Regional Water Quality Issues:
Algae and Associated Drinking Water Challenges

Workshop – September 2011

A Cooperative Research and Implementation Program
Arizona State University (Tempe, AZ)
Paul Westerhoff
Chao-An Chiu, Jacelyn Rice, Kyle Doudrick, David Hanigan

Salt River Project
Central Arizona Project
City of Tempe
City of Peoria
City of Glendale
City of Chandler
Arizona Water
Agenda

Purpose: Provide a forum to review and discuss on-going regional water quality issues, in particular algae-associated issues.

- 830 am  Snacks and coffee
- 845 am  Introductions and key questions
- 900am  Water Quality Update and Overview (Westerhoff)
- 925am  Taste and Odors in Canals – Will it ever happen again? (Westerhoff)

Water Supplies in light of climate changes
- 935am  Water quality responses under different climatic situations (Chiu)
- 905-10am  Stretch
- 1005 am  How much wastewater is in our drinking water supply (Rice)
- 1015am  Groundwater – how do we deal with nitrate (Doudrick)

Treatment of organics and T&O using Activated carbon
- 1040am  In-situ GAC regeneration: Progress and a Path Forward (Chiu)
- 1055am  Jar Testing with PAC (Hanigan)

Open Discussion on research needs for next year and feedback
- 1130am  Workshop concludes
Introductions

Name?

Affiliation?

What do you want to hear today?
Workshop will present results as water moves down through the watershed.
Salt River Above Roosevelt

High flows are between Dec 15-Mar 31 usually

Period of major T&O Challenges
Verde River Above Horseshoe Reservoir (at Tangle Creek)

Inflows bring:
- Water
- Nutrients
- DOC

All 3 high flows were in January
Hydrology Affects Water Quality
(conductance can affect algal dominance)

Lake Pleasant
Bartlett Lake
Saguaro Lake

Conductivity (μs/cm)

Reservoir Stratification over the years

Bartlett Lake winter & summer

Temperature (°C)

DO (mg/L)
Reservoirs are destratifying

Saguaro Lake
Reservoir Conditions Affect Water Quality

Lake Pleasant
Arsenic

MCL = 10 μg/L

Arsenic (μg/L)

Pleasant Hypo
Bartlett Hypo
Saguaro Hypo
Secchi Disk Depth Influenced by Inorganic Suspended Sediment and/or Organic Biomass

Low values in Bartlett: Jan-Feb due to rains
Low values in Saguaro: early summer due to algae blooms
Common Algal T&O Compounds

- Taste threshold ~ 10 ng/L
- Chlorine residual can “mask” odors
- T&O is a worldwide issue affecting the publics “confidence” in drinking waters, but is not regulated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MIB (2-methyisoborneol)</th>
<th>Geosmin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Name</td>
<td>(1-R-exo)-1,2,7,7-tetramethyl bicyclo-[2,2,1]-heptan-2-ol</td>
<td>tran-1, 10-dimethyl-trans-9-decalol</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>C₁₁H₂₀O</td>
<td>C₁₂H₂₂O</td>
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<tr>
<td>Molecular Weight</td>
<td>168 g-mole⁻¹</td>
<td>182 g-mole⁻¹</td>
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<tr>
<td>Boiling Point</td>
<td>197 °C</td>
<td>165 °C</td>
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<tr>
<td>Aqueous Solubility</td>
<td>195 mg/L</td>
<td>150 mg/L</td>
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<tr>
<td>Kᵣₒw</td>
<td>3.13</td>
<td>3.7</td>
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<tr>
<td>Henry’s Law Constant</td>
<td>5.76×10⁻⁵ atm m³-mole⁻¹</td>
<td>6.66×10⁻⁵ atm m³-mole⁻¹</td>
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<tr>
<td>Structure</td>
<td><img src="image" alt="MIB Structure" /></td>
<td><img src="image" alt="Geosmin Structure" /></td>
</tr>
</tbody>
</table>

Source: (Pirbazari et al. 1992)
Possible MIB/geosmin producing cyanobacteria

On our website:
INTERACTIVE TAXONOMIC GUIDE
http://enpub.fulton.asu.edu/pwest/tasteandodor.htm
MIB Data – Lake Pleasant

Lake Pleasant Epilimnion (R2A)

Lake Pleasant Hypolimnion (R2B)
MIB Data – Bartlett Lake

Bartlett Lake Epilimnion (R6A)

Bartlett Lake Hypolimnion (R6B)

Saguaro MIB = 0.15e^{0.21x} R^2 = 0.64
Bartlett MIB = 0.0013e^{0.35x} R^2 = 0.80
MIB Data – Saguaro Lake

Cells die and settle into darkness

Saguaro Lake Epilimnion (R9A)

Saguaro Lake Hypolimnion (R9B)
## Most Recent Data (Sept 14)

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Location</th>
<th>MIB (ng/L)</th>
<th>Geosmin (ng/L)</th>
<th>Cyclocitral (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Pleasant (August 11)</td>
<td>Eplimnion</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Lake Pleasant (August 11)</td>
<td>Hypolimnion</td>
<td>2.6</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Verde River @ Beeline</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bartlett Reservoir</td>
<td>Eplimnion</td>
<td>17.8</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Bartlett Reservoir</td>
<td>Epi-near dock</td>
<td>22.9</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Bartlett Reservoir</td>
<td>Hypolimnion</td>
<td>&lt;2.0</td>
<td>2.5</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Salt River @ BluePt Bridge</td>
<td></td>
<td>7.6</td>
<td>3.7</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Saguaro Lake</td>
<td>Eplimnion</td>
<td>34.9</td>
<td>4.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Saguaro Lake</td>
<td>Epi-Duplicate</td>
<td>35.0</td>
<td>4.1</td>
<td>&lt;2.0</td>
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<tr>
<td>Saguaro Lake</td>
<td>Epi-near dock</td>
<td>32.9</td>
<td>5.9</td>
<td>&lt;2.0</td>
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<tr>
<td>Saguaro Lake</td>
<td>Hypolimnion</td>
<td>13.1</td>
<td>2.0</td>
<td>&lt;2.0</td>
</tr>
</tbody>
</table>
Lake Destratification

**Thermally Stratified**
- Algae & MIB are on top
- Dead cells sink and release MIB

**Post-stratification**
- Algae & MIB mix with depth
- Increased MIB in outlet
- Food and O2 fuels rapid biodegradation
MIB Growth in AZ canal from below X-Con to Central Ave.

What changed after 2006?
-After long-term drought
- lower conductivity water
- Less frequent changes in water blending
- SRP cleaned out forebay below Pima in 2006
Algae Removal Demonstrations (July 2004)
Copper Application
MIB levels higher in AZ Canal system compared against South Canal system.
T&O Production Trend Summary

- Significant MIB production potential in the Arizona Canal between Pima and Central
- Historically geosmin production in Consolidated canal – but no MIB or geosmin change this year
MIB Removal at WTPs (September 2011)

Tempe Tap Water MIB = 13 ng/L; Geosmin = 3 ng/L
T&O Trends

- Saguaro Lake has consistently produced the highest levels of T&O.
- Verde River can produce T&O below Bartlett Reservoir.
- Minimal production of T&O in canals over the past ~ 5 years:
  - Prior > 50 ng/L MIB or geosmin could form in canals.
  - Significant MIB production potential in the Arizona Canal between Pima and Central.
  - Historically geosmin production in Consolidated canal – but no MIB or geosmin change this year.
Up-stream reservoirs attenuate DOC
Specific UV Absorbance at 254 nm

S UVA (L/m/mg)

Pleasant  Bartlett  Saguaro

Roosevelt Lake

- 2003 (August)  DOC = 4.9 mg/L
- 2005 data (April)
  - DOC = 6.7 mg/L
  - SUVA = 2.8 (L/mg-m)

- 2009
  - January
    - DOC = 4.2 mg/L
    - SUVA = 2.6 (L/mg-m)
  - May
    - DOC = 4.2 mg/L
    - SUVA = 2.3 (L/mg-m)

- 2011 data
  - July
    - DOC = 3.6 mg/L
    - SUVA = 1.7 (L/mg-m)
  - Sept*
    - DOC = 4 mg/L
    - SUVA = 1.7 (L/mg-m)
  - *MIB: 25 ng/L (epi) & 2 ng/L (hypolimnion)
DOC Removal by WTP


Avg DOC (mg/L)

24th Street WTP | DV WTP | VV WTP | Green WTP | NP WTP | SPT WTP | UH WTP | GL WTP | CH WTP
Removal of Size Fractions by Different Unit Processes

Molecular Weight (Da)

Time series of in-line DOC signal output
Coagulation Dose Impacts Organic Size Distribution

SEC-DOC Analysis

DOC Response vs. MW (Da)

- 0ppm
- 2.5ppm
- 5ppm
- 10ppm
- 25ppm
- 50ppm
Tempe WTPs DOC Responses

South Tempe Water Treatment Plant

- Raw water
- Pre-sedimentation
- Post-sedimentation
- Filtration Effluent
- Post-UV

JGM Water Treatment Plant

- Raw water
- Pre-Sedimentation
- Post-sedimentation
- Filtration Effluent
- Post-UV

52% 48% 30%

59% 30% 32%
Peoria and Gilbert WTP

Ozonation helps breakdown of large MW OM but won’t remove DOC significantly
Chandler Pecos SWTP Actiflo vs. Conventional Processes

**Ballasted Flocc helps in removing of large MW and medium MW organic matters.**

<table>
<thead>
<tr>
<th>Fractional Removal</th>
<th>Large MW</th>
<th>Medium MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ballasted Flocc</td>
<td>58%</td>
<td>40%</td>
</tr>
<tr>
<td>C/F/S</td>
<td>30%</td>
<td>30%</td>
</tr>
</tbody>
</table>
Membrane Filtration vs. Conventional Processes with GAC Contactors

- Membrane filtration enhances the removal of large MW OM.
- GAC removes medium and low MW OM further.

Water Campus WTP
Deep Bed GAC adsorber with conventional units

<table>
<thead>
<tr>
<th>Fractional Removal</th>
<th>Large MW</th>
<th>Medium MW</th>
<th>Low MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>51%</td>
<td>19%</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>C/F/S</td>
<td>44%</td>
<td>35%</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>GAC</td>
<td>-</td>
<td>56%</td>
<td>55%</td>
</tr>
</tbody>
</table>
Membranes Remove Some TOC

Major benefit of membranes is multi-barrier approach for pathogen reduction.
Membrane Filtration with GAC Contactors (Scottsdale)

- Membrane filtration enhances the removal of large MW OM but not medium and small MW OM.
- GAC removes medium and low MW OM further.
DOC Summary

- **DOC levels in Lakes right now**
  - Bartlett Lake (Verde River): 3.6 mg/L
  - Saguaro Lake (Salt River): 5.0 mg/L
  - Lake Pleasant (CAP): 3.4 mg/L

- Limited impact from Wallow Fire on DOC in Roosevelt Lake (yet)

- Winter rains is what transport most of the DOC into the reservoirs

- Each unit process removes different size fractions of organic matter
Potential Influences of Climate Change on Arizona Water Supply (A. Ellis) conclusions:

- Region has warmed over the past century & projected to warm during remainder of 21st century – little uncertainty
- Regional precipitation has changed little over the past century; recent drought of early 2000s evidenced in a trend back to long-term mean
- Much uncertainty in projected precipitation during rest of the century – majority of GCM-GHG models => less precipitation
- Virtually all local-to-regional hydrologic projections (indicate less runoff (-10% to -20%), but with a large range of potential outcomes (+23% to –45%)}
Water Supplies in light of climate changes

We looked at information & comments from last years workshop on what it means for water quality during extreme events, potentially more wastewater influences during droughts and potentially greater reliance on groundwater.
Water Quality Responses under Different Climate Situations

Chao-An Chiu
Paul Westerhoff
Arizona State University
School of Sustainable Engineering and The Built Environment
Civil, Environmental and Sustainable Engineering
Headlines

• Annual DOM and inflow profiles for three reservoirs.
• Spring flush and loading of DOC mass – example of Bartlett Lake (Verde River)
  – early storm
  – dry duration antecedent to first flush.
• In Case of extreme climate scenarios.
SRP and CAP Reservoir System

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Volume (m³)</th>
<th>HRT</th>
<th>Combined HRT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Pleasant</td>
<td>7.4x10⁸</td>
<td>400 days</td>
<td>4~5 years</td>
</tr>
<tr>
<td>Bartlett Lake</td>
<td>1.5x10⁸</td>
<td>150 days</td>
<td>210 days</td>
</tr>
<tr>
<td>Saguaro Lake</td>
<td>8.0x10⁷</td>
<td>70 days</td>
<td>2.5 years</td>
</tr>
</tbody>
</table>
Long-Term DOC Trends

- Lake pleasant – Some variation
- Saguaro Lake – Low variation with increasing trend of DOC.
- Bartlett Lake – largest variation with increasing trend of DOC
Annual DOM and inflow profiles

• Sources of inflow:
  – Snowmelt (early spring);
  – precipitation (storm or monsoon).

• Higher UV254 or SUVA value shows
  – Higher aromatic content;
  – Higher terrestrially-derived DOM;
  – Higher DBP formation potential.
Annual Average DOM conc. and Inflow

Lake Pleasant

- DOC increased during summer due to in-lake bioactivities.
- Summer inflow might bring autochthonous DOM into Saguaro Lake from lake upstream.
- Early spring inflow brought in terrestrial materials.

Bartlett Lake

Saguaro Lake

- DOC increased during summer due to in-lake bioactivities.
- Summer inflow might bring autochthonous DOM into Saguaro Lake from lake upstream.
- Early spring inflow brought in terrestrial materials.
Higher Variation = Vulnerable?

• Less variation of summer DOM content – autochthonous production.
• Higher variation of DOM content during early spring with some extremely high value (outliers).
Inflow vs. DOC concentration in Bartlett Lake over time

- **Inflow**
- **Bartlett Lake - Epilimnion**

<table>
<thead>
<tr>
<th>Year</th>
<th>DOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>4.0</td>
</tr>
<tr>
<td>2005</td>
<td>7.0</td>
</tr>
<tr>
<td>2008</td>
<td>6.0</td>
</tr>
<tr>
<td>2010</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Inflow (AF/month):
- 2003: 400,000
- 2005: 500,000
- 2008: 450,000
- 2010: 600,000
While we only interested in data during early spring ...

**How to calculate mass of DOC loading?**

- **Main assumption:**
  - Autochthonous DOM is negligible
  - Biological reaction is negligible
  - Evaporation is negligible
  - Water is well mixed vertically

**Define of Dry Duration (DD) Antecedent**

- **Criteria:** Average of total inflow volume (\( \text{Ave}_{\text{inflow}} \)) except inflow volume > 50% of reservoir volume.
- If month total inflow < \( \text{Ave}_{\text{inflow}} \) then this month is identified as “Dry month”, opposite as “Wet month”.
- Total amount of “Dry month” between “Wet month” before February is defined as “Dry Duration (DD)” antecedent to February.
- This “DD” factor is used to adjust the inflow (\( \text{Adj}_{\text{inflow}} \)) by:
  \[
  \text{Adj}_{\text{inflow}} = \text{Inflow}(AF) \times \log_{10}(DD)
  \]

\[
\text{Inflow loading of DOC mass (kg)} = (\text{Storage}_{\text{final}} - \text{Storage}_{\text{initial}}) + \text{outflow loading}
\]
Relationship between DOC mass loading and inflow in spring

<table>
<thead>
<tr>
<th>Year</th>
<th>Dry duration antecedent to February (month)</th>
<th>Total inflow btw Feb to Apr (AF)</th>
<th>Inflow DOC loading from Feb to Apr (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>2</td>
<td>52,967</td>
<td>47141853</td>
</tr>
<tr>
<td>2001</td>
<td>7</td>
<td>104,894</td>
<td>580783475</td>
</tr>
<tr>
<td>2002</td>
<td>10</td>
<td>30,798</td>
<td>55712055</td>
</tr>
<tr>
<td>2003</td>
<td>5</td>
<td>149,925</td>
<td>1129276819</td>
</tr>
<tr>
<td>2004</td>
<td>7</td>
<td>34,959</td>
<td>48202614</td>
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<tr>
<td>2005</td>
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<td>567,593</td>
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<td>2006</td>
<td>6</td>
<td>36,608</td>
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<tr>
<td>2007</td>
<td>18</td>
<td>23,317</td>
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<tr>
<td>2008</td>
<td>27</td>
<td>202,355</td>
<td>2717621946</td>
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<tr>
<td>2009</td>
<td>4</td>
<td>71,326</td>
<td>566331116</td>
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<tr>
<td>2010</td>
<td>7</td>
<td>298,422</td>
<td>2303591268</td>
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</tbody>
</table>

Adjusted by factor of dry duration

R² = 0.8688

R² = 0.9877
From another view of inflow and DOC mass loading – Verde River at Tangle Creek

- Loading of DOC mass strongly correlated with inflow volume in early spring.
- Early storm occurred could increase DOC mass loading.
- Lack of 2008 DOC data.
What did we observed in Bartlett Lake of Verde River system

- Loading of DOC mass into Bartlett Lake is strongly correlated to inflow volume during early spring (Feb to Apr).
- Early storm of 2003, 2005, 2008, and 2010 brought more DOC mass into Bartlett Lake than other years.
- Long term of dry duration might result in loss of DOC mass from reservoir.
- In 2008, Spring flush after long dry duration brought more DOC mass into Bartlett Lake even though the total inflow was not as high as 2010.
How about Saguaro Lake and Lake Pleasant

**Saguaro Lake**

- **Early Storm**
  - 2005
  - 2008
  - 2010

**Lake Pleasant**

- **DOC mass loading (kg)**
- **Inflow (AF)**

- **R² = 0.0526**

**Salt River Lake system**

**Lake Pleasant (off-stream)**

- **Inflow (AF)**

<table>
<thead>
<tr>
<th>Inflow (AF)</th>
<th>0.0</th>
<th>50000.0</th>
<th>100000.0</th>
<th>150000.0</th>
<th>200000.0</th>
<th>250000.0</th>
<th>300000.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

- **DOC mass loading (kg)**
- **R² = 0.2311**

<table>
<thead>
<tr>
<th>Inflow (AF)</th>
<th>0.0</th>
<th>50000.0</th>
<th>100000.0</th>
<th>150000.0</th>
<th>200000.0</th>
<th>250000.0</th>
<th>300000.0</th>
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<tr>
<td>Salt River</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
Inflow of these two lakes were regulated and relatively constant.
Take home messages

• DOC loading early of the year was associated to spring flush and impacted by early storm significantly.
• Multi-lake system (Salt River) – less impact by spring flush and early storm; in-lake autochthonous production is major concern (longer HRT).
• Single-lake system (Verde River) – vulnerable to spring flush and early storm.
• Dry duration antecedent to spring flush could increase the terrestrial DOM loading, especially in extreme case.
In Case of extreme climate scenarios

- Wildfire events
- 2005 phoenix water boil (early storm)
- Drought duration antecedent to first flush
- Long HRT vs. short HRT reservoir system.
- Expected impact:
  - Muddy water
  - High in DOC and UVA material
  - High chlorine demand
  - High in DBPs formed in drinking water
- The rain after a long drought!!
How Much Wastewater is in Our Drinking Water?

Presented By: Jacelyn Rice

NSF Award # 0855802

Why?

- Contaminants of Emerging Concern
- Possible tool for analysis/studies on WW impacts
- Implications on public perception
- Potential source of DBP Precursors
Salt and Verde River Watersheds

http://upload.wikimedia.org/wikipedia/commons/5/5a/Salt_River_Map.jpg
Verde River

Camp Verde WWTP
Present Design Flow: 0.65 MGD

Northern Gila Sanitary District
Present Design Flow: 2 MGD

USGS Gage 09508500

Discharge Statistic | Flow (CFS) | % WW
---|---|---
25th percentile | 129 | 3.2%
Mean | 220 | 1.9%
Salt River

Discharge Statistic | Flow (CFS) | % WW
---|---|---
25th percentile | 573 | 0.3%
Mean | 923 | 0.2%
# Colorado River WWTPs Breakdown

<table>
<thead>
<tr>
<th>State</th>
<th>#WWTPs in Drainage</th>
<th>2004 $Q_{\text{Design}}$ (MGD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wyoming</td>
<td>13</td>
<td>6.27</td>
</tr>
<tr>
<td>Colorado</td>
<td>79</td>
<td>69.71</td>
</tr>
<tr>
<td>Utah</td>
<td>12</td>
<td>29.40</td>
</tr>
<tr>
<td>Arizona</td>
<td>2</td>
<td>2.74</td>
</tr>
<tr>
<td>New Mexico</td>
<td>3</td>
<td>7.40</td>
</tr>
<tr>
<td>Nevada</td>
<td>4</td>
<td>151.75</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>113</strong></td>
<td><strong>267.27</strong></td>
</tr>
</tbody>
</table>

**2010 Census Data for Las Vegas Metro Area: 1.95 Million People
Current Flows are possibly closer to 195 MGD (assuming 100 gpcd)**
## Colorado River WW%

<table>
<thead>
<tr>
<th>Discharge Statistic</th>
<th>Daily Discharge (CFS)</th>
<th>Worst Case (all upstream)</th>
<th>Only Las Vegas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max (1983)</td>
<td>39600</td>
<td>1.0%</td>
<td>0.5%</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>14200</td>
<td>2.7%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Mean</td>
<td>13000</td>
<td>3.0%</td>
<td>1.6%</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>10600</td>
<td>3.7%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Min (1905)</td>
<td>4520</td>
<td>8.6%</td>
<td>4.6%</td>
</tr>
</tbody>
</table>
So.... Is this Important?

- Is treated WW effluent in our drinking water Bad?

- Does this change ones perception of the water quality or safety?

- What is your social perception? Did this presentation change your perception?
Developing a National View

GIS Model
Integrating predicted WWTP effluent with public perception

Public Threshold Data
What makes a good environmental tracer?

- Constituent should be present whenever the pollutant is present
- Compound should not accumulate on its own
- Concentration of compound should be directly related to degree of pollutant

Tracers

- Caffeine
- Sucralose
## Sucralose Occurrence across Valley

<table>
<thead>
<tr>
<th>Location</th>
<th>Sucralose (ppt)</th>
<th>Caffeine (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt River at Blue Point Bridge</td>
<td>5</td>
<td>19</td>
</tr>
<tr>
<td>Verde River at Beeline Highway</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>CAP Canal at Waddle Canal</td>
<td>180</td>
<td>17</td>
</tr>
<tr>
<td>WTP-Influent (example of 1)</td>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td>WTP-Sedimentation (example of 1)</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>WTP-Effluent (example of 1)</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>WWTP-Raw (example of 1)</td>
<td>5,400</td>
<td>51,000</td>
</tr>
<tr>
<td>WWTP-Effluent (Activated Sludge)</td>
<td>2,800</td>
<td>47</td>
</tr>
<tr>
<td>GRUSP Measure Well #1</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>GRUSP Measure Well #2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>GRUSP Measure Well #3</td>
<td>92</td>
<td>6</td>
</tr>
</tbody>
</table>
Photocatalysis: A new treatment option for nitrate mitigation

Kyle Doudrick

Ting Yang & Paul Westerhoff
Kiril Hristovski (ASU-Poly)

Funding by

[NSF] [Science Foundation Arizona]
Objectives

• 20% of drinking water wells in rural areas in the U.S. are above the EPA MCL (10 mg-N/L)
• Main cause of eutrophication in the Gulf of Mexico
• Develop a new nitrate mitigation technology
• Examine the potential for pilot scale applications
Nitrate in Central Arizona

Phoenix Metropolitan Area

- Sampled Wells
- Major Roads
- Nitrate Concentrations (mg-N/L) for 1996-1998
Nitrate Treatment Technologies

- Glendale currently uses IX treatment that produces nitrate-laden brine
- IX brine is costly to dispose
- They have investigated biological denitrification pilot scale and currently uses IX treatment as a Water Research Foundation (AwwaRF) Project with ASU (Bruce Rittmann)

<table>
<thead>
<tr>
<th>Treatment Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Exchange</td>
<td>Simple, cost-effective, low-maintenance for smaller applications</td>
<td>Disposal/treatment of brines, toxic by-products, not good for high TDS waters</td>
</tr>
<tr>
<td>Biological Denitrification</td>
<td>Non-toxic by-product, large applications, high concentrations, more cost effective than brine disposal</td>
<td>Electron donor required (H2 or organic carbon), possible microbial contamination, high-maintenance, start-up times</td>
</tr>
</tbody>
</table>
Novel Solution

• Photocatalysis (light activated catalysts)

• Advantages
  – Non-biological
  – Low maintenance
  – On/off

• Disadvantages
  – Still in research stage
  – Energy cost for UV light
Photocatalyst Mechanisms

\[
\text{Ni}^{2+} + 12\text{H}^+ + 10e^- \rightarrow \text{Nitrogen gas} + 6\text{H}_2\text{O}
\]

\[
\text{Nitrate} + 2\text{H}^+ + 2e^- \rightarrow \text{Nitrite} + \text{H}_2\text{O}
\]

\[
\text{Nitrate} + 10\text{H}^+ + 8e^- \rightarrow \text{Ammonia} + 3\text{H}_2\text{O}
\]

By-products:

- \(2\text{Nitrate} + 12\text{H}^+ + 10e^- \rightarrow \text{Nitrogen gas} + 6\text{H}_2\text{O}\)
- \(\text{Nitrate} + 2\text{H}^+ + 2e^- \rightarrow \text{Nitrite} + \text{H}_2\text{O}\)
- \(\text{Nitrate} + 10\text{H}^+ + 8e^- \rightarrow \text{Ammonia} + 3\text{H}_2\text{O}\)

\(\text{N}_2, \text{NO}_2^-, \text{NH}_3\)
Nitrate removal in DI water

**By-products**

- UV alone
  - Nitrite
- UV+Formic
  - Nitrogen gas
- P90+UV+Formic
  - Nitrogen gas
  - ~15% Ammonia
DOC (Formic acid) Management

[Formic Acid/Nitrate] Molar Ratio vs. Removal Ratio

Full DOC removal

0 2 4 6 8 10 12
0 0.4 0.8 1.2 1.6
Looking Forward...

<table>
<thead>
<tr>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preliminary experiments</td>
<td>Exploration of new photocatalysts</td>
<td>IX brine treatment preliminary studies</td>
<td>New materials</td>
</tr>
<tr>
<td>comparing commercial TiO₂</td>
<td>for improved nitrate removal rates</td>
<td>NSF funding awarded to expand study</td>
<td>Pilot-scale</td>
</tr>
<tr>
<td>photocatalysts</td>
<td></td>
<td></td>
<td>testing</td>
</tr>
</tbody>
</table>

Current Partners:
- Glendale, AZ
- Salt River Project
- 3 Private Companies
Thank You
Future Research

- Test in ion exchange brine
- Scale up to pilot
- Synthesis of new photocatalysts for:
  - Activity/Selectivity at neutral pH
  - Water as an electron donor

PhotoCat® system

Puralytics Shield ®
Increasing NaCl concentration decreases the rate of nitrate removal with P90

12% NaCl: Formic acid does not improve nitrate removal rate without a catalyst
In-situ GAC Regeneration: Progress and Path Forward

Chao-An Chiu
Paul Westerhoff
Arizona State University
School of Sustainable Engineering and The Built Environment
Civil, Environmental and Sustainable Engineering
In-Situ GAC Regeneration

• What concept is?

What does it replace?
- Operate to near complete breakthrough;
- GAC remove;
- GAC off-site transportation;
- GAC thermal regeneration;
- Transport back to site;
- GAC back-installation;
- Attrition replacement (at least 10%);
- 4-6 weeks downtime.

- Envision Process -
- Reagent preparation;
- In-column contact with GAC;
- Reagent washout;
- GAC back to operation;
- 1-2 days downtime;
- May have frequent regeneration (weeks) to make GAC more effective during peak THM control needs.
In-Situ GAC Regeneration for Surface Water Treatment Plant
(Timeline for Implementation)

**Literature Study and Nano-Fe Synthesis**
- Nano-Fe can be synthesized easily by hydrolysis of FeCl₃ in hours and preserved for months.

**Feasibility and Batch Test**
- Nano-Fe produced by 7% FeCl₃ can oxidize organics sorbed onto GAC in an hour.
- Nano-Fe can be recycled and reused.
- No-Slurry formed after oxidization.

**In-Situ GAC Regeneration Test**
- Nano-Fe can recover >80% GAC sorption capacity.
- > 5 runs of sorption-regeneration can be performed.
- Nano-Fe can be used for regeneration of GAC saturated with low conc. organics.

- 2009
- 2010
- 2011
- 2012
In-situ saturated GAC regeneration
Small-Scale Test

Three Stages:
A. Adsorption Stage
   - Fresh GAC
   - Downflow mode
   - Enforced adsorption
B. In-situ Regeneration Stage
   - Upflow mode
   - In-situ
   - 30 minutes
C. Re-Adsorption Stage
   - Regenerated GAC
   - Downflow mode
   - Enforced adsorption

Comparison of GAC adsorption capacity between stage A and C.
Demonstration of In-Situ Regeneration System

Up-Flow mode
Loaded GAC column

nFe+H₂O₂
Representative Results

- GAC adsorption capacity was recovered.
- Stage A-B-C can be repeated for 5 runs.
- Duplicate results (red dot) confirmed the feasibility.

Adsorption of phenol (1000 mg/L) onto virgin and in-situ regenerated GAC.
Test for recycle and reuse of nano-Fe

Recycle of Nano-Fe

- Simple pH adjustment
  - pH > 5 $\rightarrow$ aggregation
  - pH < 2 $\rightarrow$ re-dispersion

- Measurement of iron concentration shows no iron loss after reaction.

- Nano-Fe can be recycled and performed as fresh nano-Fe.
In-situ regeneration of GAC adsorbing different PHENOL concentrations

![Graph showing regeneration efficiency of GAC adsorbing different PHENOL concentrations]
### Comparison for Regeneration Efficiency of Sorption Capacity

**Efficiency** 

\[
Efficiency(E) = \frac{\sum_{i=1}^{n} [(C_{0,i} - C_{eq,i}) \times V_i]_{Virgin}}{\sum_{i=1}^{n} [(C_{0,i} - C_{eq,i}) \times V_i]_{regenerated}} \times 100
\]

---

<table>
<thead>
<tr>
<th>Regeneration condition</th>
<th>Efficiency (E) of Adsorption Capacity Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1\textsuperscript{st} cycle</td>
</tr>
<tr>
<td>Adsorbate (phenol)</td>
<td></td>
</tr>
<tr>
<td>Iron nanocatalyst</td>
<td>1000ppm Fresh</td>
</tr>
<tr>
<td>Iron nanocatalyst</td>
<td>1000ppm Recycled</td>
</tr>
<tr>
<td>Adsorbate (phenol)</td>
<td>1000ppm Fresh</td>
</tr>
<tr>
<td>Iron-nanoparticles</td>
<td>1000ppm Fresh</td>
</tr>
<tr>
<td>Adsorbate (phenol)</td>
<td>500ppm Fresh</td>
</tr>
<tr>
<td>Iron-nanoparticles</td>
<td>100ppm Fresh</td>
</tr>
<tr>
<td>Adsorbate (phenol)</td>
<td>50ppm Fresh</td>
</tr>
<tr>
<td>Iron-nanoparticles</td>
<td>10ppm Fresh</td>
</tr>
<tr>
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<td>100ppm Fresh</td>
</tr>
<tr>
<td>Iron-nanoparticles</td>
<td>50ppm Fresh</td>
</tr>
<tr>
<td>Adsorbate (phenol)</td>
<td>10ppm Fresh</td>
</tr>
</tbody>
</table>
### Next Step – Demonstrate In-situ Regeneration with NOM and PPCP

<table>
<thead>
<tr>
<th></th>
<th>H2O2</th>
<th>nFe/H2O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estradiol</td>
<td>80%</td>
<td>60%</td>
</tr>
<tr>
<td>Phenol</td>
<td>60%</td>
<td>40%</td>
</tr>
<tr>
<td>Sucralose</td>
<td>40%</td>
<td>20%</td>
</tr>
<tr>
<td>Caffeine</td>
<td>20%</td>
<td>0%</td>
</tr>
<tr>
<td>SRNOM</td>
<td>0%</td>
<td>10%</td>
</tr>
<tr>
<td>Atrazine</td>
<td>10%</td>
<td>0%</td>
</tr>
</tbody>
</table>

#### Why Pharmaceuticals?
- Are they significant in surface water?
Summary and Timeline for Implementation

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- Nano-Fe can be used for regeneration of GAC saturated with low conc. organics.

- 2009
- 2010
- 2011
- 2012
- 2013

Demonstrate with NOM and DBPs control
Pilot Study
Full Scale Study
Implementation Full Scale
Jar Testing with PAC

How to & Results with S-PAC

David Hanigan
Ph.D. Student

S-PAC provided by Detleff Knappe / Univ of N. Carolina
PAC

- Carbon that has been “activated”
  - Common carbon sources: Coal, peat, wood
  - Activation generates an extremely porous structure that is beneficial for adsorption
  - Surface areas of 500-2000 m$^2$/g
    - Football field=5300 m$^2$
Uses in Water Treatment

- Taste and odor organics
  - MIB, Geosmin, Cyclocitral
- Performs best on certain organics:
  - High molecular weight (large)
  - Aromatic (unsaturated bonds)
  - Hydrophobic (nonpolar, not attracted to water)
- Nontraditional uses
  - DBP precursors (THM, HAA, NDMA?)
It’s a matter of size

- **GAC**
  - Usually used in a packed column
  - Can be regenerated
  - **Particle size ~500-2000 micron**

- **PAC**
  - Not recovered, removed by coagulant or filters
  - Can be used in older facilities not designed for GAC beds
  - Sometimes used seasonally for THM/HAA precursor reduction
  - **Particle size generally less than 100 micron**

- **S-PAC**
  - Similar to PAC, with **particle size ~0.3 micron**
Size and Texture

Conventional PAC

S-PAC
SEM Images

Source: Matsui, Yoshida, Ando, Matsushita (Hokkaido University)

PAC (D50: 12 μm)

S-PAC (D50: 0.7 μm)
Jar Tests

- Commonly used for finding optimum coagulation dosage
- Instead, used in this study to compare S-PAC to WPH with and without coagulation (ferric chloride) for UVA, MIB, geosmin removal
- Saguaro Lake water spiked with MIB and Geosmin
- Add PAC (15 mg/L), mix for 30 min (100rpm)
- Add ferric (40mg/L) (2 min rapid mix)
- Floc/Sedimentation (~30 rpm) for 30 min
- Filtered (0.2 micron)
- Analyzed for UVA, Geosmin, MIB, cylcocitral
  - MIB spike contains methanol so cannot analyze for TOC
UV254 of untreated water = 7.81 m⁻¹
Based on linear relationship between UV254 and THM developed by several authors summarized in Chowdhury and Champagne, 2007

R² between .77 and .91
Conclusions and Future Research

- S-PAC has a smaller particle size than regular WPH
- S-PAC removes less taste and odor compounds than WPH under similar experimental conditions
- S-PAC removes a larger amount of UV absorbing material than WPH under similar conditions
- A greater removal of UV absorbing material generally results in reduced THM and HAA formations.

Future work
- Can S-PAC/PAC/GAC reduce NDMA formation in drinking waters impacted by wastewater?
EfOM and DBP precursor average removal after equilibration (7d) at three activated carbon dosages (all four EfOMs evaluated with 50 mg/L of PAC, the SMPs and the Nogales WWTP evaluated with 500 mg/L of PAC, and the Southerly WWT Center and the Metro District/North Complex evaluated with 1000 mg/L of PAC, all Calgon WPM) (HAAFP results for the 50 mg/L test of Southerly WWT Center not included [data out of control]) (Kranser et al., 2007)
Samples are from secondary effluent
PAC contact time is 3 hr.
Building Long-Term Datasets from Multiple Sources

Linking data is an increasing opportunity/challenge within scientific communities

We want to start with our water supply – it has been fascinating

We want your help to expand our dataset
Example Data

Salt & Verde River Lake Data (AZ DEQ)

DOC (mg/L) vs. Month-Year for Apache, Canyon, Roosevelt, Saguaro, and Bartlett.
We want to include all CAP data too

Lake Pleasant Data (AZ DEQ)

Mesa CAP Plant sees large increases in operational chemical costs seasonally despite similar bulk water qualities – why?
Treatment plants have this type of data:
For how many years is it electronically available?

24th St. WTP TOC - 2009

- Verde Raw TOC
- Deer Valley Raw TOC
- Union Hills (CAP) Raw TOC
- 24th Street Raw TOC
If cities have data – Should our project continue to measure this at each WTP?

Chandler WTP Data
Discussion

- 10 years ago TOC data was not measured as frequent as today – it would seem we can streamline canal sampling if this type of data is being collected and focus on the watershed?

- We could instead focus on molecular weight changes for example

- What type of Organic matter data over time would help your facilities?
General Discussion

- We plan to continue lake monitoring – as that is the most requested information
- We plan to continue MIB/Geosmin monitoring
- What other monitoring is critical for you?
- Is anyone using S::can and should we get it into the monitoring network?
- With a gradual shift towards GAC what issues are you having?
- What would you like to see us initiate and eventually seek outside funding?
- Open floor....