

# BASIC TECHNIQUES OF PHYTOREMEDIATION

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## Abstract

The rapid increase in population coupled with fast industrialization growth causes serious environmental problems particularly soil pollution. Farmers generally use fertilizers to appropriate soil deficiencies. Since the metals are not degradable, their accumulation in the soil above their toxic levels becomes an indestructible poison for crops. There are a number of conventional remediation technologies which are employed to remediate environmental contamination with heavy metals such as solidification, soil washing and permeable barriers. But a majority of these technologies are costly to implement and cause further disturbance to the already damaged environment. Phytoremediation, Phytoextraction or phytomining, Phytostabilization, Rhizofiltration, Rhizodegradation, Phytovolatilization is evolving as a cost-effective alternative to high-energy, high-cost conventional methods. These are considered to be a "Green Revolution" in the field of innovative cleanup technologies. Constituents amenable to phytoremediation include  $Pb^{2+}$ ,  $Sr$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{6+}$ ,  $U$ ,  $Sr$ . The plant affected soil environment can convert metals from a soluble to an insoluble oxidation state  $As$ ,  $Cd$ ,  $Cr^{6+}$ ,  $Pb$ ,  $Zn$ . Therefore, the process of remediation using micro-organisms represents a promising, largely untapped resource for new environmental biotechnologies.

**Keywords:** Accumulation, Bioremediation, Heavy Metals, Toxic Phytoremediation

## 1 INTRODUCTION

In recent years, public concerns relating to ecological threats caused by heavy metal (HM) have led to intensive research of new economical plants based remediation technologies. Conventional methods used for reclamation of contaminated soils, namely chemical, physical and microbiological methods, are costly to install and operate.[1] The rapid increase in population coupled with fast industrialization growth causes serious environmental problems, including the production and release of considerable amounts of toxic waste materials into environment [2]

Soil pollution or land pollution is major problem in the world. Soil pollution is results from buildup of contaminants, toxic compounds, radioactive

materials, chemical compounds. The most common sources of soil pollution are hydrocarbons, heavy metals (Cd, Pb, Zn, Cu, Hg and As), herbicides, pesticides, tars and PCBs. Industry is to blame for the biggest pollution disaster in the whole world. Heavy metals like Fe, Zn, Cu, Pb, As etc. are come from industrialized plants which are very much harmful for land and human being. High level of radionuclide like nitrogen and phosphorus can be found surrounding farm centers containing high population densities of livestock. Pesticides also soak into the soil and leaving lasting effects.

Farmers generally use fertilizers to appropriate soil deficiencies. Fertilizers contaminate the soil with impurities, which come from the raw materials used for their manufacture. Mixed fertilizers often contain

ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), phosphorus as  $\text{P}_2\text{O}_5$ , and potassium as  $\text{K}_2\text{O}$ . For instance, As, Pb and Cd present in traces in rock phosphate mineral get transferred to super phosphate fertilizer. Since the metals are not degradable, their accumulation in the soil above their toxic levels becomes an indestructible poison for crops. Excess potassium content in soil decreases Vitamin C and carotene content in vegetables and fruits. The vegetables and fruits grown on over fertilized soil are more horizontal to attacks by insects and disease.

Bioremediation and phytoremediation are two important techniques. "Remediate" means to solve the problem and bio-remediation means to use biological organisms to solve an environmental problem such as contaminated soil or groundwater.

## Bioremediation

Bioremediation is defined as the process whereby organic wastes are biologically degraded under controlled conditions [3] By operational definition, bioremediation is the use of living organisms, to degrade the environmental contaminants into less toxic forms. It involves naturally occurring bacteria and fungi or plants to degrade or detoxify substances hazardous to human health. Contaminant compounds are transformed by living organisms through reactions that take place as a part of their metabolic processes. Biodegradation of a compound is a result of the actions of multiple organisms. When, microorganisms are imported from contaminated site to enhance degradation that process known as bioaugmentation. For bioremediation to be effective, microorganisms must enzymatically attack the pollutants and convert them to harmless products.[4]

As bioremediation can be effective only where environmental conditions permit microbial growth and activity. It involves the manipulation of environmental parameters to allow microbial growth and degradation to proceed at a faster rate. Bioremediation has some limitations. Some contaminants, such as chlorinated organic or high aromatic hydrocarbons, are resistant

to microbial attack. They are degraded slowly; hence it is not easy to predict the rates of cleanup for a bioremediation exercise. Bioremediation techniques are typically more economical than traditional methods such as incineration. Bioremediation is based on natural attenuation the public considers it more acceptable than other technologies. Most bioremediation systems are run under aerobic conditions, but running a system under anaerobic conditions [5] may permit microbial organisms to degrade otherwise recalcitrant molecules.

Many different types of organisms such as plants can be used for bioremediation but microorganisms show the greatest potential. Microorganisms primarily bacteria and fungi are nature's original recyclers. Their capability to transform natural and synthetic chemicals into sources of energy and raw materials for their own growth suggests that expensive chemical or physical remediation processes might be replaced with biological processes that are lower in cost and more environmentally friendly. Therefore, microorganisms represent a promising, largely untapped resource for new environmental biotechnologies. Research continues to verify the bioremediation potential of microorganisms. For instance, a recent addition to the growing list of bacteria that can reduce metals is *Geobacter metallireducens*, which removes uranium, a radioactive waste from drainage waters in mining operations and from contaminated groundwater. Even dead microbial cells can be useful in bioremediation technologies. [6]

## 2 PHYTOREMEDIATION

A major environmental concern due to dispersal of industrial and urban wastes generated by human activities is the contamination of soil. Controlled and uncontrolled disposal of waste, accidental and process spillage, mining and smelting of metalliferous ores, sewage sludge application to agricultural soils are responsible for the migration of contaminants into non-contaminated sites as dust or leachate and

contribute towards contamination of our ecosystem. A wide range of inorganic and organic compounds cause contamination, these include heavy metals, combustible and putrescible substances, hazardous wastes, explosives and petroleum products. Major component of inorganic contaminants are heavy metals [7],[8] they present a different problem than organic contaminants. Soil microorganisms can degrade organic contaminants, while metals need immobilisation or physical removal. Although many metals are essential, all metals are toxic at higher concentrations, because they cause oxidative stress by formation of free radicals. Another reason why metals may be toxic is that they can replace essential metals in pigments or enzymes disrupting their function [9] Thus, metals render the land unsuitable for plant growth and destroy the biodiversity. Though several regulatory steps have been implemented to reduce or restrict the release of pollutants in the soil, they are not sufficient for checking the contamination. There are a number of conventional remediation technologies which are employed to remediate environmental contamination with heavy metals such as solidification, soil washing and permeable barriers. But a majority of these technologies are costly to implement and cause further disturbance to the already damaged environment. Phytoremediation is evolving as a cost-effective alternative to high-energy, high-cost conventional methods. It is considered to be a "Green Revolution" in the field of innovative cleanup technologies. [10]

Bioremediation by use of plants constitutes phytoremediation. Specific plants are cultivated at the sites of polluted soil. These plants are capable of stimulating the biodegradation of pollutants in the soil adjacent to roots (rhizosphere), although phytoremediation is a cheap and environment friendly clean-up process for the biodegradation of soil pollutants, it takes several years.

### History

While phytotechnologies have gained attention over the last several years, the processes have been

taking place naturally for over three centuries. Throughout the 1970s and the following decades, plants were heavily tested and used to treat soil infiltrated with metals and contaminants in wetlands. As a result, techniques for these uses are well established. [11] Widespread use of phytoremediation by federal and state governments, as well as non-governmental organizations, began in the 1980s (EPA 2005b). The use of the term phytoremediation was initiated by the EPA in 1991, and it was first used in open technical literature in 1993 by Cunningham and Berti. In the late 1990s new uses for phytoremediation were discovered, and it became known among innovative scientific technologies.[11] Phytoremediation was derived from other fields such as agronomy, forestry, chemical and agricultural engineering, microbiology, and many others. Since its inception it has developed into an independent field of study and a widely applicable technology.[12]

### Applications

Phytoremediation has been applied at several sites on the National Priorities. The diversity of pollutants to which it can be applied crude oil, metals, explosives, pesticides, chlorinated solvents and numerous other contaminants is the prime reason the technology has developed rapidly (EPA, 2005b). Phytoremediation applications can be classified based on the contaminant fate: degradation, extraction, containment, or a combination of these. Phytoremediation applications can also be classified based on the mechanisms involved. Such mechanisms include extraction of contaminants from soil or groundwater; concentration of contaminants in plant tissue; degradation of contaminants by various biotic or abiotic processes; volatilization or transpiration of volatile contaminants from plants to the air; immobilization of contaminants in the root zone; hydraulic control of contaminated groundwater (plume control); and control of runoff, erosion, and infiltration by vegetative covers.

## Degradation

Plants may enhance degradation in the rhizosphere (root zone of influence). There are measurable effects on certain contaminants in the root zone of planted areas. Several projects examine the interaction between plants and such contaminants as trinitrotoluene (TNT), total petroleum hydrocarbons (TPH), pentachlorophenol (PCP), and polynuclear aromatic hydrocarbons (PAH). Another possible mechanism for contaminant degradation is metabolism within the plant. Some plants may be able to take in toxic compounds and in the process of metabolizing the available nutrients, detoxify them. Trichloroethylene (TCE) is possibly degraded in poplar trees and the carbon used for tissue growth while the chloride is expelled through the roots. EPA has three projects underway in the field using populus species to remediate TCE.

## Extraction

Phytoextraction, or phytomining, is the process of planting a crop of a species that is known to accumulate contaminants in the shoots and leaves of the plants, and then harvesting the crop and removing the contaminant from the site. Unlike the destructive degradation mechanisms, this technique yields a mass of plant and contaminant (typically metals) that must be transported for disposal or recycling. This is a concentration technology that leaves a much smaller mass to be disposed of when compared to excavation and land filling. This technology is being evaluated in a Superfund Innovative Technology Evaluation (SITE) demonstration, and may also be a technology agreeable to contaminant recovery and recycling. Rhizofiltration is similar to phytoextraction in that it is also a concentration technology. It differs from phytoextraction in that the mechanism is root accumulation and harvest using hydroponic (soilless) growing techniques. This is useful for separating metal contaminants from water. Rhizofiltration has been demonstrated on U.S. Department of Energy

(DOE) sites for radionuclides. Volatilization or transpiration through plants into the atmosphere is another possible mechanism for removing a contaminant from the soil or water of a site. It is often raised as a concern in response to a proposed phytoremediation project, but has not been shown to be an actual pathway for many contaminants. Mercury (Hg) has been shown to move through a plant and into the air in a plant that was genetically altered to allow it to do so. The thought behind this media switching is that elemental Hg in the air poses less risk than other Hg forms in the soil. However, the technology or the associated risk has not been evaluated.

## Containment and Immobilization

A containment using plant bind the contaminants to the soil, render them non bioavailable, or immobilizes them by removing the means of transport. Physical containment of contaminants by plants can take the form of binding the contaminants within a humic molecule (humification), physical sequestration of metals as occurs in some wetlands, or by root accumulation in non harvestable plants. Certain trees sequester large concentrations of metals in their roots, and although harvesting and removal is difficult or impractical, the contaminants present a reduced human or environmental risk while they are bound in the roots. Risk reduction may also be achieved by transforming the contaminant into a form that is not hazardous, or by render contaminant into a form that is not hazardous, or by rendering the contaminant nonbioavailable. EPA and the U.S. Department of Agriculture (USDA) have ongoing research in this area. Hydraulic control is another form of containment. Groundwater contaminant plume control may be achieved by water consumption, using plants to increase the evaporation and transpiration from a site. Some species of plants use tremendous quantities of water, and can extend roots to draw from the saturated zone. Vegetative cover (evapotranspiration or water-balance cover) systems are another remediation application utilizing the

natural mechanisms of plants for minimizing infiltrating water. Originally proposed in arid and semi-arid regions, vegetative covers are currently being evaluated for all geographic regions. The effectiveness in all regions and climates needs to be assessed on a site-specific basis. Sites with requirements to collect and control landfill gas may not meet Federal requirements under the Clean Air Act if a vegetative cover is used. Hydraulic control for groundwater plumes and water balance covers are two technologies that are being applied in the field prior to model development predicting their behavior.

### 3. TYPES OF PHYTOREMEDIATION

Phytoremediation is the name given to technologies that use plants to clean up contaminated sites. Many techniques and applications are represented under phytoremediation. They differ in the way plants deal with contaminants (removal, immobilization, degradation), as well as in the type of contaminant that the plant species can target (organic or inorganic contaminant).[13]

#### 3.1 PHYTOEXTRACTION

Phytoextraction is the uptake of contaminants by plant roots and movement of the contaminants from the roots to aboveground parts of the plant. Contaminants are generally removed from the site by harvesting the plants. Phytoextraction accumulates the contaminants in a much smaller amount of material to be disposed of (the contaminated plants) than does excavation of soil or sediment. The technique is mostly applied to heavy metals and radionuclides in soil, sediment, and sludges. It may use plants that naturally take up and accumulate extremely elevated levels of contaminants in their stems and leaves<sup>14</sup>. It can also entail the use of plants that take up and accumulate aboveground significant amounts of contaminants only when special soil amendments are used. Another approach is the use of plants that trap the contaminants in their root systems and are then harvested whole (including the roots). Mercury represents a special case of metal

phytoremediation that is still being investigated. To remove this metal from soil and sediments, researchers propose to use genetically modified plants to take up the mercury and transform it into a less toxic form. The less toxic form is then vaporized out of the leaves, reducing the danger to the environment and humans.

#### Mechanism

Phytoextraction closely resembles the operations conducted in conventional agricultural farming. The area must be sufficiently dry to allow equipment traffic (either by redirecting the river's flow or by conducting the work during the summer dry season). "Natural" phytoextraction is usually conducted by planting (or transplanting) selected plant species in the contaminated soil. These plants are grown under normal farming conditions (fertilized and irrigated as necessary) until they reach their maximum size. The aboveground parts of the plants containing the contaminants are then harvested and disposed of appropriately. The plants are highly specialized, occur naturally, and can tolerate very elevated concentrations of metals that would be toxic to other plants. Typically, these plants are small, have a small and shallow root system, and grow relatively slowly<sup>13</sup>. Induced phytoextraction is conducted by growing selected fast-growing plants in the contaminated soil. Throughout the growth period, amendments are added to the soil to increase availability of metals to the plants. When the plants are mature, inducing agents (chemicals) are used to trigger accumulation of metals from the soil. The plants are then harvested and disposed appropriately. It is possible that two harvests will be conducted annually.[14]

Phytoextraction by whole plant harvesting is conducted by growing the selected plants under normal conditions, including fertilization and irrigation as necessary. Modified agricultural implements typically used to harvest below-ground crops (potatoes, beets, carrots, peanuts, etc.) are used to harvest the whole plant, including the root.

#### Media



Phytoextraction is primarily used in the treatment of soil, sediments, and sludges. It can be used to a lesser extent for treatment of contaminated water.

#### Advantages

- Phytoextraction is able to trap metal and radionuclide contaminants that are in mobile chemical forms. These forms are the most threatening to human and environmental health.
- Compared with other remediation technologies, such as excavation, materials handling is limited (similar to that in normal agricultural processes), and costs are typically lower. Usually the technology leaves the soil fertile and able to support subsequent vegetation. [15]

#### Disadvantages

- This technology is longer than other technologies: several crops are usually required to remove all the contaminants to the desired levels.
- Mercury removal is considered experimental and has shown promise using genetically modified plants that vaporize mercury.
- Most of the plants that are considered good candidates for use with this technology do not grow well under submerged (wetland) conditions. Phytoextraction has not been applied to wetlands. [15]
- Extensive treatability studies are needed before this technology can be considered for implementation in wetlands.
- Portions of the river may have to be re-routed for the duration of the treatment.
- Plants that are good phytoextraction candidates are not native to the area.
- Plants used for phytoextraction will have to be harvested over multiple growing seasons.[14]
- If soil additives are used, additional precautions must be taken to avoid leaching of the mobilized contaminants outside the area where roots can take them up.
- Accumulation of contaminants in the aboveground part of the plants may pose a risk to animals eating these plants and fences may be needed to deter grazing animals. [13]

- Phytoextraction will not directly remove organic contaminants (PCBs, DDD) from soils and sediments. However, microbial activity associated with plant roots may accelerate the degradation of these contaminants to non-toxic forms.

#### Root Depth

Phytoextraction is generally limited to the immediate zone of influence of the roots; thus, root depth determines the depth of effective phytoextraction. The root zones of most metal accumulators are limited to the top foot of soil.

#### Plants

Hyperaccumulator plants are found in the *Brassicaceae*, *Euphorbiaceae*, *Asteraceae*, *Lamiaceae*, or *Scrophulariaceae* plant families.[20] Examples include:

- *Brassica juncea* (Indian mustard) - a high-biomass plant that can accumulate Pb, Cr (VI), Cd, Cu, Ni, Zn, 90Sr, B, and Se [21],[22],[23] It has over 20 times the biomass of *Thlaspi caerulescens*. Brassicas can also accumulate metals. Of the different plant species screened, *B. juncea* had the best ability to transport lead to the shoots, accumulating >1.8% lead in the shoots (dry weight). The plant species screened had 0.82 to 10.9% Pb in roots (with *Brassica* spp. Having the highest), with the shoots having less Pb. Except for sunflower (*Helianthus annuus*) and tobacco (*Nicotiana tabacum*), other non-*Brassica* plants had phytoextraction coefficients less than one. 106 *B. juncea* cultivars varied widely in their ability to accumulate Pb, with different cultivars ranging from 0.04% to 3.5% Pb accumulation in the shoots and 7 to 19% in the roots.[21]
- *Thlaspi caerulescens* (Alpine pennycress) for Ni and Zn<sup>24</sup>.
- *Thlaspi rotundifolium* sp. *cepaefolium*, a noncrop *Brassica* and one of the few Pb accumulators mentioned in the literature.[21]
- *Alyssum wulfenianum* for Ni.[25]

- Baker<sup>20</sup> found 80 species of nickel-accumulating plants in the *Buxaceae* (including boxwood) and *Euphorbiaceae* (including cactus-like succulents) families. Some euphorbs can accumulate up to 5% of their dry weight in nickel.
- Indian mustard (*Brassica juncea*) and canola (*Brassica napus*) have been shown to accumulate Se and B. Kenaf (*Hibiscus cannabinus* L. cv. Indian) and tall fescue (*Festuca arundinacea* Schreb cv. Alta) also take up Se, but to a lesser degree than canola.[26]
- Hybrid poplar trees were used in a field study in mine tailing wastes contaminated with As and Cd.[27]
- Lambs quarter leaves had relatively higher As concentrations (14 mg/kg As) than other native plant or poplar leaves (8 mg/kg) in mine-tailing wastes.[27]
- Sunflowers took up Cs and Sr, with Cs remaining in the roots and Sr moving into the shoots.[28]
- Metal accumulator plants such as the crop plants corn, sorghum, and alfalfa may be more effective than hyper accumulators and remove a greater mass of metals due to their faster growth rate and larger biomass. Additional study is needed to quantify contaminant removal.

### 3.2 Rhizofiltration

Rhizofiltration is the adsorption or precipitation onto plant roots, or absorption into the roots of contaminants that are in solution surrounding the root zone, due to biotic or abiotic processes. Plant uptake, concentration, and translocation might occur, depending on the contaminant. Exudates from the plant roots might cause precipitation of some metals. Rhizofiltration first results in contaminant containment, in which the contaminants are immobilized or accumulated on or within the plant. Contaminants are then removed by physically removing the plant.

#### Media

Extracted groundwater, surface water, and waste water can be treated using this technology. Rhizofiltration is generally applicable to low-

concentration, high-water-content conditions. This technology does not work well with soil sediments, or sludges because the contaminant needs to be in solution in order to be sorbed to the plant system.

#### Advantages

- Either terrestrial or aquatic plants can be used. Although terrestrial plants require support, such as a floating platform, they generally remove more contaminants than aquatic plants.
- This system can be either *in situ* (floating rafts on ponds) or *ex situ* (an engineered tank system).
- An *ex situ* system can be placed anywhere because the treatment does not have to be at the original location of contamination.

#### Disadvantages

- The pH of the influent solution may have to be continually adjusted to obtain optimum metals uptake.
- The chemical speciation and interaction of all species in the influent have to be understood and accounted for.
- A well-engineered system is required to control influent concentration and flow rate.
- The plants (especially terrestrial plants) may have to be grown in a greenhouse or nursery and then placed in the rhizofiltration system.
- Periodic harvesting and plant disposal are required.
- Metal immobilization and uptake results from laboratory and greenhouse studies might not be achievable in the field.

#### Applicable Contaminants

Constituents amenable to phytoremediation include:

- **Metals:**

- a) **Lead**

- i.  $Pb^{2+}$  at a solution concentration of 2 mg/L, was accumulated in Indian mustard roots with a bioaccumulation coefficient of 563 after 24 hours.  $Pb^{2+}$  (at solution concentrations of 35, 70, 150, 300, and 500 mg/L) was accumulated in Indian mustard roots, although root adsorption of Pb saturated at 92

to 114 mg Pb/g DW root. Pb disappeared from the 300- and 500-mg/L solutions due to precipitation of lead phosphate. Pb absorption by roots was found to be rapid, although the amount of time required to remove 50% of the Pb from solution increased as the Pb concentration increased .[29]

- ii. Pb was accumulated in the roots of Indian mustard (*Brassica juncea*) in water concentrations of approximately 20 to 2,000 g/L, with bioaccumulation coefficients of 500 to 2,000.[23]
- iii. Pb at concentrations of 1 to 16 mg/L was accumulated by water milfoil (*Myriophyllum spicatum*) with a minimum residual concentration below 0.004 mg/L.[31]

#### b) Cadmium

$\text{Cd}^{2+}$  (2 mg/L) was accumulated in Indian mustard roots with a bioaccumulation coefficient of 134 after 24 hours.[30] Cd was accumulated by the roots of Indian mustard (*Brassica juncea*) in water concentrations of about 20 to 2,000 g/L, with bioaccumulation coefficients of 500 to 2,000. The seedlings removed 40 to 50% of the Cd within 24 hours at a biomass loading of 0.8 g dry weight/L solution. The Cd went from 20 g/L to 9 g/L within 24 hours. After 45 hours, the Cd reached 1.4% in the roots and 0.45% in the shoots. Cd saturation was reached in the roots in 12 hours and in the shoots in 45 hours. Removal of competing ions in the solution increased the uptake 47-fold. [23] Cd at concentrations of 1 to 16 mg/L was accumulated by water milfoil (*Myriophyllum spicatum*) with a minimum residual concentration of approximately 0.01 mg/L.[31]

#### c) Copper

$\text{Cu}^{2+}$  (6 mg/L) was accumulated in Indian mustard roots with a bioaccumulation coefficient of 490 after 24 hours<sup>30</sup>. Cu at concentrations of 1 to 16 mg/L was accumulated by water milfoil (*Myriophyllum spicatum*) with a minimum residual concentration of approximately 0.01 mg/L.

#### d) Nickel

$\text{Ni}^{2+}$  (10 mg/L) were accumulated in Indian mustard roots with a bioaccumulation coefficient of 208 after 24 hours.[30] Ni was accumulated by the roots of Indian mustard (*Brassica juncea*) in water concentrations of about 20 to 2,000 g/L, with bioaccumulation coefficients of 500 to 2,000<sup>23</sup>. Ni at concentrations of 1 to 16 mg/L was accumulated by water milfoil (*Myriophyllum spicatum*) with a minimum residual concentration of approximately 0.01 mg/L.[31]

#### e) Zinc

$\text{Zn}^{2+}$  (100 mg/L) was accumulated in Indian mustard roots with a bioaccumulation coefficient of 131 after 24 hours.[30] Zn at concentrations of 1 to 16 mg/L was accumulated by water milfoil (*Myriophyllum spicatum*) with a minimum residual concentration of approximately 0.1 mg/L.[31]

#### f) Chromium

- 1)  $\text{Cr}^{6+}$  (4 mg/L) was accumulated in Indian mustard roots with a bioaccumulation coefficient of 179 after 24 hours. The roots contained  $\text{Cr}^{3+}$ , indicating reduction of  $\text{Cr}^{6+}$  [30]
- 2) Cr (VI) was accumulated by the roots of Indian mustard (*Brassica juncea*) in water concentrations of about 20 to 2000 g/L, with bioaccumulation coefficients of 100 to 250.

#### • Radionuclides:

##### a) Uranium

U was studied using sunflowers in bench-scale and pilot-scale engineered systems.[30]

##### b) Cesium

- 1) Cs was used with sunflowers in bench-scale and pilot-scale engineered systems. Co = 200 g/L, decreased noticeably after 6 hours, then went below 3 g/L after 24 hours.
- 2) Cs was accumulated in the roots of Indian mustard (*Brassica juncea*) in water concentrations of approximately 20 to 2,000 g/L, with bioaccumulation coefficients of 100 to 250.



### c) Strontium

- 1) Sr was used with sunflowers<sup>30</sup>. Co = 200 g/L, went to 35 g/L within 48 hours, then down to 1 g/L by 96 hours.
- 2) Sr was accumulated in the roots of Indian mustard (*Brassica juncea*) in water concentrations of approximately 20 to 2,000 g/L.[23] Rhizofiltration has not been evaluated for use with nutrients or organics.

#### Root depth

Rhizofiltration occurs within the root zone in water. For rhizofiltration to occur, the water must come into contact with the roots. Engineered systems can be designed to maximize this contact zone by matching the depth of the unit to the depth of the roots. Groundwater may be extracted from any depth and piped to an engineered hydroponic system for ex-situ treatment. The depth of treatable groundwater is a function of the extraction system, not the rhizofiltration treatment system. For *in situ* technologies, such as natural water bodies, the depth of the roots might not be the same as the depth of the water body. The water must be adequately circulated in such cases to ensure complete treatment, which is likely to become more difficult as the depth of the water increases.

#### Plants

The following are examples of plants used in rhizofiltration systems:

- Terrestrial plants can be grown and used hydroponically in rhizofiltration systems. These plants generally have a greater biomass and longer, faster growing root systems than aquatic plants. Seedlings have been proposed for use instead of mature plants because seedlings do not require light or nutrients for germination and growth for up to 2 weeks.[23]
- Under hydroponic conditions, 5 dicots (broadleaf crops), 3 monocots (cereals), 11 cool season grasses, and 6 warm season grasses were each effective in accumulating Pb in their roots after three days of exposure to 300 mg/L Pb. The maximum lead concentration on a dry weight basis was 17% in a cool season grass (colonial bent grass), and the

minimum was 6% in a warm season grass (Japanese lawn grass). The dicot Indian mustard (*Brassica juncea*) was also effective in taking up other metals.[30]

- Sunflowers (*Helianthus annuus* L.) removed concentrated Cr<sup>6+</sup>, Mn, Cd, Ni, Cu, U, Pb, Zn, and Sr in laboratory greenhouse studies.[23] Sunflowers also were more effective than Indian mustard (*Brassica juncea*) and bean (*Phaseolus coccineus*) in removing uranium. Bioaccumulation coefficients for uranium in the sunflowers were much higher for the roots than for the shoots.
- At a field site in Chernobyl, Ukraine, sunflowers were grown for 4 to 8 weeks in a floating raft on a pond. Bioaccumulation results indicated that sunflowers could remove 137 Cs and 90 Sr from the pond.
- Aquatic plants have been used in water treatment, but they are smaller and have smaller, slower-growing root systems than terrestrial plants.
- Floating aquatic plants include water hyacinth (*Eichhornia crassipes*), pennywort (*Hydrocotyle umbellata*), duckweed (*Lemna minor*), and water velvet (*Azolla pinnata*).
- The floating aquatic plant water milfoil (*Myriophyllum spicatum*), at a biomass density of 0.02 kg/L, rapidly accumulated Ni, Cd, Cu, Zn, and Pb. The plant accumulated up to 0.5% Ni, 0.8% Cd, 1.3% Cu, 1.3% Zn, and 5.5% Pb by weight.[31]
- Wetland plants can be used in engineered or constructed beds to take up or degrade contaminants. Hydroponically-grown plants concentrated Pb, Cr (VI), Cd, Ni, Zn, and Cu onto their roots from wastewater. Lead had the highest bioaccumulation coefficient, and zincs the lowest.[22]

### 3.3 Phytostabilization

Phytostabilization is defined as (1) immobilization of a contaminant in soil through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants, and (2) the use of plants and plant roots to prevent contaminant migration via wind and water erosion, leaching, and

soil dispersion. Phytostabilization occurs through root-zone microbiology and chemistry, and/or alteration of the soil environment or contaminant chemistry. Soil pH may be changed by plant root exudates or through the production of CO<sub>2</sub>. Phytostabilization can change metal solubility and mobility or impact the dissociation of organic compounds. The plant affected soil environment can convert metals from a soluble to an insoluble oxidation state.

Phytostabilization can occur through adsorption, precipitation, complexation, or metal valence reduction.[32] Plants can also be used to reduce the erosion of metal contaminated soil. The term phytolignification has been used to refer to a form of phytostabilization in which organic compounds are incorporated into plant lignin.[33] Compounds can also be incorporated into humic material in soils in a process likely related to phytostabilization in its use of plant material.

#### **Media**

Phytostabilization is used in the treatment of soil, sediments, and sludges.

#### **Advantages**

- This technology reduces the mobility, and therefore the risk, of inorganic contaminants without removing them from their location. This technology does not generate contaminated secondary waste that needs treatment.
- Compared with other remediation technologies, such as excavation, materials handling is limited (similar to that for agricultural processes), and costs are typically lower.
- Usually the technology enhances the soil fertility. It may combine treatment with ecosystem restoration.

#### **Disadvantages**

- The contaminants remain in place. The vegetation and soil may require long-term maintenance to prevent rerelease of the contaminants and future leaching.

- Vegetation may require extensive fertilization or soil modification using amendments.
- Plant uptake of metals and translocation to the aboveground portion must be avoided.
- The root zone, root exudates, contaminants, and soil amendments must be monitored to prevent an increase in metal solubility and leaching.
- Phytostabilization might be considered to only be an interim measure.
- Contaminant stabilization might be due primarily to the effects of soil amendments, with plants only contributing to stabilization by decreasing the amount of water moving through the soil and by physically stabilizing the soil against erosion.

#### **Applicable Contaminants**

Phytostabilization has not generally been examined in terms of organic contaminants. The following is a discussion of metals and metal concentrations, with implications for phytostabilization:

- **Arsenic:**  
As (as arsenate) might be taken up by plants because it is similar to the plant nutrient phosphate, although poplar leaves in a field study did not accumulate significant amounts of as Poplars were grown in soil containing an average of 1250 mg/kg As.[27]
- **Cadmium:**  
Cd might be taken up by plants because it is similar to the plant nutrients Ca, Zn, although poplar leaves in a field study did not accumulate significant amounts of Cd.[27] Poplars were grown in soil containing an average of 9.4 mg/kg Cd. Plants were grown in mine waste containing up to 160 mg/kg Cd.
- **Chromium:**  
Indian mustard (*Brassica juncea*) might be able to reduce Cr<sup>6+</sup> to Cr<sup>3+</sup>.
- **Copper:**  
Mine wastes containing copper were stabilized by grasses.
- **Mercury:**

Mercury might be one of the leading candidates for the phytostabilization of metals, although additional study is required.[32]

- **Lead:**

Pb in leachate was 22 g/mL in soil containing Indian mustard (*Brassica juncea*) compared to 740 µg/mL in soil without plants. Mine wastes containing lead were stabilized by grasses. 625 µg/g Pb was used in a sand-Perlite mixture that supported Indian mustard (*Brassica juncea*) soil with 1660 mg/kg Pb had less than 50% plant cover. Plants in soil with 323 mg/kg Pb exhibited heavy chlorosis. Plants were grown in mine waste containing up to 4500 mg/kg.

- **Zinc:**

Mine wastes containing zinc were stabilized by grasses soil with 4230 mg/kg Zn had less than 50% plant cover. Plants in soil with 676 mg/kg Zn exhibited heavy chlorosis. Plants were grown in mine waste containing up to 43,750 mg/kg Zn.

### **Root depth**

The root zone is the primary area affecting chemically moderated immobilization or root precipitation. Plants can be selected for their root depth; for example, poplars can be used for remediation of soil to a depth of 5 to 10 feet. The impact of the roots may extend deeper into the soil, depending on the transport of root exudates to lower soil depths.

### **Plants**

Metal-tolerant plants are required for heavy-metal-contaminated soils. *Brassica juncea* has been shown to reduce leaching of metals from soil by over 98%<sup>23</sup>. The following grasses have been used to reduce metals leaching:

- Colonial bentgrass (*Agrostis tenuis* cv Goginan) for acid lead and zinc mine wastes.
- Colonial bentgrass (*Agrostis tenuis* cv Parys) for copper mine wastes.
- Red fescue (*Festuca rubra* cv Merlin) for calcareous lead and zinc mine wastes.

Native and tame grasses and leguminous forbs including big bluestem (*Andropogon gerardi* Vit.), tall fescue (*Festuca arundinacea* Schreb.), and soybean (*Glycine max* (L.) Merr.) were studied to determine their effectiveness in remediating mine wastes. In addition, hybrid poplars were evaluated in a field study at a Superfund site to determine their metal tolerance.[27]

### **3.4 Rhizodegradation**

Rhizodegradation is the breakdown of an organic contaminant in soil through microbial activity that is enhanced by the presence of the root zone. Rhizodegradation is also known as plant-assisted degradation, plant-assisted bioremediation, plant-aided *in situ* biodegradation, and enhanced rhizosphere biodegradation.

Root-zone biodegradation is the mechanism for implementing rhizodegradation. Root exudates are compounds produced by plants and released from plant roots. They include sugars, amino acids, organic acids, fatty acids, sterols, growth factors, nucleotides, flavanones, enzymes, and other compounds.[34] The microbial populations and activity in the rhizosphere can be increased due to the presence of these exudates, and can result in increased organic contaminant biodegradation in the soil. Additionally, the rhizosphere substantially increases the surface area where active microbial degradation can be stimulated. Degradation of the exudates can lead to co-metabolism of contaminants in the rhizosphere.[36]

Plant roots can affect soil conditions by increasing soil aeration and moderating soil moisture content, thereby creating conditions more favorable for biodegradation by indigenous microorganisms. Thus, increased biodegradation could occur even in the absence of root exudates. One study raised the possibility that transpiration due to alfalfa plants drew methane from a saturated methanogenic zone up into the zone where the methane was used by methanotrophs that co-metabolically degraded TCE.[37] The chemical and physical effects of the

exudates and any associated increase in microbial populations might change the soil pH or affect the contaminants in other ways.

### Advantages

- Contaminant destruction occurs *in situ*.
- Translocation of the compound to the plant or atmosphere is less likely than with other phytoremediation technologies since degradation occurs at the source of the contamination.
- Mineralization of the contaminant can occur.
- Low installation and maintenance cost as compared to other remedial options.

### Disadvantages

- Development of an extensive root zone is likely to require substantial time.
- Root depth can be limited due to the physical structure or moisture conditions of the soil.
- The rhizosphere might affect an increase in the initial rate of degradation compared to a non rhizosphere soil, but the final extent or degree of degradation might be similar in both rhizosphere and non rhizosphere soil.
- Plant uptake can occur for many of the contaminants that have been studied. Laboratory and field studies need to account for other loss and phytoremediation mechanisms that might complicate the interpretation of rhizodegradation. For example, if plant uptake occurs, phytodegradation or phytovolatilization could occur in addition to rhizodegradation.
- The plants need additional fertilization because of microbial competition for nutrients.
- The exudates might stimulate microorganisms that are not degraders, at the expense of degraders.
- Organic matter from the plants may be used as a carbon source instead of the contaminant, which could decrease the amount of contaminant biodegradation. In laboratory sediment columns, debris from the salt marsh plant *Spartina alterniflora* decreased the amount of oil biodegradation. This could have been due to competition for limited oxygen and nutrients between the indigenous oil-

degrading microorganisms and the microorganisms degrading plant organic matter.

### Applicable Contaminants

The following contaminants are amenable to rhizodegradation:

- **TPH** (total petroleum hydrocarbons)
  - Several field sites contaminated with crude oil, diesel, heavier oil, and other petroleum products were studied for phytoremediation by examining TPH disappearance. Rhizodegradation and humification were the most important disappearance mechanisms, with little plant uptake occurring. Phytoremediation was able to bring TPH levels to below the plateau level found with normal (non-plant-influenced) bioremediation.[38]
  - High initial petroleum hydrocarbon contents (2,000 to 40,000 mg/kg TPH) were studied at several field sites. Plant growth varied by species, but the presence of some species led to significantly greater TPH disappearance than with other species or in unvegetated soil.
- **PAHs** (polycyclic aromatic hydrocarbons)
  - Chrysene, benzoanthracene, benzopyrene, and di benzoanthracene had greater disappearance in vegetated soil than in no vegetated soil.[39]
  - Anthracene and pyrene had greater disappearance in vegetated soils than in unvegetated soil.[40]
  - Pyrene was mineralized at a greater rate in a planted system than in an unplanted system[41]
  - Pyrene at 150 mg/kg was used in an experiment with crested wheatgrass.[41]
  - Anthracene and pyrene at 100 mg/kg were used in a study with grasses and a legume .
  - 10 mg/kg PAH (chrysene, benzoanthracene, benzopyrene, dibenzoanthracene) had greater disappearance in vegetated soil than in non vegetated soil.
  - PAHs at 1,450 to 16,700 mg/kg (in soil also contaminated with PCP) strongly inhibited germination and growth of eight species of grasses.[42]

- **BTEX** (Benzene, toluene, ethylbenzene, and xylenes)
  - Soil from the rhizosphere of poplar trees had higher populations of benzene-, toluene-, and o-xylene degrading bacteria than did nonrhizosphere soil. Root exudates contained readily biodegradable organic macromolecules.[43]
- **Pesticides**
  - Atrazine, metolachlor, and triflural in herbicides: Soil from the rhizosphere had increased degradation rates compared to nonrhizosphere soil. The experiments were conducted in the absence of plants to minimize effects of root uptake.[17]
  - Parathion and diazinon organophosphate insecticides: Mineralization rates of the radiolabeled compounds were higher in rhizosphere soil (soil with roots) than in nonrhizosphere soil (soil without roots). Diazinon mineralization in soil without roots did not increase when an exudate solution was added, but parathion mineralization did increase .[44]
  - Propanil herbicide: An increased number of gram negative bacteria were found in rhizosphere soil. It was hypothesized that the best propanil degraders would benefit from the proximity to plant roots and exudates.[45]
  - 2, 4-D herbicide: Microorganisms capable of degrading 2, 4-D occurred in elevated numbers in the rhizosphere of sugar cane, compared to nonrhizosphere soil. The rate constants for 2,4-D biodegradation were higher in rhizosphere soil than in nonrhizosphere soil.[46]
  - 2, 4, 5-T herbicide: The rate constants for 2,4,5-T biodegradation were higher in rhizosphere soil than in nonrhizosphere soil.
  - Increased degradation of 0.3 g/g trifluralin, 0.5 g/g atrazine, and 9.6 g/g metolachlor occurred in rhizosphere soil compared to nonrhizosphere soil.[18]
  - Parathion and diazinon at 5 g/g had greater mineralization in rhizosphere soil than in nonrhizosphere soil.[44]
  - Rhizosphere soil with 3 g/g propanil had increased numbers of gram-negative bacteria that could rapidly transform propanil.[45]
- **Chlorinated solvents**
  - Greater TCE mineralization was measured in vegetated soil as compared to non vegetated soil.[19]
  - TCE and TCA dissipation was possibly aided by rhizosphere biodegradation enhanced by the plant roots.
  - TCE at 100 and 200 g/L in groundwater was used in a soil and groundwater system.[38]
  - TCA at 50 and 100 g/L in groundwater was used in a soil and groundwater system.[38]
- **PCP** (pentachlorophenol)
  - PCP was mineralized at a greater rate in a planted system than in an unplanted system. [41]
  - 100 mg PCP/kg soil was used in an experiment with hycrest crested wheatgrass [Agropyron desertorum (Fisher ex Link) Schultes] .
  - Proso millet (Panicum miliaceum L.) seeds treated with a PCP-degrading bacterium germinated and grew well in soil containing 175 mg/L PCP, compared to untreated seeds.[47]
  - PCP at 400 to 4100 mg/kg (in soil also contaminated with PAHs) strongly inhibited germination and growth of eight species of grasses.[42]
- **PCBs** (polychlorinated biphenyls)
  - Compounds (such as flavonoids and coumarins) found in leachate from roots of specific plants stimulated the growth of PCB-degrading bacteria.[48], [49]
- **Surfactants**
  - Linear alkylbenzene sulfonates (LAS) and linear alcohol ethoxylate (LAE) had greater mineralization rates in the presence of root microorganisms than in nonrhizosphere sediments.[50]
  - LAS and LAE at 1 mg/L had greater mineralization rates in the presence of root microorganisms than in non rhizosphere sediments.[50]

#### Root depth

Because the rhizosphere extends only about 1 mm from the root and initially the volume of soil occupied by roots is a small fraction of the total soil volume, the soil volume initially affected by the rhizosphere is



limited. With time, however, new roots will penetrate more of the soil volume and other roots will decompose, resulting in additional exudates to the rhizosphere. Thus, the extent of rhizodegradation will increase with time and with additional root growth. The effect of rhizodegradation might extend slightly deeper than the root zone. If the exudates are water soluble, not strongly sorbed, and not quickly degraded, they may move deeper into the soil. Contaminated groundwater can be affected if it is within the influence of roots.

### Plants

Plants that produce exudates that have been shown to stimulate growth of degrading microorganisms or stimulate co-metabolism will be of more benefit than plants without such directly useful exudates. The type, amount, and effectiveness of exudates and enzymes produced by a plant's roots will vary between species and even within subspecies or varieties of one species. The following are examples of plants capable of rhizodegradation:

- Red mulberry (*Morus rubra* L.), crabapple [*Malus fusca* (Raf.) Schneid], and orange [*Maclura pomifera* (Raf.) Schneid] produced exudates containing relatively high levels of phenolic compounds, at concentrations capable of stimulating growth of PCB-degrading bacteria.[51]
- Spearmint (*Mentha spicata*) extracts contained a compound that induced cometabolism of a PCB.[49]
- Alfalfa (*Medicago sativa*) appears to have contributed to the dissipation of TCE and TCA through exudates on soil bacteria.[38]
- A legume [*Lespedeza cuneata* (Dumont)], Loblolly pine [*Pinus taeda* (L.)], and soybean [*Glycine max* (L.) Merr., cv Davis] increased TCE mineralization compared to non vegetated soil.[18]
- At a Gulf Coast field site, the use of annual rye and St. Augustine grass led to greater TPH disappearance after 21 months than that experienced with the use of sorghum or an unvegetated plot.[52]

- At one field site, although white clover did not survive the second winter, concentrations of TPH were reduced more than with tall fescue or bermudagrass with annualrye, or bare field.[52]
- PAH degradation occurred through the use of the following mix of prairie grasses: big bluestem (*Andropogon gerardi*), little bluestem (*Schizachyrium scoparius*), Indiangrass (*Sorghastrum nutans*), switchgrass (*Panicum virgatum*), Canada wild rye (*Elymus canadensis*), western wheatgrass (*Agropyron smithii*), side oats grama (*Bouteloua curtipendula*), and blue grama (*Bouteloua gracilis*).[39]
- Fescue (*Festuca arundinacea* Schreb), a cool-season grass; sudangrass (*Sorghum vulgare* L.) and switchgrass (*Panicum virgatum* L.), warm-season grasses; and alfalfa (*Medicago sativa* L.), a legume, were used to study PAH disappearance; greater disappearance was seen in the vegetated soils than in unvegetated soils.[40]
- Hycrest crested wheatgrass [*Agropyron desertorum* (Fischer ex Link) Schultes] increased mineralization rates of PCP and pyrene relative to unplanted controls.[41]
- In PAH and PCP contaminated soil, a mix of fescues [hard fescue (*Festuca ovina* var. *duriuscula*), tall fescue (*Festuca arundinacea*), and red fescue (*Festuca rubra*)] had higher germination rates and greater biomass relative to controls than did a mix of wheatgrasses [western wheatgrass (*Agropyron smithii*) and slender wheatgrass (*Agropyron trachycaulum*)] and a mix of little bluestem (*Andropogon scoparius*), Indiangrass (*Sorghastrum nutans*), and switchgrass (*Panicum virgatum*).[42]
- Bush bean (*Phaseolus vulgaris* cv. "Tender Green") rhizosphere soil had higher parathion and diazinon mineralization rates than nonrhizosphere soil.[44]
- Rice (*Oryza sativa* L.) rhizosphere soil had increased numbers of gram-negative bacteria, which were able to rapidly transform propanil.[45]

- Kochia sp. rhizosphere soil increased the degradation of herbicides relative to nonrhizosphere soil.[19]
- Cattail (*Typha latifolia*) root microorganisms produced greater mineralization rates of LAS and LAE than did nonrhizosphere sediments.
- Hybrid poplar tree (*Populus deltoides* X *nigra* DN-34, Imperial Carolina) rhizosphere soil contained significantly higher populations of total heterotrophs, denitrifiers, pseudomonads, BTX degraders, and atrazine degraders than did nonrhizosphere soil.[43]

### 3.5 Phytodegradation

Phytodegradation (also known as Phytotransformation) is the breakdown of contaminants taken up by plants through metabolic processes within the plant, or the breakdown of contaminants external to the plant through the effect of compounds (such as enzymes) produced by the plants.

#### Mechanism

The main mechanism is plant uptake and metabolism. Additionally, degradation may occur outside the plant, due to the release of compounds that cause transformation. Any degradation caused by microorganisms associated with or affected by the plant root is considered rhizodegradation.

#### Uptake

For phytodegradation to occur within the plant, the compounds must be taken up by the plant. One study identified more than 70 organic chemicals representing many classes of compounds that were taken up and accumulated by 88 species of plants and trees.[54] A database has been established to review the classes of chemicals and types of plants that have been investigated in regard to their uptake of organic compounds.[55] Uptake is dependent on hydrophobicity, solubility, and polarity. Moderately hydrophobic organic compounds (with log  $K_{ow}$  between 0.5 and 3.0) are most readily taken up by and translocated within plants. Very soluble

compounds (with low sorption) will not be sorbed onto roots or translocated within the plant. Hydrophobic (lipophilic) compounds can be bound to root surfaces or partitioned into roots, but cannot be further translocated within the plant.[35],[37] Nonpolar molecules with molecular weights <500 will sorb to the root surfaces, whereas polar molecules will enter the root and be translocated.[57]

Plant uptake of organic compounds can also depend on type of plant, age of contaminant, and many other physical and chemical characteristics of the soil. Definitive conclusions cannot always be made about a particular chemical. For example, when PCP was spiked into soil, 21% was found in roots and 15% in shoots after 155 days in the presence of grass.[56] In another study, several plants showed minimal uptake of PCP.[58]

#### Metabolism

Metabolism within plants has been identified for a diverse group of organic compounds, including the herbicide atrazine.[59] the chlorinated solvent TCE<sup>[60]</sup> and the munition TNT.[61] Other metabolized compounds include the insecticide DDT, the fungicide hexachlorobenzene (HCB), PCP, the plasticizer diethylhexylphthalate (DEHP), and PCBs in plant cell cultures.

#### Plant-Formed Enzymes

Plant-formed enzymes have been identified for their potential use in degrading contaminants such as munitions, herbicides, and chlorinated solvents. Immunoassay tests have been used to identify plants that produce these enzymes.[11]

#### Media

Phytodegradation is used in the treatment of soil, sediments, sludges, and groundwater. Surface water can also be remediated using phytodegradation.

#### Advantages

Contaminant degradation due to enzymes produced by a plant can occur in an environment, free of microorganisms (for example, an environment in

which the microorganisms have been killed by high contaminant levels). Plants are able to grow in sterile soil and also in soil that has concentration levels that are toxic to microorganisms. Thus, phytodegradation potentially could occur in soils where biodegradation cannot.

### Disadvantages

- Toxic intermediates or degradation products may form. In a study unrelated to phytoremediation research, PCP was metabolized to the potential mutagen tetrachlorocatechol in wheat plants and cell cultures.
- The presence or identity of metabolites within a plant might be difficult to determine; thus contaminant destruction could be difficult to confirm.

### Applicable Contaminants

Organic compounds are the main category of contaminants subject to phytodegradation. In general, organic compounds with a log  $k_{ow}$  between 0.5 and 3.0 can be subject to phytodegradation within the plant. Inorganic nutrients are also remediated through plant uptake and metabolism. Phytodegradation outside the plant does not depend on log  $k_{ow}$  and plant uptake.

### Organics

#### Chlorinated solvents

- The plant-formed enzyme dehalogenase, which can dechlorinate chlorinated compounds, has been discovered in sediments.[11]
  - TCE was metabolized to trichloroethanol, trichloroacetic acid, and dichloroacetic acid within hybrid poplar trees. In a similar study, hybrid poplar trees were exposed to water containing about 50 ppm TCE and metabolized the TCE within the tree.[60]
  - Minced horseradish roots successfully treated wastewater containing up to 850 ppm of 2, 4-dichlorophenol.[62]
- #### Herbicides
- Atrazine in soil was taken up by trees and then hydrolyzed and dealkylated within the roots, stems, and leaves. Metabolites were identified within the

plant tissue, and a review of atrazine metabolite toxicity studies indicated that the metabolites were less toxic than atrazine.[59]

- The plant formed enzyme nitrilase, which can degrade herbicides and has been discovered in sediments.
- A qualitative study indicated that the herbicide bentazon was degraded within black willow trees, as indicated by bentazon loss during a nursery study and by identification of metabolites within the tree. Bentazon was phytotoxic to six tree species at concentrations of 1000 and 2000 mg/L. At 150 mg/kg, bentazon metabolites were detected within tree trunk and canopy tissue samples.[63]
- Atrazine at 60.4 g/kg (equivalent to about 3 times field application rates) was used to study phytodegradation in hybrid poplars.[59]
- The herbicide bentazon was phytotoxic at concentrations of 1,000 to 2,000 mg/L, but allowed growth at 150 mg/L.[63]

#### Insecticides

- The isolation from plants of the enzyme phosphatase, which can degrade organophosphate insecticides, may have phytodegradation applications.[11]

#### Munitions

- The plant-formed enzyme nitroreductase, which can degrade munitions, has been discovered in sediments; this enzyme, from parrot feather, degraded TNT.[11]
- Hybrid poplar trees metabolized TNT to 4-amino- 2, 6-dinitrotoluene (4-ADNT), 2-amino- 4,6-dinitrotoluene (2-ADNT), and other unidentified compounds.[61]
- TNT concentrations in flooded soil decreased from 128 to 10 ppm with parrot feather.

#### Phenols

- Chlorinated phenolic concentrations in wastewater decreased in the presence of oxidoreductase enzymes in minced horseradish roots.[62]

### Inorganics

- **Nutrients:** Nitrate will be taken up by plants and transformed to proteins and nitrogen gas.[64]

### Root depth

Phytodegradation is generally limited to the root zone and possibly below the root zone if root exudates are soluble, nonsorbed, and transported below the root zone. The degree to which this occurs is uncertain.

### Plants

The aquatic plant parrot feather (*Myriophyllum aquaticum*) and the algae stonewort (*Nitella*) have been used for the degradation of TNT. The nitroreductase enzyme has also been identified in other algae, ferns, monocots, dicots, and trees.[11] Degradation of TCE has been detected in hybrid poplars and in poplar cell cultures, resulting in production of metabolites and in complete mineralization of a small portion of the applied TCE. Atrazine degradation has also been confirmed in hybrid poplars (*Populus deltoides* x *nigra* DN34, Imperial Carolina).[59] Poplars have also been used to remove nutrients from groundwater.[64]

Black willow (*Salix nigra*), yellow poplar (*Liriodendron tulipifera*), bald cypress (*Taxodium distichum*), river birch (*Betula nigra*), cherry bark oak (*Quercus falcata*), and liveoak (*Quercus virginiana*) were able to support some degradation of the herbicide bentazon.[64]

### 3.6 Phytovolatilization

Phytovolatilization is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant through contaminant uptake, plant metabolism, and plant transpiration. Phytodegradation is a related phytoremediation process that can occur along with Phytovolatilization.

### Media

Phytovolatilization has mainly been applied to groundwater, but it can be applied to soil, sediments, and sludges.

### Advantages

- Contaminants could be transformed to less-toxic forms, such as elemental mercury and dimethyl selenite gas.
- Contaminants or metabolites released to the atmosphere might be subject to more effective or rapid natural degradation processes such as photodegradation.

### Disadvantages

- The contaminant or a hazardous metabolite (such as vinyl chloride formed from TCE) might be released into the atmosphere. One study indicated TCE transpiration, but other studies found no transpiration.
- The contaminant or a hazardous metabolite might accumulate in vegetation and be passed on in later products such as fruit or lumber. Low levels of metabolites have been found in plant tissue.

### Applicable Contaminants

#### • Organics

Chlorinated solvents include TCE, 1, 1,1-trichloroethane (TCA) and carbon tetrachloride. In two years, hybrid poplars removed >97% of the 50-ppm TCE from the water. 100 and 200 µg/L TCE in groundwater was studied using alfalfa.[27] 50 and 100 µg/L TCE in groundwater were studied using alfalfa (Narayanan *et al.*, 1995). In one year, 95% of 50- ppm carbon tetrachloride was removed by hybrid poplars.[60]

#### • Inorganics

The inorganic contaminants Se and Hg, along with As, can form volatile methylated species. Selenium has been taken up and transpired at groundwater concentrations of 100 to 500 µg / L and at soil concentrations of 40 mg/L. Genetically engineered plants were able to germinate and grow in 20-ppm Hg ++ and then volatilize the Hg; 5 to 20 ppm Hg ++ was phytotoxic to unaltered plants.[65]

### Root depth

The contaminant has to be within the influence of the root of the plant. Since groundwater is the target media, contaminated groundwater up gradient of the plants may flow into the area of influence of the plants. Contaminated water may also be pumped and watered on plants.

### Plants

Plants used for phytovolatilization include:

- University of Washington researchers have extensively studied the use of poplars in the phytoremediation of chlorinated solvents. In these studies, transformation of TCE was found to occur within the tree.[60]
- Alfalfa (*Medicago sativa*) has been studied by Kansas State University researchers for its role in the phytovolatilization of TCE.
- Black locust species were studied for use in remediating TCE in groundwater.[60]
- Indian mustard (*Brassica juncea*) and canola (*Brassica napus*) have been used in the phytovolatilization of Se. Selenium (as selenite) was converted to less toxic dimethyl selenite gas and released to the atmosphere. Kenaf (*Hibiscus cannabinus* L.cv. Indian) and tall fescue (*Festuca arundinacea* Schreb cv. Alta) have also been used to take up Se, but to a lesser degree than canola.[26]
- A weed from the mustard family (*Arabidopsis thaliana*) genetically modified to include a gene for mercuric reductase converted mercuric salts to metallic mercury and released it to the atmosphere.[65]

### 3.7 Hydraulic Control

Hydraulic control is the use of plants to remove groundwater through uptake and consumption in order to contain or control the migration of contaminants. Hydraulic control is also known as phytohydraulics or hydraulic plume control.

### Media

Hydraulic control is used in the treatment of groundwater, surface water, and soil water.

### Advantages

- An engineered pump-and-treat system does not need to be installed.
- Costs will be lower.
- Roots will penetrate into and be in contact with a much greater volume of soil than if a pumping well is used.

### Disadvantages

- Water uptake by plants is affected by climatic and seasonal conditions; thus, the rate of water uptake will not be constant. Water uptake by deciduous trees will slow considerably during winter.
- Groundwater removal is limited by the root depth of the vegetation.

### Root depth

Hydraulic control by plants occurs within the root zone or within a depth influenced by roots, for example:

- The effective rooting depth of most crops is 1 to 4 feet. Trees and other vegetation can be used to remediate groundwater in water table depths of 30 feet or less.[66]
- Plant roots above the water table can influence contaminants in the groundwater by interfacing through the capillary fringe. Fe, U, and P diffused upward from the water table and were absorbed by barley roots that were 10 cm (3.9 in) above the water table interface.[67]
- The placement depth of roots during planting can be varied. Root depth, early tree growth, and nitrogen accumulation were enhanced by placing poplar tree root balls closer to shallow groundwater during planting.[66]

### Plants

- Cottonwood and hybrid poplar trees were used at seven sites in the East and Midwest to contain and treat shallow groundwater contaminated with heavy metals, nutrients, or pesticides.[66] Poplars were



used at a site in Utah to contain groundwater contaminated with gasoline and diesel. Passive gradient control was studied at the French Limited Superfund site using a variety of phreatophyte trees; native no deciduous trees were found to perform the best.[68]

## CONCLUSION

Phytoremediation is an eco friendly approach for remediation of contaminated soil and water using plants comprised of two components, one by the root colonizing microbes and the other by plants themselves, which accumulates the toxic compounds to further non toxic metabolites. Various compounds viz., organic synthetic compounds, xenobiotics, pesticides, hydrocarbon and heavy metals, are among the contaminants that can be effectively remediated by plants.

Phytoremediation is comprised of several different techniques that utilize vegetation, its related enzymes, and other complex processes. Collectively, these processes are able to isolate, destroy, transport, and remove organic and inorganic pollutants from contaminated media.

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