

## Bioremediation: Phytoremediation

Phytoremediation is defined as the use of green plants to remove, contain, or render harmless contaminants in soils and sludges. Phytoremediation may be conducted surficially in near surface soils, in situ in the deep aquifer, or ex-situ for contaminated liquids treatment (extracted groundwater or surface water). Plants have been used for wastewater treatment applications over the past 300 years, and began to be used for treatment of slurries and metal contamination in the mid 1970s. However, there are still few contaminated sites where phytoremediation has been used for full-scale clean-up. Investigation into the use of plants for remediation of contaminated sites is currently a rapidly evolving area of research. In June 1997 at the International Business Communication's Second Annual International Phytoremediation Conference, estimates of the U.S. market for phytoremediation [were] \$3 to \$7 million, largely for removal of organic compounds from groundwater and heavy metals from soils; the overall market in the U.S. should grow to \$24 to \$50 million by the year 2000 (Environmental Protection, Sept. 1997). This chapter includes: a summary of the ways plants are useful in remediation, specific types of plants which are widely used, the application of plants for treatment of specific classes of contaminants, and costs associated with phytoremediation. Finally, some general comments on the future of phytoremediation are made.

### 1. Mechanisms of Plant-Based Remediation

There are six primary ways that plants are used for waste treatment and site remediation:

1. Stimulation of microorganism bioactivity in the root-zone/rhizosphere
2. enzymes from plant tissues can precipitate and bind aromatic pollutants
3. enzymes from plant tissues can degrade organic compounds
4. adsorb/sequester organics on plant roots (phytostabilization; in situ stabilization)
5. heavy metal and/or radioactivity **hyper-accumulation** in the plant tissue for soil and/or water remediation (phytoextraction, rhizofiltration)
6. phytovolatilization

Each of these phytoremediation applications will be discussed in more detail below.

#### 1.1 Stimulation of microbe bioactivity in the root-zone (aka the rhizosphere)

Plants can stimulate microbe (bacteria and fungi) bioactivity in the root-zone/rhizosphere by the excretion of bio-enhancing compounds. Typically, there are 10 to 100 times higher microbe concentrations in the rhizosphere compared to the bulk soil. The plant-excreted root exudates provide a carbon and nitrogen source for soil bacteria. The excreted compounds commonly include amino acids, carbohydrates, polysaccharides, flavinoids, and phenols. Specifically, it has been shown that flavonoids can support the growth of PCB-degrading bacteria. In addition, the phenols excreted by crabapple, sumac, mulberry, and asparagus plants can stimulate PCB-degrading bacteria and inhibit other microbes. Enhanced herbicide degradation has also been found in the presence of root exudates.

In addition, plants can excrete surfactants, which will increase the bioavailability of the contaminant to the soil microbes. For example, leguminous plants (soybeans) have been shown to aid bioremediation of oil-contaminated soil due to surfactant secretion.

From the perspective of the plants, it has been shown that the presence of contaminants can affect the root density of the plants. A decrease in fescue root density was observed in oil-contaminated soil (30,000 mg/kg TPH), while conversely aromatics contamination increased the root growth of alpine bluegrass.

#### 1.2 Enzymes from plant tissues can precipitate and bind aromatic pollutants

It has been found in laboratory studies that oxido-reductase enzymes present in the leaves, stems, and roots of plants can precipitate and bind aromatic compounds. When

crushed plant matter and H<sub>2</sub>O<sub>2</sub> as electron acceptor were added to water containing dichlorophenol (DCP), the DCP became bound into the plant matter. By comparing different treatment conditions, an optimal “size” of the crushed material and concentration of plant material, pH range (3-8), and the potential for “reuse” of the plant material was found.

### 1.3 Enzymes from plant tissues can degrade organic compounds

In addition to precipitation and binding of aromatic compounds, other intracellular plant enzymes can degrade and transform organic compounds. For example, the nitroreductase in plants rapidly degrades explosives and other nitroaromatics. Carreira (1995) reported that nitroreductase and laccase enzymes completely degraded trinitrotoluene (TNT) to form new plant biomass (i.e. lignin), and also reported the development of an immunospecific assay to screen native plants for nitroreductase activity (Carreira 1). In lab studies it has been shown that hairy root cultures can degrade TNT, and in addition some common aquatic plants degrade TNT. Based on the evidence of explosives degradation by plants, the U.S. Army Environmental Center is developing program to use constructed wetlands to degrade TNT and RDX (Bader 1).

Another plant enzyme, a dehalogenase, has been used for halogenated hydrocarbon degradation \*(Wolfe 1). In addition, poplar trees have been demonstrated to have the ability to dealkylate and hydrolyze atrazine, with radiolabeled lab studies showing that atrazine metabolites are incorporated into plant roots and leaves.

\*halogens include chloride, bromide, fluoride,.... therefore, dehalogenase will degrade compounds including trichloroethene (TCE).

### 1.4 Adsorb/sequester organics (in situ stabilization)

In-situ stabilization of contaminants can take many forms including:

a) prevent migration of the contaminant with the groundwater, due to the water flux to the plant (localized gradient toward the plant)

b) contaminants that are ions can be transported across root-cell membranes; therefore, the contaminant is now present in the plant roots. It will remain in the root when the plant is alive (and is therefore technically still in-situ) but can be re-released if the plant dies.

c) adsorption of organic compounds into roots

Some organic compounds can be taken up into the plant root, but again the compound has the potential to be re-released if the plant dies.

d) entrapment of organics in the lignin fraction of plants (lignification)

if the organic compound becomes trapped in the lignin of the plant, the likelihood of re-release is decreased since the chemical is now incorporated into the lignin structure.

Note that for adsorption or entrapment, the lipophilicity (“fat loving nature”) of the compound important (rule of thumb:  $\log K_{ow} > 0$  for compound to partition from water into roots)

An example of phytostabilization is being tested for copper smelter tailing near Anaconda, Montana, (Neuman et al. 1997) using selected grasses and legumes. Another study looked at the binding of metals (Cu<sup>+2</sup>, Ni<sup>+2</sup>, Cd<sup>+2</sup>, Cr<sup>+3</sup>, Pb<sup>+2</sup>, and Zn<sup>+2</sup>) to shoot biomass of alfalfa (Tiemann et al. 1997); the highest binding affinity in short term studies occurred at pH 5 with 19.7, 4.11, 7.1, 7.7, 43, and 4.9 mg metal bound per gram of biomass. No Cr(VI) was removed. The apparent mechanism of this binding is oxygen or nitrogen ligands for Ni<sup>+2</sup>, and nitrogen ligands for Cr<sup>+3</sup>.

### 1.5 Hyper-accumulation of heavy metals and/or radioactivity

certain types of plants hyper-accumulate materials (concs in biomass >100x to 1000x conventional plants), and then plant biomass harvested and the toxic elements concentrated and reclaimed or disposed

growing, harvesting, processing plant biomass fairly inexpensive  
processing = digesting, ashing, smelting, kiln processing, leaching

accumulation coefficient (AC) = toxic element conc in biomass / conc in soil  
range: <1 to >10; phytoremediation feasible when AC greater than 10-40

phytotoxicity threshold = max conc in plant material which is toxic to the plant,  
mg metal/kg plant material

characteristic uptake curves for different soil and contaminant regimes for different plants determine optimal harvest (genetic and environmental conditions)  
same plants may uptake more than one contaminant for multi-component clean-up  
can concentrate in different parts of the plants: roots, leaves, stalk, sap  
concs in plant tops from 1,800 to 51,600 mg/kg for Cd, Cu, Co, Pb, Ni, Zn  
phytotoxicity may limit the maximum amount of contaminant that can be accum.  
soil pH manipulation can affect uptake rates  
ex. *Thlaspi caerulescens* Zn, Co, Ni, Cd, Mo, Pb, Mn in shoot tissue (121,000 ppm)  
*Alsyum*: Ni  
*Betyka oedyka* : Pb; other selected plants accumulate up to 1% Pb in their tissue  
tree sap 25% Ni, plants up to 3% Zn  
radioactive compounds (max mass per ton dry plant mass):  
Sr (11.5 kg), Cs (9.4 kg), U (0.46 kg), Th (0.32 kg) in Russia

### 1.6 “phytovolatilization”

Phytovolatilization is plant conversion of compounds from solid forms in the soil or dissolved in groundwater into gaseous forms that are excreted from the plant.

Two examples of phytovolatilization are:

selenium: plants remove Se and convert to non-toxic gas (Terry 1)  
organic compounds by poplar trees (Burken and Schnoor 1997). Experiments tested the movement and fate of VOCs in poplar trees, and found that BTEX, TCE, and chlorinated benzene moved through the plant and volatilized into the environment.

more details on selenium and TCE volatilization are presented in the later sections.

### 1.7 Genetically Engineered Plants

Researchers are also in the process of developing and testing so-called “evolved” plants. These plants are produced through genetic engineering.

- plant breeding, protoplast fusion, biotechnology - get “super-accumulating” varieties
- insertion of bacterial genes into plants

Example1: mercury resistance via mercuric ion reductase which reduces thiol-mercury salts (Hg<sup>+2</sup>) to metallic Hg, *Arabidopsis* plants (Meagher 1)

Example2: sMMO for TCE degradation into poplar trees (Strand, UW)

## **2. Plants used in Phytoremediation Applications**

### 2.1 Poplar Trees

Poplar trees have been found to be useful for a variety of phytoremediation applications. Special hybrids have been developed with the following capabilities (Aitchison et al. 1997; <http://www.interlog.com/~ihn/nuc8.htm>):

- very fast growing, hardy, and tolerant of high organics concentrations
- extensive root systems, with the ability to penetrate the soil several feet down, sometimes to groundwater tables
- transpiration of large quantities of water (absorbing water from soil and emitting it as water vapor through foliage),
- long life spans,
- ability to grow on low-fertility soil
- pre-formed root initials that allow rooting along the entire buried depth
- release of exudates that may stimulate microbes in the rhizosphere and promote ecosystem diversity
- direct uptake of organics, sometimes coupled with enzymatic transformation of these compounds to less toxic metabolites

Hybrid poplar trees have been used as buffers and caps to prevent pollutants--for instance, from landfills--from reaching waterways and groundwater. The poplar-tree systems were developed at the University of Iowa and are now being used commercially by Ecolotree, Inc., of Iowa City, Iowa, a private spinoff company. Since 1990, Ecolotree has installed caps and buffers at 30 permitted sites in 11 States and Europe.

Seven landfills in Virginia, Iowa, and Oregon are using poplar trees to manage water. An example of a full-scale Ecolotree Cap is at Lakeside Landfill in Beaverton, Oregon. In its seventh year of operation, the cap has been successful in keeping the landfill free of leachate problems. Another full-scale site at Riverbend Landfill in McMinnville, Oregon, uses an Ecolotree Buffer of 14.3 acres of hybrid poplars to transpire landfill leachate, which is irrigated onto the poplar stand. According to the company, this is an effective, low-cost alternative to pumping the leachate to a wastewater treatment facility.

Ecolotree has also planted the hybrid poplars as buffer systems to filter water and air, while stopping erosion and degrading pollutants in the soil. For example, in Amana, Iowa, poplars were planted in four rows along a stream in an effort to intercept nitrate pollutants from nearby farmland before they reached the stream and groundwater. According to Ecolotree president, Louis Licht, in the second year of establishment, the tree-lined stream contained 50 percent less nitrate nitrogen and 85 percent less sediment compared to an adjacent unbuffered watershed. Nitrate nitrogen in groundwater flowing through the buffer was also decreased significantly. Ecolotree Buffer systems have also been used at agrochemical dealerships owned by Clarence Cooperative of Clarence, Iowa. The hybrid poplars have been used to remove chemicals at urea fertilizer spills, old herbicide-equipment rinsing areas, and perimeter buffers as a final filter for surface and ground water.

Chevron has a phytoremediation project in Ogden, Utah using poplar trees, where the climate is nearly ideal for phytoremediation. Chevron operated a fuel terminal at Ogden from 1950 to 1989, and numerous small, accidental spills have contaminated the site. Removing and incinerating or landfilling the soil would have cost Chevron an estimated \$850,000, which encouraged Chevron to experiment with phytoremediation at a much lower cost. Both the local community and state regulators support phytoremediation at the site. The Logan, Utah-based PHYTOkinetics Inc. was contracted for the projects and greenhouse research for a \$70,000; the U.S. EPA continues to monitor cleanup progress and conduct sampling. "The poplar hybrids can suck up much of the hydrocarbon-impacted groundwater at a high rate. We are testing the ability of the poplars as hydraulic barriers to intercept the groundwater before leaving," according to Chevron's Project Hydrologist Sheldon Nelson. (<http://www.envirobiz.com/newsdaily/960502e1.htm>)

Poplar tree research is continuing at the University of Iowa, focusing on the fate and movement of solvents, ammunition (such as TNT), herbicides, fuels, and organic intermediaries for various plastics. Other organizations involved in poplar research include the University of Washington, EPA Laboratory in Athens, Georgia, the National Salinity Laboratory in Riverside, California, the Bioresource Engineering Department at Oregon State University, and Phytokinetics of North Logan, Utah. Phytokinetics has commercial applications using poplar technologies, which have been used in several States to remediate groundwater.

In his field research, Jerald Schnoor, a professor at the University of Iowa, has found that poplar trees can break down between 10% and 20% of atrazine in soil. The poplars absorb atrazine through their roots and break it down, possibly by the enzymes dehalogenase and laccase, to several harmless compounds, including short-chain metabolites. The trees also stimulate bacteria living around the trees' roots to attack and degrade atrazine. The sugars, alcohols, and volatile acids secreted by the plant roots enhance the rate of microbial transformation of atrazine. In sandy soil, virtually 100% of the atrazine was metabolized.

At the University of Washington, Stuart Strand and Milton Gordon have found in lab experiments using small poplar trees that monooxygenase enzymes break down trichloroethylene to carbon dioxide. Although the majority of TCE is transpired to the atmosphere, the breakdown is still significant as a potential cleanup technique. The plant enzymes appear to be solely responsible for the breakdown, with the same results achieved in tissue culture experiments in the laboratory. The researchers are currently testing poplar trees in the field to see if the lab results are borne out.  
([http://ehpnet1.niehs.nih.gov/docs/1995/103\(12\)/innovations.html](http://ehpnet1.niehs.nih.gov/docs/1995/103(12)/innovations.html))

The ability of hybrid poplar trees (*Populus deltoids* X *P. trichocarpa*) to absorb and metabolize trichloroethylene (TCE) from a simulated aquifer is under investigation at the University of Washington (<http://www.niehs.nih.gov/sbrp/newweb/resprog/resprj95/uwprj95.htm>; Drs. Milton P. Gordon and Stuart Strand). Poplars are able to grow in the presence of high levels of TCE and to transpire and metabolize the compound. TCE is converted to trichloroethanol, trichloroacetic acid, and two polar compounds whose structures will be determined. Researchers will determine which clones metabolize the largest proportion of TCE absorbed by the plants. The extent of metabolism will be augmented by introducing genes which are known to metabolize TCE. The best clones will be studied in greenhouse-scale experiments to determine their ability to adsorb and detoxify TCE. Finally, field studies will be conducted in collaboration with the Occidental Chemical Corporation at a site at the Port of Tacoma. In conjunction with these studies, a collaborative study will determine the effect of the ingestion of TCE-treated poplar tissue on insects that normally feed on poplar. These insects will in turn be fed to starlings or their chicks to determine whether there is any effect on the birds resulting from this exposure. Development of an experimental biomarker for detection of below-ground TCE contamination will also be investigated.

In initial studies, axenic cultures of poplar tissues were used to examine the metabolism of trichloroethylene (TCE) without the interference of soil microorganisms, microflora and microfauna. Radiolabeled TCE studies were conducted. Under these conditions, TCE was converted to trichloroethanol, trichloroacetic acid, dichloroacetic acid and a small amount of CO<sub>2</sub>. Some of the TCE is incorporated into the plant as insoluble, nonextractable material. There are also a number of lipid soluble compounds produced, the identity of which is under investigation by GC-MS and/or MS-MS.

In greenhouse studies, poplar shoots were grown in plastic pipes. After eight months the TCE-exposed plants were about 75% the size of the control plants. The major difference noted was that very few fine roots of the exposed plants penetrated into the sand zone which contained the TCE, in comparison to control plants, in which the fine roots

filled the sand layer. Chemical analysis of the roots, stems and leaves of the plants fed TCE showed that the same group of metabolites were present as those found in the exposed poplar cell cultures. In addition, in a study in an inert chamber it was found that approximately 1% of the TCE was transpired by the poplars per week.

In addition to laboratory studies, a field trial was established in collaboration with Occidental Chemical Corporation at a highly instrumented site near Tacoma, WA. A series of twelve "test plots", double walled cells each measuring 3.7mX6.1mX1.5m deep, were constructed. Liquid was added to the bottom of the cells with a T shaped input pipe with a 1/40 slope toward the output well. Four cells were planted with 30cm rooted cuttings of hybrid poplars, and two of these cells were dosed with water containing about 15mg TCE/liter. The other two cells received only water, while a fifth cell, which did not have trees and served as a nonvegetated control, also received water containing 15mg TCE/liter. The purpose of this experiment was to determine the ability of the poplars to remove TCE from contaminated water under outdoor conditions approaching those found in the field. About nine weeks after injection of TCE into the cells, a breakthrough of TCE and related metabolites, particularly cis-1,2-dichloroethylene, occurred in the cells which did not contain trees. In cells with trees, very little TCE could be detected in the effluent until after leaf drop. The stems, roots and leaves of the trees exposed to TCE showed the products of oxidative metabolism, which were also seen in the green house studies and tissue culture experiments. These experiments will be continued for an additional year. Over the course of a two year period, about 6 moles of TCE were added to the cells. In cells containing trees only about 2 to 4% of the input TCE remained in the effluent as compared to 68% in the nonvegetated controls. Each of the trees consumed over 2000 liters of water during their second growing season, which is considered a minimal amount to keep the trees healthy. A similar study in progress indicates that poplar hybrids also can take up carbon tetrachloride. It thus appears that hybrid poplars can be used to remediate spills of trichloroethylene and carbon tetrachloride.

In conclusion, the results of the above experiments show that TCE can undergo oxidation to chloromethyl derivatives, trichloroethanol, dichloroethanol, trichloroacetic acid, or complete mineralization to CO<sub>2</sub>. Plant uptake coupled with TCE metabolism serves to remove TCE from groundwater.

Attempts are now underway to modify trees so that they can degrade chlorinated hydrocarbons efficiently. Initial work has included the optimization of a procedure for the transformation of hybrid poplars. Copies of the gene encoding mammalian cytochrome, P4502E1, have been obtained. P4502E1 is a liver P450 known to be involved in the metabolism of TCE. Plasmids containing the genes for auxiliary proteins, P450 oxidoreductase and cytochrome B5, have also been obtained which may complex with and help stabilize the P450. The plasmid vector for inserting these genes into poplars via agrobacterial transformation is in preparation. Once produced the genetically modified trees will be tested to determine if their ability to degrade chlorinated hydrocarbons has been enhanced. If successful, phytoremediation may become an efficient means to remediate TCE-contaminated Superfund sites, as the method involves simply planting trees and letting them grow.

## 2.2 Sunflowers

Sunflowers have been used successfully in rhizofiltration applications. Successful rhizofiltration techniques require identification of species of plants that have the ability to process large quantities of water and sequester certain contaminants in plant biomass. A special strain of sunflower that, when grown hydroponically on rafts, has removed radionuclides from water. The system was developed and patented by Phytotech, Inc. According to the company, the sunflower rhizofiltration system can successfully reduce uranium, strontium, and cesium levels in water to below cleanup standards set by the U.S.

Environmental Protection Agency (EPA). Accumulation of uranium occurs primarily in the roots, whereas strontium and cesium accumulate throughout the plant.

The system has worked effectively at test sites near the Chernobyl nuclear plant in Ukraine, as well as at a DOE site in Ohio. Phytotech estimates the cost to remove radionuclides from water would be between \$2 and \$6 per 1,000 gallons, including disposal costs. A standard treatment of microfiltration and precipitation would cost nearly \$80 per 1,000 gallons, according to DOE estimates. If approved by EPA regulators and site owners, the process could be commercialized within 1 year. (<http://www.interlog.com/~ihn/nuc8.htm>)

### 2.3 Indian Mustard

The Indian mustard plant (*Brassica juncea*) can extract both heavy metals and radionuclides from soil. The Indian mustard is a high-biomass crop that traditionally has been grown in Southeast Asia as a source of cooking oil. ARS's Water Management Research Laboratory in Fresno, California, has had success in using Indian mustard to dramatically reduce selenium levels in soil (<http://www.interlog.com/~ihn/nuc8.htm>). In some areas of California where irrigation is vital to agriculture, evaporation ponds for drainage water may leave a high selenium residue behind. Making Indian mustard part of a proper crop rotation can help control selenium levels and minimize the selenium load deposited into the agricultural effluent. In addition, some of the harvested mustard can be blended with hay and fed to animals in nearby areas where selenium deficiency is a problem. In order to see if *Brassica* species used for selenium uptake could be used as viable oil crops, scientists currently are evaluating the effects of higher selenium concentrations on oil content.

Based on Indian mustard germplasm collected by ARS, studies conducted by Phytotech, Rutgers University, and the International Institute of Cell Biology have also shown that Indian mustard has the ability to accumulate heavy metals such as lead, chromium, cadmium, nickel, and zinc. The approach requires adding a chelating agent to the soil to solubilize the soil lead, and allow it to move from the roots into the shoots. Field trials are being conducted this year in Trenton, New Jersey. However, it is not clear whether future environmental regulation will allow adding such high levels of chelating agents to the soil, as increased mobilization of contaminants may pose a threat to ground water. Phytotech has also had some success in using Indian mustard to remove radionuclides such as cesium-137 and strontium-90 at a site near Chernobyl.

Norman Terry, a professor of plant biology at the University of California at Berkeley, is exploring the possibility of using Indian mustard to remove naturally occurring selenium from soil. A necessary nutrient, selenium can leach into water. In high amounts, this metal can poison wildlife and livestock. In laboratory research, Terry has found that Indian mustard not only takes up selenium but converts it into dimethyl selenide, a gas which he describes as relatively nontoxic. They are currently working on genetically altering the plants to increase the volatilization. According to Terry, there are huge amounts of this gas in the atmosphere from volcanoes, soil, and plants, and it is continually recycled; therefore, the amount that would be added via phytoremediation would be negligible. ([http://ehpnet1.niehs.nih.gov/docs/1995/103\(12\)/innovations.html](http://ehpnet1.niehs.nih.gov/docs/1995/103(12)/innovations.html))

## 3. Classes of Compounds treated with Plants

### 3.1 Explosives

There has been a lot of recent research into plant-based remediation of explosives-contaminated soils and groundwater.

Poplar trees have been shown to rapidly uptake TNT from hydroponic solutions, with most of the TNT remaining immobilized in the roots. TNT within the plant was transformed to

metabolites such as 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, and 2,4-diamino-6-nitrotoluene in the roots and stems. There was no significant production of CO<sub>2</sub> from the TNT. When the TNT was present in soil, it was less bioavailable for uptake due to sorption competition. The poplar trees were also shown to be affected by toxicity from the TNT; over less than 14 days exposed to 5 mg/L no significant effects were seen, but over extended time periods the trees died. (Thompson and Schnoor; 1997). Behavior of the poplars in the presence of RDX was significantly different, with much slower uptake from water, 60% translocation to the leaves within 48 hours of initial uptake, and no significant transformation of the RDX within the plant.

Treatment of TNT and RDX in wetland systems was also investigated (Best et al. 1997; Miller et al. 1997) Eurasian water milfoil growing in a beaver pond absorbs TNT from runoff of contaminated soil.

These plants, and the variety of poplars studied by Schnoor, contain the enzyme nitroreductase, which can rapidly break down TNT. Steve McCutcheon at EPA's research lab in Athens, GA, and his colleague David Young at Auburn University have tested Eurasian milfoil on 2-4 inches of soil from the Alabama Army ammunition plant that is contaminated with 5,000 ppm of TNT. The soil, which contained little natural bacterial activity, was put in small plastic pools, covered with water, and the plants were added. Within a week the dissolved TNT was near detection; and a few days it was below detection limits. The TNT is broken down and becomes part of the lignin or plant structure. Toxicity analysis is needed to determine if the TNT breakdown products represent a residual risk. However, indications of low residual toxicity are that tadpoles and snails have thrived in the pools with the plants, but are unable to live in the control pools that do not contain the plants. In 1999, the EPA and the Army Environmental Center planned to field test the plants on a one-eighth of an acre wetland at an Army ammunition plant in Milan, Tennessee. ([http://ehpnet1.niehs.nih.gov/docs/1995/103\(12\)/innovations.html](http://ehpnet1.niehs.nih.gov/docs/1995/103(12)/innovations.html))

### 3.2 Heavy Metals and Radionuclides

Potential remediation sites for heavy metals include abandoned mines and smelting operations, military sites, and nuclear energy and waste sites. Because of the high cost of current heavy-metal remediation methods, soil phytoremediation offers a potentially cost effective alternative, and is therefore widely studied. In a recent presentation at a phytoremediation conference in Arlington, Virginia, Scott Cunningham, a scientist at Dupont Central Research and Development in Newark, Delaware, compared potential costs: remediation of 10 acres contaminated with lead using current technologies could cost as much as \$12 million (including planning and documenting the project, and actual decontamination) versus potential phytoremediation costs as little as \$500,000. In addition, many phytoremediation costs can be spread out over the life of the project (which may be years), whereas traditional remediation technologies typically call for large up-front expenditures. This lower cost potential of phytoremediation is driving organizations like Dupont, Phytotech, Argonne National Laboratory, DOE's Office of Science and Technology, and USDA's Agricultural Research Service (ARS) to research the removal or stabilization of heavy metals by plants. Much of the research is centered on hyperaccumulators, plants that absorb levels of metal that would be toxic to most other plants. (<http://www.interlog.com/~ihn/nuc8.htm>)

Though many hyperaccumulator plants are relatively small in size (low biomass) and take a long time to grow, several species are showing some promise as heavy metal phytoextractors. One such plant is Alpine pennycress (*Thalaspis caerulescens*), which hyperaccumulates zinc and smaller amounts of cadmium. Field trials are currently being conducted by ARS at a Superfund cleanup site in Palmerton, Pennsylvania, to test ways to remove zinc and cadmium. The site is managed by the Zinc Corporation of America, and is thought to have been contaminated by a zinc smelter that operated in Palmerton from 1890 to 1980. The low harvestable biomass of pennycress is a restricting factor that scientists

from USDA, the University of Maryland, and the University of Sheffield in the United Kingdom are trying to overcome. *Thalassia* strains are being collected and crossbred in an attempt to maximize cadmium and zinc concentration in the plant, as well as create plants that grow faster and taller. This work will also likely lead to genetic screening in an attempt to isolate genes responsible for metal uptake, so they can potentially be transferred to other higher yielding biomass plants.

Another potential technology for heavy metal remediation is phytostabilization, also referred to as IINERT (in-place inactivation and environmental restoration). This technology is currently being investigated by Dupont and others for use at sites where extraction is logistically difficult. The objective is to use soil amendments to reduce the bioavailability of the metals in the soil matrix. Certain plants are then grown to trap the remaining contaminants in the roots. This further reduces the bioavailability of the metals to other plants and animals and helps prevent leaching and off-site migration of the metals (2). Contaminants are likely to be phytostabilized more quickly than they can be phytoextracted. However, phytostabilization is not yet accepted by EPA, as research is still needed to determine overall effectiveness and long-term stability achieved by this technology.

Phytoremediation may leave topsoil in usable condition and reduce the amount of contaminated material to be landfilled or incinerated, distinct advantages over the chemical and engineering technologies used now to treat contaminated soil. For example, phytoremediation of toxic heavy metals actually reduces the volume of contaminated material. For example, removing heavy metal-contaminated soil from two and a half acres to a depth of about 18 inches creates about 5,000 tons of soil that must be disposed of in a hazardous landfill. In contrast, plants that take up the metal and are burned leave a residue of between 25 and 30 tons of ash to be disposed (a huge reduction in mass). ([http://ehpnet1.niehs.nih.gov/docs/1995/103\(12\)/innovations.html](http://ehpnet1.niehs.nih.gov/docs/1995/103(12)/innovations.html))

Phytoremediation of metal-contaminated soils may also have direct health benefits. It is specifically attractive for widespread lead contaminated soils (which resulted from the use of leaded gasoline). The ground cover with plants reduces wind-entrainment of the soil and dust, and may also limit the direct hand-to-mouth exchange of dirt in children. There have been a few lead phytoremediation demonstration project in New Jersey, including one where plants are being used to remove lead from lagoon sediments near a facility where lead tetraethyl was made for leaded gasoline. ([http://ehpnet1.niehs.nih.gov/docs/1995/103\(12\)/innovations.html](http://ehpnet1.niehs.nih.gov/docs/1995/103(12)/innovations.html))

### **Disadvantages of Phytoremediation**

- time-consuming, may take several growing seasons to clean a site
- vegetation containing bioaccumulated toxic heavy metals may pose a risk to wildlife that eats the plants (food chain effects)
  - example: insects eat the plants (although generally plants containing hyperaccumulated metals are avoided by insects, according to Ensley), then then subsequent movement up the food chain
- engineering sites to prevent flooding and erosion
- use of chemicals, potentially, such as chelating agents to free metals and other contaminants from soil particles to allow them to be taken up by the plants
- highly toxic sites may inhibit growth of the plants

### **4. Costs**

A “hypothetical” example was used to compare the costs of phytoremediation versus soil Washing to remediate metal and/or radioactive contaminated soils. The site was a U.S. DOE site located in the western U.S. at which there is a 0.5-hectare area chemical waste disposal pond contaminated with Cd, Zn, and 137-Cs in the top 50 cm of soil. Information on the clean closure concentrations of the compounds required, the

hyperaccumulation properties of selected plants (species, metal specific), the accumulation coefficient for the plants (species, metal specific), and biomass productivity of the plants at the site was given. For the calculation, the costs associated with phytoremediation included:

- seeding plants
- watering and nutrient/fertilizer addition
- harvesting plants
- “destruction” of plants (such as drying, ashing, ash disposal and air poll control)
- time to meet clean-up limits (# growing seasons)

By comparison, the costs associated with soil washing included:

- digging up contaminated soil
- mechanical mixing of “washing” basin, chemical addition
- liquid waste stream treatment and residual solids disposal

Note that both phytoremediation and soil washing are considered “innovative treatment technologies” by EPA). The costs estimated are shown in the Table below:

Activity	Cost Estimate, \$ Phytoremediation	Cost Estimate, Soil Washing
Site preparations	63,000	61,000
Production/processing	395,000	1,336,000
Waste mgmt/disposal	35,000	175,000
Project closeout	18,000	62,000
EH&S, design, proj mgmt	153,000	490,000
<b>Overall Estimated Cost</b>	<b>664,000</b>	<b>2,124,000</b>
<b>Cost per metric ton soil</b>	<b>200</b>	<b>600</b>

\* total soil treated = 2,500 m<sup>3</sup> @ 1,420 kg/m<sup>3</sup>

This analysis determine that phytoremediation would be 1/3 the cost of soil washing. In particular, there are major economy of scale savings with phytoremediation. This can be considered a conservative estimate for phytoremediation costs since low accumulation factors for the plants were assumed in the analysis.

Other cost estimates for phytoremediation systems include: \$10,000 per acre for planting; total remediation costs including maintenance, monitoring, and verification of \$60 to \$100 thousand per acre; for sunflower treatment of radioactive-contaminated groundwater \$2 to \$6 / thousand gallons of water. [RIMS] ; \$80 / cy for metal and radioactive contaminated soil (Rashalee Levine; [http://ehpnet1.niehs.nih.gov/docs/1995/103\(12\)/innovations.html](http://ehpnet1.niehs.nih.gov/docs/1995/103(12)/innovations.html)).

Comparative technology costs, according to the president of Phytotech Burt Ensley, such as soil washing metal-contaminated soil can cost about \$250 per cubic yard; an EPA project cleaned 19,000 tons of contaminated soil at a cost of \$400 per ton (one ton is roughly equivalent to one cubic meter). Incineration costs range from \$400 to \$1200 per ton (for explosives). And an incineration project to clean up explosives-contaminated soil at the Department of Energy's Idaho National Engineering Laboratory cost \$4,000 per ton to clean hot spots at the naval proving ground. ([http://ehpnet1.niehs.nih.gov/docs/1995/103\(12\)/innovations.html](http://ehpnet1.niehs.nih.gov/docs/1995/103(12)/innovations.html)). All of these other costs are significantly higher than predicted phytoremediation costs.

## 5. The Future of Phytoremediation

Though phytoremediation technologies are still primarily in research and development phases, various applications have shown potential for success. This has helped to increase interest and research in both public and private sectors, in an attempt to develop phytoremediation into a commercially viable industry. Some key technical hurdles

that must be overcome for an industry to develop and grow are  
(<http://www.interlog.com/~ihn/nuc8.htm>):

- identifying more species that have remediative abilities,
- optimizing phytoremediation processes, such as appropriate plant selection and agronomic practices,
- understanding more about how plants uptake, translocate, and metabolize contaminants,
- identifying genes responsible for uptake and/or degradation for transfer to appropriate high-biomass plants,
- decreasing the length of time needed for phytoremediation to work,
- devising appropriate methods for contaminated biomass disposal, particularly for heavy metals and radionuclides that do not degrade to harmless substances, and protecting wildlife from feeding on plants used for remediation.

In addition to technical barriers, government regulations will also determine the overall success of phytoremediation. Because the remediation industry is compliance driven, phytoremediation technologies must demonstrate their effectiveness at meeting State and Federal regulations. This simply might not be possible in all situations with many current phytoremediation technologies, due to the nature of the contamination (for example, the age of contamination and relative bioavailability of the contaminants). For these technologies, changes in regulatory status and/or continuing technical improvements will be necessary for commercialization. Also, for more heavily contaminated sites, the phytoremediation process runs into the problems with RCRA waste classification. "When contaminated soils are "managed" they become a hazardous waste, triggering RCRA's Land Disposal Restrictions (LDR) and Minimum Technology Requirement (MTR)," according to Dave Sanders, Chevron spokesperson. As a "managed" hazardous waste meeting the LDR requirement, it must be disposed of with the best available technology — incineration. MTR prohibits phytoremediation by requiring landfill liners to be laid under the soil, before it can be spread out and seeded. Many facilities may delay phytoremediation because they don't want to trigger LDR and MTR. "The RCRA regulations are looked upon as an impediment for phytoremediation at refineries," said Nelson. There have been recent efforts to reform the RCRA barrier in federal legislative and regulatory committees. Altering or providing temporary exemption from the LDR and MTR requirements, as was done with underground storage tanks would "open the door to a wide number of remedial technologies like phytoremediation and bioremediation," stated Sanders. (<http://www.envirobiz.com/newsdaily/960502e1.htm>)

Because of all the factors needed for success, the likely size and growth rate of a phytoremediation industry are difficult to predict. Because contaminated soils tend to present more bioavailability problems, Scott Cunningham of Dupont believes most initial phytoremediation successes will come in treatment of contaminated surface and ground waters. Industry sources suggest potential sites for soil phytoremediation are areas with low to moderate amounts of contaminants near the surface. Because it may take a relatively long time for phytoremediation to work, the first target contaminants will also likely have to pose no immediate threat to health or risk of further environmental damage.

How soon phytoremediation will succeed as an industry is also uncertain. It offers many potential advantages over traditional remediation technologies, particularly its public acceptance and considerably lower cost. If these factors continue to drive government and private research and development, phytoremediation technologies could continue to evolve. If so, some industry experts believe commercialization of certain technologies could occur within the next 5 years.

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