Arsenic: Municipal Industrial Sources and Biosolids Sinks

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Potential negative impacts to Biosolids from Arsenic Water Treatment Plant backwash

- Answers not exactly clear. More questions than answers
  - Circumstantial evidence might suggest there are impacts, some data inconclusive.
  - What do we mean by negative impact? IPP definition of pass through and interference? If concentrating what is acceptable?
Discussion Summary

- Provide some background of the issue
- Present data and develop more questions
- Discuss possible wwtp remedies to reduce As headwork loading
- Raise awareness in IPP/BS industrial regarding potential impacts and encourage more research.
Regulatory Background of Arsenic

The previous drinking water standard was established at 50 ppb in 1975.

In 1996, Congress amended the SDWA and directed EPA to propose a new arsenic regulation.
Arsenic Rulemaking

- **Final Arsenic Rule**
  - January 22, 2001
  - 10.0 ppb standard for arsenic
  - Enforceable on January 23, 2006
Arsenic Rule

- New MCL applies to all CWSs and NTNCWs
- Estimate that ~450 MI systems will exceed MCL
Arsenic Occurrence

- Naturally occurring element
- Found throughout the United States
- Weathers from rocks and soils
- Primarily found in ground waters
- Also associated with wood preserving, mining, agriculture, pulp and paper production, burning of fossil fuels
Percentage of Community Water Systems with Mean Arsenic above 10 ppb

Reg. 1: New England
Reg. 2: Mid Atlantic
Reg. 3: Southeast
Reg. 4: Midwest
Reg. 5: South Central
Reg. 6: North Central
Reg. 7: West

States without compliance data

Regions adapted from Frey and Edwards, 1997
Michigan's Arsenic Levels

Highest level for county in the DEQ Ground Water Data Base.

- >50 ug/L
- >20 ug/L
- >10 ug/L
- Less Than 10 ug/L
Arsenic Water Chemistry

Arsenic Species

As (III) - \( \text{H}_3\text{AsO}_3^0 \), \( \text{H}_2\text{AsO}_3^{-1} \), \( \text{HAsO}_3^{-2} \)

As (V) - \( \text{H}_3\text{AsO}_4^0 \), \( \text{HAsO}_4^{-1} \), \( \text{AsO}_4^{-2} \)
For maximum As removal
oxidize As (III) to As (V)
before applying treatment

\[
\text{III} \rightarrow \text{V}
\]
As III Oxidation

Effective!

- Free Chlorine
- Potassium Permanganate
- Ozone
- Solid Oxidizing Media (MnO₂ solids)

Ineffective

- Chloramine
- Chlorine Dioxide
- UV Radiation
Typical Arsenic water treatment options

- Conventional iron removal
- Modified iron removal
- Anion exchange
- Adsorptive media
  - Iron based
  - Alumina based
Conventional Iron Removal

- If you can remove iron, you can usually remove arsenic.
- Oxidation converts arsenic (III), arsenite, to arsenic (V), arsenate.
- Ratio of iron to arsenic should be at least 20:1 for effective removal of As.
- Most ground waters in MI are in As (III) state, so a strong oxidant (\(\text{Cl}_2\), \(\text{KmMnO}_4\)) may have to be used to covert to (III) to (V).
- Backwash will contain both Fe and As.
 Adsorption medias

- **Adsorption** is contaminant removal from water by attachment onto the surface of a porous solid.

  - **Advantage** - Binds and removes some of the As in backwash.
  - **Disadvantage** - Varying levels of success and Costs associated with periodic removal / disposal of spent media.
Conventional iron, modified iron and anion removal systems are backwashed/regenerated every 1-7 days and will contain arsenic in the backwash water.

Adsorption based medias are backwashed every 7-30 days depending a raw water quality.

Backwash water from adsorptive media MAY contain elevated levels of As, depending how system is designed (i.e. is As bound to the naturally occurring iron in the raw water or is adsorbed onto the media?)
# Backwash Disposal Options

## Liquid Residuals
Brine, Backwash Water, Rinse Water, Acid Neutralization Water, Concentrate

<table>
<thead>
<tr>
<th>Disposal Option</th>
<th>Waste Type</th>
<th>Applicable Authority</th>
<th>Key Considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge directly to surface waters</td>
<td>Non-hazardous</td>
<td>CWA</td>
<td>- NPDES Permit</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Appropriate receiving body</td>
</tr>
<tr>
<td><strong>Discharge to a Publicly Owned Treatment Works (POTW)</strong></td>
<td>Non-hazardous</td>
<td>CWA</td>
<td>- Meet MAHL, POTW and state requirements</td>
</tr>
<tr>
<td>Injection to a Class 1 UIC Well</td>
<td>Hazardous, Non-hazardous, &amp; Mixed</td>
<td>SDWA/UIC Regs.</td>
<td>- Expensive, complex, and few wells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Permit required</td>
</tr>
<tr>
<td>Injection to a Class V UIC Well</td>
<td>Non-hazardous</td>
<td>SDWA/UIC Regs.</td>
<td>- Injection prohibited if it will endanger an underground source of drinking water</td>
</tr>
</tbody>
</table>
ATP backwash disposal alternatives

- NPDES Gen Permit –
    - Difficult to obtain with convention iron removal system
  - Presently ATP with adsorptive media more likely candidate for general permit....
    - However some discussion with permits unit of applying the Rule 57 number of 10 ug/l to all surface water discharges.
Some in wastewater industry expressed concerns regarding POTWs receiving As backwash.

- Inhibition of unit process?
- As precipitant concentrating in the residuals?

Others felt impacts were unlikely or minimal

- Mass balance -
Mass Balance

- **Original Water System**
  - All arsenic from wells & eventual to WWTP
    - Concentration & Flow Constant
  - Exception Losses (Minor) from distribution system
    - Sprinkling and Fire Hydrants
IPP Perspective-

- Part 23 Rules -R323.2303(1)
  - “...non domestic user may not introduce into any POTW any pollutant that causes pass-through or interference...”
    - Interference roughly defined as a discharge inhibits process or sludge processes, use or disposal.

- Not aware of unit process inhibition from As backwash.
- Q -Is the backwash inhibiting sludge process use or disposal?
# TABLE 1 -- CEILING POLLUTANT CONCENTRATIONS

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ceiling Concentration (milligrams per kilogram (on a dry weight basis))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>75</td>
</tr>
<tr>
<td>Cadmium</td>
<td>85</td>
</tr>
<tr>
<td>Copper</td>
<td>4300</td>
</tr>
<tr>
<td>Lead</td>
<td>840</td>
</tr>
<tr>
<td>Mercury</td>
<td>57</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>75</td>
</tr>
<tr>
<td>Nickel</td>
<td>420</td>
</tr>
<tr>
<td>Selenium</td>
<td>100</td>
</tr>
<tr>
<td>Zinc</td>
<td>7500</td>
</tr>
</tbody>
</table>

# TABLE 3 -- POLLUTANT CONCENTRATIONS

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration (milligrams per kilogram (on a dry weight basis))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>41</td>
</tr>
<tr>
<td>Cadmium</td>
<td>39</td>
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<tr>
<td>Copper</td>
<td>1500</td>
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<tr>
<td>Lead</td>
<td>300</td>
</tr>
<tr>
<td>Mercury</td>
<td>17</td>
</tr>
<tr>
<td>Nickel</td>
<td>420</td>
</tr>
<tr>
<td>Selenium</td>
<td>100</td>
</tr>
<tr>
<td>Zinc</td>
<td>2800</td>
</tr>
</tbody>
</table>
Let's look at the data!
Caro BS MG/KG vs Year

BW Tank Upgrade

As WTP On-Line

Year
2002 2003 2004 2005 2006 2007 2008 2009 2010

[As] Mg/Kg

[As] MG/KG
Caro ATP backwash tank

- Original design ineffective - outlet at bottom of tank
- Raised outlet and allow backwash to settle
- Use City owned vac truck to periodically remove As precipitant
- Place As precipitant on wwtp drying beds and landfill.
Sandusky As Concentrations

Sandusky BS MG/KG vs Year

As WTP On-Line

Year

[As] Mg/Kg

[As] MG/KG
Mass Balance

- $Q = \text{Flow Rate, GPD}$
- $C = \text{Concentration, mg/l}$
- $M = \text{Mass, Lbs/Day}$

$C \times Q \times 8.34 \times 10^{-6} = M$
# Sandusky Drinking Water and Biosolids Summary

## Drinking Water

<table>
<thead>
<tr>
<th>Year</th>
<th>Total Gals. Pumped</th>
<th>Ave. Arsenic Concentration (µg/l)</th>
<th>Lbs. Arsenic Produced</th>
<th>Dry Tons Applied</th>
<th>Arsenic Concentration (mg/kg)</th>
<th>lbs. Arsenic in biosolids</th>
<th>Difference Lbs. Arsenic Produced &amp; Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>107,237,000</td>
<td>12</td>
<td>10.73</td>
<td>180</td>
<td>3.54</td>
<td>1.27</td>
<td>9.46</td>
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<tr>
<td>2003</td>
<td>102,620,000</td>
<td>12</td>
<td>10.27</td>
<td>249</td>
<td>1.19</td>
<td>0.59</td>
<td>9.68</td>
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<tr>
<td>2004</td>
<td>91,572,000</td>
<td>12</td>
<td>9.16</td>
<td>243</td>
<td>10.5</td>
<td>5.10</td>
<td>4.06</td>
</tr>
<tr>
<td>2005</td>
<td>102,605,000</td>
<td>12</td>
<td>10.27</td>
<td>90</td>
<td>17</td>
<td>3.08</td>
<td>TBD</td>
</tr>
<tr>
<td>2006</td>
<td>96,369,000</td>
<td>12</td>
<td>9.64</td>
<td>85</td>
<td>16.15</td>
<td>2.75</td>
<td>6.90</td>
</tr>
<tr>
<td>2007</td>
<td>99,035,000</td>
<td>12</td>
<td>9.91</td>
<td>80</td>
<td>29.7</td>
<td>4.75</td>
<td>5.16</td>
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<tr>
<td>2008</td>
<td>93,588,000</td>
<td>12</td>
<td>9.37</td>
<td>71</td>
<td>33.25</td>
<td>4.72</td>
<td>4.64</td>
</tr>
<tr>
<td>2009</td>
<td>92,799,000</td>
<td>12</td>
<td>9.29</td>
<td>53</td>
<td>28.8</td>
<td>3.05</td>
<td>6.23</td>
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<tr>
<td>2010</td>
<td>96,919,000</td>
<td>12</td>
<td>9.70</td>
<td>15</td>
<td>46.5</td>
<td>1.40</td>
<td>8.30</td>
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<tr>
<td>Total (2)</td>
<td>882,744,000</td>
<td>12</td>
<td>88.35</td>
<td>976</td>
<td>20.74</td>
<td>40.48</td>
<td>47.87</td>
</tr>
</tbody>
</table>

**Notes:**
- (2) Indicates total data across all years.

Summary of Table - Sandusky

- Pounds of Arsenic from WTP – Similar
- Pounds of Arsenic to Field - Similar
- Tons of BS to Field – Lower
- Concentration of Arsenic in BS – Higher
  - %VS stayed the same
  - Q – where is the remaining As going?

Mass = Concentration X Volume
<table>
<thead>
<tr>
<th>Year</th>
<th>Total Gals. Pumped</th>
<th>Arsenic Concentration (μg/l)</th>
<th>Lbs. Arsenic Produced</th>
<th>Dry Tons Applied</th>
<th>Arsenic Concentration (mg/kg)</th>
<th>lbs. Arsenic Applied</th>
<th>Difference Lbs. Arsenic Produced &amp; Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>111,155,460</td>
<td>17</td>
<td>15.76</td>
<td>60</td>
<td>26</td>
<td>3.12</td>
<td>12.64</td>
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<tr>
<td>2003</td>
<td>112,693,750</td>
<td>17</td>
<td>15.98</td>
<td>50</td>
<td>74</td>
<td>7.40</td>
<td>8.58</td>
</tr>
<tr>
<td>2004</td>
<td>108,439,680</td>
<td>17</td>
<td>15.37</td>
<td>56</td>
<td>48</td>
<td>5.38</td>
<td>10.00</td>
</tr>
<tr>
<td>2005</td>
<td>99,240,458</td>
<td>17</td>
<td>14.07</td>
<td>31</td>
<td>32.9</td>
<td>2.04</td>
<td>12.03</td>
</tr>
<tr>
<td>2006</td>
<td>100,429,450</td>
<td>17</td>
<td>14.24</td>
<td>34</td>
<td>35.6</td>
<td>2.42</td>
<td>11.82</td>
</tr>
<tr>
<td>2007</td>
<td>134,590,000</td>
<td>17</td>
<td>19.08</td>
<td>77</td>
<td>43.1</td>
<td>6.64</td>
<td>12.44</td>
</tr>
<tr>
<td>2008</td>
<td>153,506,000</td>
<td>17</td>
<td>21.76</td>
<td>75</td>
<td>42.3</td>
<td>6.35</td>
<td>15.42</td>
</tr>
<tr>
<td>2009</td>
<td>154,436,000</td>
<td>17</td>
<td>21.90</td>
<td>51</td>
<td>71.23</td>
<td>7.27</td>
<td>14.63</td>
</tr>
<tr>
<td>2010</td>
<td>121,095,000</td>
<td>17</td>
<td>17.17</td>
<td>0</td>
<td>85.78</td>
<td>0.00</td>
<td>17.17</td>
</tr>
<tr>
<td>Total(1)(3)</td>
<td>542,961,450</td>
<td>17</td>
<td>76.98</td>
<td>237</td>
<td>48.06</td>
<td>22.78</td>
<td>54.20</td>
</tr>
</tbody>
</table>
Cass City Mass Balance -

- Where is the remaining As going
  - Out the Pipe?? Not Likely.

- Average As Effluent data from 2010 around 3 ug/l with a flow of .204 mgd = about 2 lbs of As a year.
Summary of Table – Cass City

- Pounds of Arsenic from WTP – Similar
- Pounds of Arsenic to Field - Similar
- Tons of BS to Field – Variable
- Concentration of Arsenic in BS – Variable

Mass = Concentration X Volume
Complicating variables in analyzing data

- Sampling dates relative to land application and reporting dates
- Pounds of Biosolids generated vs land applied
- Lab data errors. Is the Biosolids As digestion acid extraction procedures accurately determining true As concentrations in Biosolids?
- How does Iron Arsenate effect extraction?
Final Summary –
More ??s than answers

- Seems to be some correlation between Arsenic removal WTPs and additional [As] in Biosolids
- Installation and maintaining an As Backwash tank may offer solution for negative BS impacts.
- Concerns remain over lagoons receiving As backwash
- More in-depth research and analysis needed.
  - Are differences in WWTP operations and sludge reduction effect As levels?
  - Need better Mass Balance/ Better Data including As in WWTP Effluent. Where is the remaining As going?
  - Lab accuracy. How is matrix interference effecting bs As concentrations? Are the Lab extraction procedures accurately accounting for all [As] in BS.
Questions?

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