- Project Background & Objectives
- Project Approach & Key Findings
- Reuse Nutrient Survey
- Marker Selection & Behavior
- Field Sampling Results
- Study Conclusions
- Future Work for Tool Development
Project
Background & Objectives
Nutrient loading is a major cause of water quality impairment

Vital to understand water reuse’s contribution toward nutrient impairment of waterways

Many TMDLs have nutrient load allocations associated with reclaimed water irrigation
What factors impact nutrient application rate estimation and subsequent loading to water bodies?
Characterize reclaimed water irrigation as a nutrient source

Identify conservative marker(s) for assessing reclaimed water volumetric load contributions

Translate volumetric load contributions to nutrient loads from source concentrations and fate and transport behavior
Project Approach & Key Findings
Establish Nutrient/Marker Concentrations in Reclaimed Water

Marker Occurrence in other Sources and Transport Fate

Positive and Negative Site Control Studies
Study Approach

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
Project Key Findings

- Sucralose can 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.
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 absent in stormwater ponds & present in irrigation collection ponds
Reuse Nutrient Survey
96 samples were collected from WWTP effluents, WWTP ponds, and golf course ponds.

45 reuse plants with capacities ranged from 0.01 to 35 mgd (2007 capacity) were covered.
Location of Eight Plant Follow-Up Survey
## Nitrogen and Phosphorus Data Summary

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average (mg/L)</th>
<th>Median (mg/L)</th>
<th>Min (mg/L)</th>
<th>Max (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Phosphorus</td>
<td>2.03</td>
<td>1.30</td>
<td>0.02</td>
<td>16.0</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>7.92</td>
<td>6.10</td>
<td>0.13</td>
<td>29.1</td>
</tr>
</tbody>
</table>
Nutrients in 50 Plant Survey and 8 Plant Follow-up Survey
Marker
Selection & Behavior
Two Types of Markers

– Conservative Source Markers: source specific stable concentrations with conservative transport behavior

– Nutrient Fate Markers: mimic environmental fate properties of nutrients
# 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>
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
## Marker Presence in US Waterways with and without Municipal Wastewater 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>1310</td>
<td>45</td>
<td>92</td>
</tr>
<tr>
<td>Iohexal (10)</td>
<td>4780</td>
<td>45</td>
<td>100</td>
</tr>
</tbody>
</table>

Sucralose Presence in Reuse Effluent Independent of Treatment
<table>
<thead>
<tr>
<th>Compound</th>
<th>Reuse Water (n=8)</th>
<th>Septic Tank* (n=8)</th>
<th>Rain-water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucralose</td>
<td>29,000 ± 6,000</td>
<td>40,000 ± 24,700</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>230 ± 8</td>
<td>16 ± 20</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Atenolol</td>
<td>1,300 ± 880</td>
<td>8.1 ± 6.3</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Iohexol</td>
<td>5,400 ± 3500</td>
<td>&lt;10 ± 0.7</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Galaxolide</td>
<td>1,000 ± 300</td>
<td>2,700 ± 2,700</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Gd Anomaly</td>
<td>30 ± 14</td>
<td>1.5 ± 1.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* Units are in ng/L and only 4 samples for carbamazepine, atenolol, and iohexol in reuse water
# 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*
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

Tallahassee Region

HOOT
(suspended nitrifiers)

FAST – 3 Tanks
(fixed nitrifiers)

FAST – Dual Chamber
(fixed nitrifiers)
Conventional Septic Systems

Loxahatchee Region

- Manhole cover removed
- Bottle inverted through scum
- Wastewater sample collected
• PBTS EFFLUENT RESULTS:
  – $T_{N_{\text{mean}}}$ = 30 mg/L (prior study)
  – $T_{N_{\text{mean}}}$ = 22 mg/L (this study) (5.2 to 31 mg/L range)
  – $T_{P_{\text{mean}}}$ = 7.7 mg/L (this study) (5.1 to 9.6 mg/L range)

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

• Marker consistently $>$100 times MRL:
  – Sucralose
  – Ratio of markers might distinguish septic from reuse
# Fate Behavior from Bench-scale 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>

*Yes = >10% adsorption, >15% biodegradation, >10% photolysis*
Field Sampling Results
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 golf courses irrigating with reclaimed water and groundwater
- Assess capability to distinguish reuse effluent from stormwater and septic infiltration
Field Sampling Event: Golf Courses

- Sampled stormwater runoff and stormwater ponds from two golf courses
  - Golf Course A: Groundwater Irrigation
  - Golf Course B: Reclaimed Water
- Controlled irrigation
- Both golf courses apply fertilizer
- Samples obtained after rain event from:
  - Water used for irrigation (end of pipe)
  - Stormwater runoff
  - Stormwater pond
### 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>δC13 (‰)</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>1,100</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>3800</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>29</td>
<td>3.5</td>
</tr>
</tbody>
</table>

*Note: The numbers in red are the values of interest.*
Field Sampling Event: Retention Ponds RW

- Objective: Evaluate level of markers and nutrients in retention ponds located in residential areas irrigating with reclaimed water.
- Uncontrolled irrigation.
- Wastewater treated to advance waste treatment levels - 5/5/3/1 mg/L (BOD$_5$/SS/TN/TP).
- No septic influence.
# Field Sampling Event: Retention Ponds RW

<table>
<thead>
<tr>
<th>Compound</th>
<th>Units</th>
<th>Woodberry</th>
<th>Calusa</th>
<th>Van Dyke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen</td>
<td>mg/L</td>
<td>2.9</td>
<td>0.74</td>
<td>0.84</td>
</tr>
<tr>
<td>Total-P</td>
<td>mg/L</td>
<td>0.26</td>
<td>0.1</td>
<td>0.027</td>
</tr>
<tr>
<td>Sucralose</td>
<td>ng/L</td>
<td>3,300</td>
<td>4,400</td>
<td>5,500</td>
</tr>
<tr>
<td>Gd Anomaly</td>
<td>ng/L</td>
<td>2</td>
<td>4</td>
<td>3</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>&lt;PQL</td>
<td>28</td>
<td>&lt;PQL</td>
</tr>
<tr>
<td>Atenolol</td>
<td>ng/L</td>
<td>29</td>
<td>21</td>
<td>14</td>
</tr>
</tbody>
</table>

1 Total nitrogen was present as organic nitrogen at all sites with exception of Woodberry which had 0.61 mg/L of ammonia
## 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
Field Sampling Event: Canals/Septic

- Objective: Assess the presence of markers and nutrients in canals adjacent to areas with septic systems.
- Canals discharge into the Loxahatchee River, Florida’s only Wild and Scenic River.
- 29 sample locations plus two reference points located in a non-urbanized area.
- Samples taken during Florida’s dry and wet seasons.
### Field Sampling Result: Canals/Septic

<table>
<thead>
<tr>
<th>Compound</th>
<th>Units</th>
<th>Septic System</th>
<th>Canals Dry Season</th>
<th>Canals Wet Season</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen</td>
<td>mg/L</td>
<td>32 -130</td>
<td>0.67 - 18</td>
<td>0.74 - 1.84</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>mg/L</td>
<td>5.3 -15</td>
<td>0.012 - 1.7</td>
<td>0.012 - 0.16</td>
</tr>
<tr>
<td>Sucralose</td>
<td>ng/L</td>
<td>40,000 - 80,000</td>
<td>ND$^1$ - 750</td>
<td>ND$^1$ - 310</td>
</tr>
</tbody>
</table>

$^1$ND=non-detect; however sucralose was found in all samples except the 2 reference locations when levels between the MDL and PQL were included.
Presence of Sucralose in Loxahatchee Canals (Dry Season)
Presence of Sucralose in Loxahatchee Canals (Wet Season)

Reference Samples in Natural Areas

Sucralose
- Non Detected
- >100 ng/L

Nitrogen
- >2.0 mg/L

Note: All sites had TN concentrations below reference level (i.e. <2 mg/L)
Study
Conclusions
1) Identified sucralose as a master diagnostic tool to distinguish wastewater derived nonpoint sources
2) Absence of sucralose indicates <1% loading
3) Sucralose concentration estimates wastewater load fraction in receiving water
4) Secondary microconstituents can be developed to utilize in tandem with sucralose in order to differentiate between septic and reuse sources of wastewater derived nonpoint loading
Sucralose?

- YES: Subtract sucralse from WW NPDES discharge
  - YES: Remaining sucralse?
    - YES: Sucralse >3µg/L?
      - YES: Gd anomaly x 1000 <1.0
        - YES: Determine actual reuse loading based on site specific evaluation
      - NO: Non-point runoff has sucralse?
        - YES: Determine actual reuse loading based on site specific evaluation
        - NO: Waterbody not impacted by septic or reuse
          - YES: Determine actual reuse loading based on site specific evaluation
  - NO: Waterbody not impacted by septic or reuse
    - YES: Determine actual reuse loading based on site specific evaluation

- NO: WW nutrient load <1%
  - Calculate potential maximum % nutrient load based on % sucralse
  - Calculate volumetric load based on % sucralse
  - Determine actual reuse loading based on site specific evaluation
Next Steps for Tool Development
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
TMDL Process

303d list

Total Maximum Daily Load

NUTRIENT SOURCE
- Stormwater
- Reclaimed water
- Septic effluent
- WWTP effluent
- Air deposition
- Fertilizer

Identify Nutrient Source Contribution

Basin Management Action Plan (BMAP)
WRRF Nutrient Tool in TMDL Process

NUTRIENT SOURCE
- Stormwater
  ✓ Reclaimed water
  ✓ Septic effluent
  ✓ WWTP effluent
- Air deposition
- Fertilizer

Total Maximum Daily Load

WRRF Nutrient Tool

Identify Nutrient Source Contribution

303d list

Basin Management Action Plan (BMAP)

WRRF Nutrient Tool is expected to provide a proven and well-tested tool that can clearly identify the source and quantity of nutrient loading to support the Basin Management Action Plan (BMAP).