Phytoremediation of Arsenic

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CE 421
Introduction

Arsenic is listed as the #1 hazardous substance according to the U.S. Agency for Toxic Substances and Disease Registry

Arsenic Background

Sources of Arsenic contamination:
- mine waste (primarily sulfide, iron and tin)
- tanneries
- metal smelters
- geothermal activity

Arsenic has been used in the following:
- embalming fluids
- paint pigments
- insecticides
- herbicides
- defoliants
- metal alloys
**Arsenic Background**

- Poisonous effects of arsenic date back to 17th and 18th centuries when it was used to kill several kings, termed "Poison of kings".

- Minnesota, Wisconsin, Michigan, North Dakota, and South Dakota have elevated amounts of arsenic in groundwater.

- 10 ppb World Health Organization drinking water standard, estimated that over 50 million people worldwide are drinking water with arsenic concentrations in excess of this standard.

- Highly toxic due enzyme inhibition, is suspected as causal agent in various forms of cancer and skin lesions.

- Arsenic poisoning symptoms include severe stomach pain, nausea, headaches and usually leads to death if untreated.
Effects of Arsenic Poisoning

Skin lesions

(source: www.sos-arsenic.net, 2006)
Most Common Soil Arsenic Species

- Arsenic is typically found in the soil in the following forms: Arsentate, Arsenite, dimethyl arsenic acid and monomethyl arsenic acid

- Inorganic forms arsenate, or As (V), and arsenite, or As (III), most common in soil

- Arsenate prevails under aerobic conditions, is less toxic and less mobile than arsenite, due to stronger soil sorption
Current Arsenic Remediation Techniques

- **Soil removal** - excavation
- **Capping** - place hard cover over soil
- **Solidification and stabilization** - inject polymers and other stabilizing compounds into ground
- **Acid-washing** - Use aqueous acidic solution to extract water-soluble arsenic

Disadvantages: $400,000 per hectacre, safety, some don’t remove arsenic
Phytoremediation: The removal of a substance from the air, soil, or water via a microorganism or plant.

Several subdivisions of phytoremediation: phytovolatilization, phytoextraction, phytostabilization, and rhizofiltration.
Why use phytoremediation?

- Low Cost
- Environmentally-friendly
- Much lower occupational risk
- Arsenic is a chemical analog to phosphorus (i.e. it’s easily taken up by plants)
Why is arsenic toxic for most plants?

- Arsenic toxicity threshold for most plants is (40-200) mg As per kg DW depending on soil conditions.

- Arsenate replaces phosphate when taken up, and disrupts production of ATP, which results in cell death.

- Arsenic is inhibitory towards cell function because it reacts with sulfydryl enzymes and disrupts their activity.
Arsenic Accumulating Plants

- *Pteris* ferns
- *Pityrogramma calomelanos*
- *Lemna gibba* (duckweed)
- *Lepidium sativum* (watercress)
- *Lupinus albus* (white lupin)
- Mustard Plants
Factors affecting arsenic accumulation

Arsenic sorption to soil is the primary process that immobilizes this metal, depends on soil pH, amount of organic matter, and texture.

- **Soil pH**: Arsenate absorbed to soil (4-7), Arsenite (7-10)
- **Presence of Ferric and Aluminum arsenic compounds** (lower water solubility)
- **Bioavailability** (water solubility)
Definitions of a hyperaccumulator

- Plant accumulates greater than 1000 mg of contaminant per kg DW (Brooks, 1998)
- Bio-concentration Factor (BF) > 1, ratio of plant to soil arsenic concentration
- Translocation Factor (TF) > 1, ratio of aboveground biomass to root system arsenic concentration
- Accumulation concentration of a contaminant greater than 100 times than the highest value for a non-hyperaccumulating plant
Why use a hyperaccumulator?

- Decrease amount of time needed to remediate contaminated area
- Reduce volume of contaminated biomass
- Makes phytoremediation a realistic option
Arsenic hyperaccumulators

- *Pteris vittata, biaurita, quadriaurita, and ryukyuensis*

- *Pityrogramma calomelanos*
Mechanisms of arsenic accumulation

- Take up arsenate in the soil and reduce it to arsenite in plant tissue
- Translocate arsenic from roots to shoots via xylem sap
- Chelate free arsenic in cytoplasm and bind it to cell wall via phytochelatins (PCs)
- Vacuolar storage also reduces free arsenic in the cytoplasm
- Mycorrhizal symbiosis, which enhances nutrient absorption area and uptake kinetics (allows for improved phosphate and arsenate uptake)
### Table 1. Arsenic concentrations in P. vittata

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Soil Arsenic (ppm)</th>
<th>Plant Arsenic (ppm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 weeks</td>
<td>6 weeks</td>
</tr>
<tr>
<td>Control</td>
<td>6</td>
<td>755</td>
<td>438</td>
<td></td>
</tr>
<tr>
<td>As-contaminated soil*</td>
<td>400</td>
<td>3,525</td>
<td>6,805</td>
<td></td>
</tr>
<tr>
<td>Low As¹</td>
<td>50</td>
<td>5,131</td>
<td>3,216</td>
<td></td>
</tr>
<tr>
<td>Medium As¹</td>
<td>500</td>
<td>7,849</td>
<td>21,290</td>
<td></td>
</tr>
<tr>
<td>High As¹</td>
<td>1,500</td>
<td>15,861</td>
<td>22,630</td>
<td></td>
</tr>
</tbody>
</table>

*Arsenic-contaminated soil was collected from the site where P. vittata was obtained

¹ Artificially contaminated soil was spiked with three levels of water-soluble potassium arsenate

(Source: Ma et. al, 2001)
Figure 2. Concentration of arsenic per kg dry weight of *P. calomelanos* for different regions of the plant (Visoottiviseth et al., 2002).
Disposal of Plant Biomass

- Significant amounts of arsenic can leach from biomass (threat to groundwater) (Tu et al., 2003)
- Arsenite in biomass oxidizes back to arsenate
- Marine algae capable of biotransforming arsenic into non-toxic forms (Francesconi et al., 2002)
- Biomass can NOT be burned, results in release of toxic $\text{As}_2\text{O}_3$
Conclusions

- Many plants have demonstrated capability for phytoremediation of arsenic contaminated soils (*P. vittata, P. calomelanos*, etc.)
  1) Plants translocate arsenic in roots to shoots
  2) Plants reduce As(V) to As(III) in plant tissue

- Question which remains:
  Why do plants transform arsenate into arsenite (more toxic form) in plant biomass?

- More research still needed to discover arsenic-accumulating plants that grow over a range of climates and soil conditions