FEASIBILITY ANALYSIS FOR THE TREATMENT OF 1,4-DIOXANE ON LONG ISLAND

Prepared by:
Christopher Melillo
Manhattan College/ D&B Engineers and Architects, P.C.
• Introduce 1,4-dioxane
• Review the hydrology & history of Long Island
• Investigate the occurrence of 1,4-dioxane on Long Island
• Discuss current treatment technologies on Long Island
• Review treatment options for 1,4-dioxane
• Conduct a feasibility analysis on the 1,4-dioxane treatment options
CHEMICAL STRUCTURE OF 1,4-DIOXANE

- Boat conformation
- Hydrogen atoms have elliptical orbit path
- Transitional dipole moment (polar and non-polar)
SOURCES OF 1,4-DIOXANE

• Chemical stabilizer for chlorinated solvents
  • Co-contaminant with 1,1,1-trichloroethane (TCA)
• Aircraft maintenance solutions
  • Deicing
  • Degreasing (applied with TCA solution)
• Solvent for coating systems
• Impurity in antifreeze
• Impurity in personal care products
**CHEMICAL CHARACTERISTICS OF 1,4-DIOXANE**

- Colorless
- Faint odor
- Low Henry law constant
- Low octanol-water partition coefficient ($K_{ow}$)
- Historically known to be resistant to biodegradation

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>1,4-Dioxane</th>
<th>1,1,1-TCA</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mole)</td>
<td>88.106</td>
<td>13.4</td>
<td>131.39</td>
</tr>
<tr>
<td>Melting Point [°F(°C) at 760 mm Hg]</td>
<td>53.24 (11.8)</td>
<td>-22.72 (-30.4)</td>
<td>-120.46 (-84.7)</td>
</tr>
<tr>
<td>Boiling Point [°F(°C) at 760 mm Hg]</td>
<td>213.98 (101.1)</td>
<td>165.38 (74.1)</td>
<td>188.96 (87.2)</td>
</tr>
<tr>
<td>Flash Point [°F(°C) at 760 mm Hg]</td>
<td>41-64.4 (5-18)</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Density (g/mL at 20°C)</td>
<td>1.0329</td>
<td>1.3</td>
<td>1.46</td>
</tr>
<tr>
<td>Water Solubility (mg/L at 20°C)</td>
<td>Miscible</td>
<td>950</td>
<td>1,280</td>
</tr>
<tr>
<td>Vapor Density (air=1)</td>
<td>3.03</td>
<td>4.54</td>
<td>4.53</td>
</tr>
<tr>
<td>Octanol-Water Partition Coefficient ($K_{ow}$)</td>
<td>0.27</td>
<td>2.49</td>
<td>2.61</td>
</tr>
<tr>
<td>Vapor Pressure (mm Hg at 20°C)</td>
<td>30</td>
<td>100</td>
<td>69</td>
</tr>
<tr>
<td>Henry's Law Constant (atm m3/mole)</td>
<td>4.88x10^{-6}</td>
<td>0.0172</td>
<td>9.85x10^{-3}</td>
</tr>
<tr>
<td>Dipole moment (at 20°C)</td>
<td>Transitional</td>
<td>1.9</td>
<td>0.81</td>
</tr>
</tbody>
</table>
HEALTH EFFECTS OF 1,4-DIOXANE

• EPA is currently unable to determine the health effects of 1,4-dioxane

• Categorized by the Integrated risk Information System (IRIS) as “ Likely to be carcinogenic to humans”

• Strong evidence of 1,4-dioxane’s carcinogenic effect on animals (rats, mice & guinea pigs)

• Tumor promoter in the liver
GEOHYDROLOGY OF LONG ISLAND

- Upper glacial aquifer utilized in less densely populated areas of Suffolk County
- Most municipal wells pump from Magothy Aquifer
- Lloyd aquifer utilized by coastal municipal water suppliers
- Lloyd protected from excessive pumping in 1986
NATURALLY OCCURRING CONSTITUENTS IN LONG ISLAND’S AQUIFERS

• High Iron concentrations found in Magothy and Lloyd Aquifers above secondary contaminant standard (0.3 parts per million [mg/L])
# LAND USE AND TYPICAL CONTAMINANTS OF LONG ISLAND

<table>
<thead>
<tr>
<th>LAND USAGE</th>
<th>CONTAMINANTS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agriculture</strong></td>
<td>Ammonia, Nitrate (NO₂)</td>
</tr>
<tr>
<td><strong>Household waste systems &amp; Landfills</strong></td>
<td>Synthetic organic compounds (SOCs)</td>
</tr>
<tr>
<td>(suburbanization &amp; urbanization)</td>
<td>Halogenated compounds (THMs)</td>
</tr>
<tr>
<td></td>
<td>Personal care products</td>
</tr>
<tr>
<td><strong>Aviation Industry</strong></td>
<td>Volatile Organic Compounds (VOCs)</td>
</tr>
<tr>
<td>(70 air fields &amp; 20 manufacturers)</td>
<td>• 1,1,1-trichloroethane (TCA)</td>
</tr>
<tr>
<td></td>
<td>• 1,1,2-trichloroethelyene (TCE)</td>
</tr>
<tr>
<td></td>
<td>• MTBE, Freon, metals, paint sludge, etc.</td>
</tr>
</tbody>
</table>
1,4-DIOXANE OCCURRENCE IN LONG ISLAND AQUIFERS

Unregulated monitoring Rule 3 (UCMR3) Results

• 31 out of 41 water suppliers from Nassau and Suffolk detected 1,4-dioxane

• Levels varied from 0.07 ppb to 34 ppb

• Additional treatment required if 0.35 ppb becomes standard (1x10^{-6} cancer risk level [EPA-IRIS])

• Iron will be a major inhibitor for 1,4-dioxane removal.

High 1,4-dioxane
High Iron
11.7%

Low 1,4-dioxane
High Iron
12.9%

Low 1,4-dioxane
Low Iron
34.4%

High 1,4-dioxane
Low Iron
41.0%

Nassau County Water supply characterized by Iron & 1,4-dioxane concentration

High Iron >0.3 ppm (secondary standard)

High 1,4-dioxane >0.35 ppb (Cancer risk level)
LONG ISLAND TREATMENT TECHNOLOGIES
ION EXCHANGE

• Physical/chemical process where less harmful ions are exchanged with the contaminant of concern (COC)

• For an exchange to occur, the Resin must have
  • Same ionic charge as COC
  • Lower valance electron charge than COC
  • Lower atomic number than COC
  • Used for Nitrate removal

NOT EFFECTIVE AT REMOVING
1,4-DIOXANE

• Electronegative oxygen molecules with a partial negative charge

• Transitional dipole moment

Figure 16-2
Schematic framework of functional cation exchange resin: (a) resin initially immersed in an aqueous solution containing $B^+$ cations and $X^-$ anions; (b) cation exchange resin in equilibrium with aqueous solution of $B^+$ cations and $X^-$ anions.
LONG ISLAND TREATMENT TECHNOLOGIES
PACKED TOWER AERATION SYSTEM (PTAS)

• Interaction between VOCs solution and air result in vaporization of VOCs
• For absorption to occur, the following chemical characteristics must be satisfied
  • Insoluble contaminant
  • Volatile contaminant (high Henry’s Law constant)

NOT EFFECTIVE AT REMOVING 1,4-DIOXANE
• High solubility (miscible)
• Low Henry’s Law constant

<table>
<thead>
<tr>
<th>1,4-dioxane</th>
<th>TCA</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry’s Law Constant (atm m³/mole)</td>
<td>4.88x10⁻⁶</td>
<td>0.0172</td>
</tr>
</tbody>
</table>
1,4-DIOXANE TREATMENT TECHNOLOGIES
GRANULAR ACTIVATED CARBON (GAC)

- Physisorption/chemisorption process uses carbon media to adsorb contaminants
- For removal to occur, the following chemical characteristics must be satisfied
  - Insoluble contaminant
  - Non-polar

1,4-dioxane characteristics
- High solubility (miscible)
- Transitional dipole moment (polar and nonpolar)

However
- Case studies show traditional carbon’s capability of 1,4-dioxane removal
- Low treatment flow rate (0.5 gal/min)
- High influent concentrations (1,000ppb)
1,4-DIOXANE TREATMENT TECHNOLOGIES
GRANULAR ACTIVATED CARBON (GAC)

Ideal Adsorption Theory
- Competitive interaction between cocontaminants
- 1,1,1-TCA dominant adsorptive characteristics
- TCA inhibits absorbance of 1,4-dioxane

Engineered Carbon Media
- Nano enhanced media like titanium Dioxide (TiO$_2$)
- Manganese Oxide (MnO)

Conclusion
- Not effective at 1,4-dioxane removal at high flow rates & influent concentrations
- High operational cost for engineered media replacement
1,4-DIOXANE TREATMENT TECHNOLOGIES
ADVANCED OXIDATION $\text{H}_2\text{O}_2$/UV

- The Hydrogen peroxide/UV light AOP is effective at removing 1,4-dioxane.
- Currently one pilot plant in operation on Long Island (SCWA).

**Treatment Process**
- $\text{H}_2\text{O}_2$ is mixed into the chamber with influent water.
- $\text{H}_2\text{O}_2$ and UV light react to create a Hydroxyl Radical.
- Hydroxyl radicals attacks the hydrogen atoms of influent compound.

**4 Mechanisms of Chemical Decomposition**
- Photolysis of hydrogen peroxide.
- Scavenging of hydroxyl radicals.
- UV light adsorption to influent compounds.
- Photolysis of influent compounds.

**Chemical Formulas**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-dioxane</td>
<td>$\text{C}_4\text{O}_2\text{H}_8$</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>$\text{C}_2\text{H}_3\text{Cl}_3$</td>
</tr>
<tr>
<td>TCE</td>
<td>$\text{C}_2\text{HCl}_3$</td>
</tr>
</tbody>
</table>

**Chemical Reactions**

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow \cdot 2\text{OH} \]

\[ \text{HOCl} + h\nu \rightarrow \cdot \text{OH} + \cdot \text{Cl} \]
**1,4-DIOXANE TREATMENT TECHNOLOGIES**

**ADVANCED OXIDATION \( \text{H}_2\text{O}_2/\text{UV} \)**

**Disadvantages**

- Post treatment is required to remove residual hydroxyl radical concentration (GAC)
- Influent turbidity needs to be monitored and controlled
- Multiple undesirable byproducts can be produced through the chemical destruction reactions
- High Operational cost due to energy usage

**Not a Feasible Option with High Iron Concentrations**

- Iron precipitate will cause scaling and high turbidity
- Prevent the photolysis reactions from occurring
- Need additional iron treatment to minimize influent iron concentrations

![Typical UV treatment vessels](image-url)
1,4-DIOXANE TREATMENT TECHNOLOGIES
SYNTHETIC MEDIA (AMBERSORB™)

• Same filter media used for ion exchange resin
• Activated through pyrolysis
• Hydrophobic media captures 1,4-dioxane
• Zero headspace treatment design prevents precipitation of iron during treatment
• Pore structure is engineered to be uniform

Ambersorb 560
1,4-DIOXANE TREATMENT TECHNOLOGIES
SYNTHETIC MEDIA (AMBERSORB™)

Ambersorb Treatment Process
1,4-DIOXANE TREATMENT TECHNOLOGIES
SYNTHETIC MEDIA (AMBERSORB™)

Advantages
• Captures 1,4-dioxane at low influent concentrations
• In-place regeneration using low pressure steam
• Can be regenerated thousands of times with consistent removal capacity (0.04ppb)
• Media is resistant to biofouling

Disadvantages
• Additional treatment required during backwashing (GAC filters)
• Large treatment footprint

GAC & Ambersorb’s absorptive capacity of 1,4-dioxane

GAC & Ambersorb's absorptive capacity of 1,4-dioxane

2 mg/g

34ppb
1,4-DIOXANE REMEDIATION TECHNOLOGIES
BIOSTIMULATION & BIOAUGMENTATION

- Not a well head treatment technology
- 1,4-dioxane can be removed through in-situ bioremediation
- Organisms CB1190 are capable of 1,4-dioxane consumption
- Retard the 1,4-dioxane plume movement

**Biostimulation**
- Low populations of CB1190 are present in the aquifers
- Oxygen and nutrients are dosed into the aquifer to ‘stimulate’ population growth

**Bioaugmentation**
- No CB1190 organisms are present in the aquifers
- CB1190, Oxygen and nutrients are dosed into the aquifer to ‘augment’ population growth

**Biostimulation process**

<table>
<thead>
<tr>
<th>Initial plume concentration</th>
<th>final plume concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5 ppb</td>
<td>0.35 ppb</td>
</tr>
<tr>
<td>0.3 ppb/week</td>
<td></td>
</tr>
</tbody>
</table>

= 24 week = 6 months
1,4-DIOXANE TREATMENT TECHNOLOGIES
BIOSTIMULATION & BIOAUGMENTATION

**Treatment Process**
- Collect samples to determine CB1190 presence
- Test CB1190 survival capability in aquifer environment
- Determine stimulant concentrations needed for CB1190 population growth
- Monitor population growth and removal rates

**Advantages**
- In-situ (little/no operational footprint)
- Low operational and Capital cost

**Disadvantages**
- ICSO will cause iron to precipitate and clog pores and increase iron concentrations are municipal wells
- Adding foreign organisms and stimulants may cause undesirable effects in the aquifer (bacteria adaptation)

Bioremediation injection well arrangement
# 1,4-DIOXANE TREATMENT TECHNOLOGIES
## FEASIBILITY ANALYSIS

<table>
<thead>
<tr>
<th>Description</th>
<th>A.O.P. (HP/UV)</th>
<th>Amersorb</th>
<th>Bioaugmentation &amp; Biostimulation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Location of Treatment</strong></td>
<td>Ex-situ</td>
<td>Ex-situ</td>
<td>In-situ</td>
</tr>
<tr>
<td><strong>Capital Cost</strong></td>
<td>Medium</td>
<td>High</td>
<td>Low/Medium</td>
</tr>
<tr>
<td><strong>Operational Cost</strong></td>
<td>High</td>
<td>Medium</td>
<td>None/Low</td>
</tr>
<tr>
<td><strong>Chemicals Required</strong></td>
<td>peroxide</td>
<td>Steam</td>
<td>Oxidant</td>
</tr>
<tr>
<td><strong>Post Treatment Required</strong></td>
<td>Yes (GAC)</td>
<td>Yes (GAC)</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Treatment Byproducts</strong></td>
<td>Yes</td>
<td>No</td>
<td>Unknown</td>
</tr>
<tr>
<td><strong>Treatment Equipment Footprint</strong></td>
<td>Medium</td>
<td>High</td>
<td>Low/None</td>
</tr>
</tbody>
</table>

### Influent Water-Low Iron Concentrations
- Pre Treatment Required | No | No | N/A |
- Post Treatment Required | Yes | No | N/A |
- Treatment Byproducts | Yes | No | Unknown |
- Treatment Equipment Footprint | Medium | High | Low/None |

### Influent Water-High Iron Concentrations
- Pre Treatment Required | Yes | No | N/A |
- Post Treatment Required | Yes | No | N/A |
- Treatment Byproducts | Yes | No | Unknown |
- Treatment Equipment Footprint | Medium | High | Low/None |

**QUESTIONS?**