Issues of Arsenic in Florida Soils:
(i) Impacts of Treated Wood
(ii) Mobilization of Naturally Occurring Arsenic

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CCA – Treated Wood
• A major topic of interest in Florida in past decade.
• As you know, Florida has relatively low arsenic concentrations in the environment.
• CCA-treated wood was the largest import of a product containing arsenic.

Background on CCA-Treated Wood
• CCA: Chromated Copper Arsenate
• The predominant wood preservative used in the United States in recent history

Why do we need wood preservatives?
• To prevent accelerated decay of wood
  • Fungi
  • Bacteria
  • Insects

Typical Uses
• Decks, Boardwalks

Typical Uses
• Fences
Typical Uses

- Utility Poles

Typical Uses

- Building Construction

Typical Uses

- Playgrounds

The Treatment Process

- CCA is a chemical solution that is prepared at a chemical plant.
- The CCA solution is then transported to a wood preservation plant.
The Treatment Process

- Several types of CCA-solution standardized by the industry
- TYPE C
  - 47.5% Cr as CrO\textsubscript{3}
  - 18.5% Cu as CuO
  - 34.0% As as As\textsubscript{2}O\textsubscript{5}

The Treatment Process

CCA

Untreated Wood Product

Treatment Cylinder

Drying and Fixation

To Market

Different Products Contain Different Amounts of CCA

- CCA-treated wood products are rated by their standard retention value (in units of lbs of CCA per ft\textsuperscript{3} of wood).
- Retention value requirements are set by the AWPA.

Note

- Concentrations of As in CCA-treated wood for typical residential applications
  - 0.25 pcf
    - As = 1,700 mg/kg; Cr = 2,000 mg/kg
  - 0.40 pcf
    - As = 2,700 mg/kg; Cr = 3,200 mg/kg

Chemistry of CCA Treatment

- Based on the reduction of hexavalent chromium to trivalent chromium
- This process has been termed “fixation”
- Fixation is a function of:
  - Time
  - Temperature
  - Wood species and condition
Chemistry of CCA-Treatment

Treating Solution

- \( \text{Cr}_2\text{O}_3 \)
- \( \text{CuO} \)
- \( \text{As}_2\text{O}_3 \)

Treated Wood

- \( \text{CrAsO}_4 \)
- \( \text{Cu(OH)CrAsO}_4 \)
- \( \text{CuCrO}_4 \)
- \( \text{Cr(OH)}_3 \)
- \( \text{Cr}^{6+}/\text{wood complexes} \)
- \( \text{Cr}^{3+}/\text{wood complexes} \)
- \( \text{Cu}^{2+}/\text{wood complexes} \)
- \( \text{As}_2\text{O}_5 \)

Focused on CCA-Treated Wood?

- Arsenic has been a focus of special attention in Florida in recent years
- Relatively low risk-based cleanup concentrations (e.g. \( SCTL_{Res} = 0.8 \text{ mg/kg} \))
- Relatively low background soil concentrations

Amount of Arsenic Imported Into Florida in CCA-Treated Wood

28,600 tons of As, Cumulative

1600 tons As imported per year

Disposed to date: 1600 tons

Future disposal (for that imported through 2000): 24,100 tons

Soil Contamination with As

- Two potential sources
  - At the treatment plant
    - Spills, leaks, improper handling
  - Around the wood products (in service)

Arsenic Contamination during In-Service Use

Possible mechanisms

1. Debris from construction (sawdust)
2. Abrasion of wood particles from wood surface
3. Leaching of metals from wood into water and into underlying soil
Debris from Construction

- Impact on site contamination dependent on construction techniques and debris management techniques
- If debris left on site, there will be potential "hot spots"

Reminder
As concentrations in wood ~ 2,000+ mg/kg

Lebow et al. 2000

- "...although the rate of release from construction debris is much greater than from the wood used in the structure, the greater volume of wood used in the structure will cause the structure itself to contribute the bulk of preservative released."

Abrasion of Wood

- Anecdotal observations suggest that in some settings, the wood is abraded in substantial amounts.
- Impact of this has not been measured.

Leaching of Metals from CCA-Treated Wood

- While the metals in CCA are "fixed" to the wood during the treatment process, the metal compounds in the wood are still "relatively" water soluble

Laboratory Leaching Studies

- Several methods
  - Batch tests
  - Tanks tests

Synthetic Precipitation Leaching Procedure (SPLP)
Rainwater leaching test at 20:1 Liquid to Solid Ratio (18 hours)

SPLP Results

Results of Nine New CCA-treated Wood Samples
Impact of pH

Summary of Leaching

- Arsenic, copper and chromium do leach from CCA-treated wood over time
- Several variables impact the rate and extent which As, Cr, and Cu leach
- Leaching generally occurs:  
  As > Cu > Cr

Contamination of Soils near CCA-treated Structures

- Metals that leach from CCA-treated structures can result in soil contamination
- Several studies have been conducted to evaluate the concentration of metals in soils underneath CCA-treated structures

Florida Study

- Total of 73 soil samples collected from under a total of nine treated wood structures.
- Total of 73 control soil samples taken at a minimum distance of 50 to 100 ft from the structure.
- Soil samples were collected from within the upper 1 inch of surface soil.
- One soil core was collected from each site.
Results of Florida Study

**Site** | Beneath Deck | Control
---|---|---
BP | 41.6 | 2.6
BR | 10.7 | 0.3
PP | 9.6 | 0.5
TB | 17.2 | 2.3
MG | 34.0 | 1.4
AD | 33.9 | 2.0
TP | 4.3 | 1.1
OP | 79.1 | 0.7
OVERALL | 28.5 | 1.3
Vertical Distribution of Arsenic in Soil

- Soil core measurements

Other studies have found As to be concentrated in the upper horizon of the soil.

Mass balance results on some core samples indicate that while arsenic may be concentrated in the upper soil horizon, some arsenic migrates with water.

Risk of Arsenic in Soil

- Florida’s residential direct exposure risk standard for As is 2.1 mg/kg (used to be 0.8 mg/kg).
- Soils near CCA-treated wood structures will have concentrations that exceed this amount.
CCA-Treated Wood Status

- CCA-treated wood has been phased out from residential applications.
- Newer wood products contain more copper.
- A lot of CCA-treated wood remains to be disposed.

Simulated Landfills
Current Situation with CCA-Treated Wood in Florida

- CCA-treated wood leaches enough arsenic to be characterized as a hazardous waste if not otherwise excluded in the regulations
- CCA-treated wood is currently allowed to be disposed in unlined C&D debris landfills in Florida
- The FDEP is developing new rules that would require unlined disposal facilities to identify and remove CCA-treated wood prior to disposal

Fate of CCA-Treated Wood under Unlined Landfills

- Will arsenic travel through the soils underneath the landfills or in the aquifer sediments?
- While arsenic is relatively mobile in landfills, we know that arsenic binds to naturally to certain soil minerals, particularly iron oxide minerals.
74 sites total

- Visual Inspection Suggests Likely Exceedance
- Visual Inspection Suggests Possible Exceedance

Arsenic isotherm study

- Langmuir isotherm
- Equation $q = (q_{max} K C) / (1 + K C)$
- At low concentration range, $q_{max} K$ equal to $K_d$ value

Method

- Inject As(V) and As(III) into oxidizing and reducing condition, analyze the arsenic concentration in water and soil phase.

As speciation

- After As(V) inject into reducing condition 1 day, in water phase, 50-80% arsenic remain As(V), 20-50% are As(III). It indicate As(V) reduce very quick under reducing condition.

Compare to As(V), As(III) distribute more in water phase.

Compare to oxidizing condition, arsenic distribute more in water phase under reducing condition.

Model Set-Up

- Depth to Groundwater Table = 2 ft (limestone)
- 7 ft (coastal flatland)
- 10 ft (upland flatland)
- Depth of Groundwater = 30 ft
- Wells screened from water table down 20 ft

Arsenic Concentration (mg/L)

- Soil #1

- K = $10^{-3}$ cm/sec
- Kd = 0 L/kg
- K = $10^{-3}$ cm/sec
- Kd = 29 L/kg

Detection Well at 50 ft from Toe

Compliance Well at 100 ft from Toe

Direction of Groundwater Flow

MYGRT – Pollutant Transport Model

- Leaching from Contaminated Area
- + Receptor Well
- Unsatuated Zone
- Saturated Zone
- Ambient Groundwater Flow
The relationship between iron and arsenic

• We know arsenic binds with iron oxides in soil.
• Oxidized iron is used to remove arsenic from drinking water
  • As drinking water standard is 0.01 mg/L
• What happens if the iron in the soil is disrupted?

\[
\frac{1}{4} (\text{solid CH}_2\text{O}) + \text{FeOOH} (s) + 2H^+ = \frac{1}{4} \text{CO}_2 + \frac{7}{4} \text{H}_2\text{O} + \text{Fe}^{2+} \text{dissolved}
\]
### Typical Range of Iron Concentrations

<table>
<thead>
<tr>
<th>µg/L</th>
<th>mg/L</th>
<th>µg/L</th>
<th>mg/L</th>
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<tr>
<td>10</td>
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<tr>
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<td>100,000</td>
<td>100</td>
</tr>
<tr>
<td>1,000,000</td>
<td>1000</td>
<td>1,000,000</td>
<td>1000</td>
</tr>
</tbody>
</table>

**Health Benchmark**

<table>
<thead>
<tr>
<th>Sample Date</th>
<th>Iron (µg/L)</th>
</tr>
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<tbody>
<tr>
<td>9/19/1991</td>
<td>101</td>
</tr>
<tr>
<td>6/15/1994</td>
<td>102</td>
</tr>
<tr>
<td>3/11/1997</td>
<td>103</td>
</tr>
<tr>
<td>12/6/1999</td>
<td>104</td>
</tr>
<tr>
<td>9/1/2002</td>
<td>105</td>
</tr>
<tr>
<td>5/28/2005</td>
<td>106</td>
</tr>
<tr>
<td>2/22/2008</td>
<td>107</td>
</tr>
</tbody>
</table>

**SMCL**

Health-based risk level

- P-17 MW-2
- 5A
- 6
- 7
- 8D
- 9
- 11
- 12
- 13
- 14
- 15
- 16
- P21
- 22
- 24
- 25
- 26
- 27
- Leachate
Elevated Iron Concentrations are Impacting Landfill Operations at Some Facilities

Exceedances of iron in landfill groundwater monitoring wells and iron impacts on surface waters in the vicinity of landfills has elevated this issue to one a major concern and research interest.

Let’s now examine some basic facts about iron and what might be causing iron releases at landfill.

Iron

- Fourth most abundant element on earth
- Exists in different forms

Form of Iron

- Iron exists in different forms
- As part of different chemical compounds
  - Iron oxides (e.g., hematite) \( \rightarrow \) \( \text{Fe}_2\text{O}_3 \)
  - Iron oxyhydroxides (e.g., geothite) \( \rightarrow \) \( \text{FeO(OH)} \)
  - Steel \( \rightarrow \) Fe alloy
- Iron will exist in different oxidation states depending on the chemical compound
What Does Oxidation State Mean?

- “The sum of negative and positive charges in an atom, which indirectly indicates the number of electrons it has accepted or donated.” — *wikipedia definition*

- Zero valent iron → Fe
- Ferrous iron → Fe$^{+2}$
- Ferric iron → Fe$^{+3}$

### Hematite

- $\text{Fe}_2\text{O}_3$

\[-2 \times 3 = -6\]
\[X \times 2 = 6\]
\[X = +3 \rightarrow \text{Fe}^{+3} \rightarrow \text{Ferric iron}\]

### Geothite

- $\text{FeO(OH)}$

\[-1 \times 1 = -1\]
\[-2 \times 1 = -2\]
\[X \times 1 = 3\]

\[X = +3 \rightarrow \text{Fe}^{+3} \rightarrow \text{Ferric iron}\]

### Total Iron in Florida Soils, mg/kg

(Dr. Lena Ma, HCSHWM Report #99-7)

<table>
<thead>
<tr>
<th>TYPE</th>
<th>mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultisols-19%</td>
<td>1,220</td>
</tr>
<tr>
<td>Entisols-22%</td>
<td>1,200</td>
</tr>
<tr>
<td>Spodosols-28%</td>
<td>330</td>
</tr>
<tr>
<td>Histosols-10%</td>
<td>3,500</td>
</tr>
<tr>
<td>Inceptisols-3%</td>
<td>1,440</td>
</tr>
<tr>
<td>Mollisols-4%</td>
<td>2,060</td>
</tr>
<tr>
<td>Alfisols-14%</td>
<td>980</td>
</tr>
</tbody>
</table>

### Forms of Iron in Soil

- Fe$^{+3}$ minerals
  - Goethite $\alpha$-FeOOH
  - Akaganeite $\beta$-FeOOH
  - Lepidocrocite $\gamma$-FeOOH
  - Ferroxyhyte $\delta$-FeOOH
  - Ferrihydrite Fe$_2$HO$_8$
  - Hematite $\alpha$-Fe$_2$O$_3$
  - Maghemite $\gamma$-Fe$_2$O$_3$
  - Magnetite Fe

- Fe$^{+2}$ minerals
  - Siderite FeCO$_3$
  - Pyrite FeS$_2$
  - Pyrrhotite FeS
  - Fe$^{+2/+3}$ minerals
  - Magnetite Fe$_3$O$_4$
Iron from Soils

- As described earlier, iron exists naturally in soils.
- What can cause iron to be released?
- Dissolution:
  - Chemical conditions (e.g., pH change so iron dissolves)
  - Redox change

Biological Influence

- In the environment, many redox reactions are biologically mediated.
- Consider the biodegradation of a carbon compound:
  \[ C_6H_{10}O_5 \rightarrow 6CO_2 + 24e^- \]

### Summary of Basic Hypothesis

**Reductive Dissolution**

- Iron occurs naturally in the solid phase as Fe^{3+}.
  - Under reducing conditions, iron can be biologically reduced to Fe^{2+}.
  \[ \frac{1}{4}[CH_2O] + \frac{1}{8}NO_3^- + \frac{1}{4}H^+ = \frac{1}{4}CO_2 + \frac{1}{10}N_2 + \frac{1}{2}H_2O \]
- This results in iron exceedances in groundwater.
- When groundwater hits the atmosphere again (at a seep or creek), the iron precipitates back out of solution.

**Fe^{2+} (dissolved) \rightarrow Fe^{3+} (solid)**

### Experimental Activities

- Can we replicate the "reductive dissolution" phenomenon in the laboratory using soils from landfills sites?
- What test procedures can we use?
  - Biological
  - Chemical
- What soil properties impact iron reductive dissolution?
Biological reducing test for soils

0 10 20 30 40 50
0 50 100 150 200
Time (days)
Ferrous conc. (mg/kg)

ORP (mv)

0 100 200 300 400

0 200 400 600 800 1000 1200
30 days bio.reducing Fe2+ (mg/kg)

Amorphous Fe (mg/kg)
y = 0.1595x + 10.471
R² = 0.8075

What conditions have to occur in the groundwater for this reaction to occur?

Iron is "reductively dissolved" from solid phase

\[
\frac{1}{4} (CH_4O) + FeOOH(s) + 2H^+ = \frac{1}{4} CO_2 + \frac{7}{4} H_2O + Fe^{2+}
\]

Organic matter is consumed.
(abiotic reduction would be an exception)

Iron must be the preferred electron acceptor.
→ No (or little) oxygen!!

Consider conditions prior to a landfill. Since the aquifer is at equilibrium with atmosphere (w.r.t. dissolved oxygen), the iron stays in the solid phase.

Amorphous Iron

Vadose Zone
Aquifer

An unlined landfill is constructed.

Vadose Zone
Aquifer

If organic matter is discharged into the aquifer, it can be used by bacteria as a food source. Once oxygen is used up (along other more favorable electron acceptors), iron will be utilized, resulting in reductive dissolution.
Another factor is landfill gas. It is important to understand that landfill gas will move down if that is the path of least resistance.

What is the role of landfill gas?
- Displaces oxygen
- Adds organic matter

\[ \frac{1}{4} \left( CH_4 + Fe(OH)_3(s) + 2H^+ \right) \rightarrow \frac{1}{4} CO_2 + \frac{3}{2} H_2O + Fe^{3+} \]

The displacement of air from the vadose zone can limit reaeration and promote oxygen depletion.

Consider a liner. Can it have an impact?

Can the liner sufficiently cut off reaeration such that iron reducing conditions develop?

Observations at Unlined Landfills in Florida

Observations at Lined Landfills in Florida

Summary of Basic Hypothesis
- What would cause this to happen?
  - Organic matter is consumed at a rate greater than can be supplied by oxygen
- Causes:
  - So much organic matter is added to the aquifer that all of the oxygen is used up by the aerobic organisms and then other organisms (iron reducing bacteria) become dominant (leachate, landfill gas)
  - The natural rate of recharge of oxygen to the aquifer is interrupted so that naturally occurring organic matter is now consumed by iron reducing bacteria (displacement of oxygen by landfill gas, interruption of recharge by the liner?)
  - A combination of both
What conditions have to occur in the groundwater for this reaction to occur?

\[
\frac{1}{4} \text{[CH}_2\text{O]} + \text{FeOOH(s)} + 2H^+ = \frac{1}{4} \text{CO}_2 + \frac{7}{4} \text{H}_2\text{O} + \text{Fe}^{2+}
\]

Iron is "reductively dissolve" from solid phase

Organic matter is consumed. (abiotic reduction would be an exception)

Iron must be the preferred electron acceptor.

\[ \rightarrow \text{No (or little) oxygen!!} \]

Iron is naturally occurring in the soil in the Fe\(^{3+}\) form. When reducing conditions develop, iron-reducing bacteria (IRB) can transform solid-phase Fe(III) to dissolved phase Fe(II).

Naturally occurring iron in soil

Dissolved iron in groundwater

Note: IRB will only flourish when DO is low.

Organic Matter Release with Iron Release

Organic matter is consumed.

(Reaction between iron (II) and hydrogen peroxide)

Iron must be the preferred electron acceptor.

\[ \rightarrow \text{No (or little) oxygen!!} \]

The Issue May be More than Iron

- The relationship between iron release and arsenic release is well established
Fundamental Hypothesis: Part 2

- The Fe(III) iron minerals contain bound such that when Fe(III) dissolves, As is released into solution. Also, Fe(III) minerals contain sufficient organic matter to act as carbon source (needed unless the groundwater contains sufficient carbon source).

![Iron mineral](image1)

Soil Structure

Close up of Iron Mineral

![Arsenic Release during Biological Reducing Test](image2)

- Column Test

Filled with bulk soil sample

Condition: Aerobic / anaerobic
Flow rate: 100 mL / day
Initial DO: 9.4 mg/L (aerobic)
0.5-1.0 mg/L (anaerobic)

![Remediation Strategies?](image3)

- Reaerate the vadose zone