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Remediation engineering: design concepts
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10.1 INTRODUCTION

Phytoremediation is the use of plants to remediate contaminated soil or groundwater. This technique can be used for the remediation of inorganic contaminants as well as organic contaminants. Most of the activity in phytoremediation takes place in the rhizosphere—in other words, the root zone. Phytoremediation of inorganic contaminants can be further categorized into phytostabilization and phytoextraction.¹

Phytostabilization is the use of plants to stabilize contaminated soil by decreasing wind and water erosion and also decreasing water infiltration and the subsequent leaching of contaminants. Phytoextraction is the removal of inorganic contaminants by above-ground portions of the plant. When the shoots and leaves are harvested, the inorganic contaminants are reclaimed or concentrated from the plant biomass or can be disposed.

Plants have been used for remediation in the past. A number of free-floating aquatic and aquatic emergent plant species and their associated microorganisms have been used for more than a decade in constructed wetlands for municipal and industrial wastewater treatment.² Several fast-growing tree plantations have been established and are under active study for their potential use in wastewater cleanup in land discharge systems.³,⁴

Plant species can be selected to extract and assimilate or extract and chemically decompose target organic contaminants. Heavy metals can be taken up and bioaccumulated in plant tissues. Many inorganic compounds considered to be contaminants are, in fact, vital plant nutrients that can be absorbed through the root system for use in growth and development. Heavy metals can be taken up and bioaccumulated in plant tissues. Organic chemicals such as PAHs and pesticides can be absorbed and metabolized by plants and trees.

The advantages of phytoremediation are the low capital costs, aesthetic benefits, minimization of leaching of contaminants, and soil stabilization. The operational cost of phytoremediation is also substantially less and involves mainly fertilization and watering for maintaining plant growth. In the case of heavy metals remediation, additional operational costs will also include harvesting, disposal of contaminated plant mass, and repeating the plant growth cycle.

The limitations of phytoremediation are that the contaminants present below rooting depth will not be extracted and that the plant or tree may not be able to grow in the soil at every contaminated site due to toxicity. In addition, the remediation process can take years for contaminant concentrations to reach regulatory levels and thus requires a long-term commitment to maintain the system.

Phytoremediation is most suited for sites with moderately hydrophobic contaminants such as benzene, toluene, ethylbenzene, xylenes, chlorinated solvents, PAHs, nitrotoluene ammunition wastes, excess nutrients such as nitrate, ammonium, and phosphate, and heavy metals.
10.2 PHYTOREMEDIATION MECHANISMS OF ORGANIC CONTAMINANTS

Plants and trees remove organic contaminants utilizing two major mechanisms: (1) direct uptake of contaminants and subsequent accumulation of nonphytotoxic metabolites into the plant tissue, and (2) release of exudates and enzymes that stimulate microbial activity and the resulting enhancement of microbial transformations in the rhizosphere (the root zone).

10.2.1 Direct Uptake

Not all organic compounds are equally accessible to plant roots in the soil environment. The inherent ability of the roots to take up organic compounds can be described by the hydrophobicity (or lipophilicity) of the target compounds. This parameter is often expressed as the log of the octanol–water partitioning coefficient, $K_{ow}$. Direct uptake of organics by plants is a surprisingly efficient removal mechanism for moderately hydrophobic organic compounds. There are some differences between the roots of different plants and under different soil conditions, but generally the higher a compound’s log $K_{ow}$, the greater the root uptake.

Hydrophobicity also implies an equal propensity to partition into soil organic matter and onto soil surfaces. Root absorption may become difficult with heavily textured soils and soils with high native organic matter. There are several reported values available in the literature regarding the optimum log $K_{ow}$ value for a compound to be a good candidate for phytoremediation (as an example, log $K_{ow} = 0.5$ to 3.0; log $K_{ow} = 1.5$ to 4.0). It was also reported that compounds that are quite water soluble (log $K_{ow} <0.5$) are not sufficiently sorbed to the roots or actively transported through plant membranes.

From an engineering point of view, a tree could be thought of as a shell of living tissue encasing an elaborate and massive chromatography column of twigs, branches, trunk, and roots. The analogous resin in this system is wood, the vascular tissue of the tree, and this “resin” is replenished each year by normal growth. Wood is composed of thousands of hollow tubes, like the bed of a hollow fiber chromatography column, with transpirational water serving as the moving phase. The hollow tubes are actually dead cells, whose death is carefully programmed by the tree to produce a water-conducting tissue which also functions in mechanical support. A complex, cross-linked, polymeric matrix of cellulose, pectins, and proteins embedded in lignin forms the walls of the tubes. The cell wall matrix is chemically inert, insoluble in the majority of solvents, and stable across a wide range of pH.

Once an organic chemical is taken up, a plant can store (sequestration) the chemical and its fragments in new plant structures via lignification, or it can volatilize, metabolize, or mineralize the chemical all the way to carbon dioxide, water, and chlorides (Figure 10.1). Detoxification mechanisms may transform the parent chemical to nonphytotoxic metabolites, including lignin, that are stored in various places in plant cells. Many of these metabolic capacities tend to be enzymatically and chemically similar to those processes that occur in mammalian livers, and one report equated plants to “green livers” due to the similarities of the detoxification process.

Different plants exhibit different metabolic capacities. This is evident during the application of herbicides to weeds and crops alike. The vast majority of herbicidal compounds have been selected so that the crop species are capable of metabolizing the pesticide to nontoxic compounds, whereas the weed species either lack this capacity or metabolize it at too slow a rate. The result is the death of the weed species without the metabolic capacity to rid itself of the toxin.

The shear volume and porous structure of a tree’s wood provides an enormous surface area for exchange or biochemical reactions. Some researchers are attempting to augment the inherent metabolic capacity of plants by incorporating bacterial, fungal, insect, and even mammalian genes into the plant genome.
10.2.2 Degradation in Rhizosphere

In natural plant ecosystems, indigenous soil microorganisms present in the rhizosphere (root zone of the plants) are found in mutual relationships with plants. The microflora that responds to the presence of living roots is distinctly different from the characteristic soil population, due to the plant creating a unique subterranean habitat for microorganisms. The plant, in turn, is markedly affected by the population it has stimulated, since the root zone is the area from which mineral nutrients are obtained. The rhizosphere is often divided into two general areas, the inner rhizosphere at the very root surface and the outer rhizosphere embracing the immediately adjacent soil. The microbial population is larger in the inner zone where the biochemical interactions are most pronounced and root exudates are concentrated.

Different plant species often establish somewhat different subterranean floras. The differences are attributed to variations in rooting habits, tissue composition, and excretion products of the plant. The primary root population is determined by the habitat created by the plant; the secondary flora, however, depends upon the activities of the initial population. The age of the plant also alters the microbial population in the rhizosphere.

The roots of the plants exude a wide spectrum of compounds including sugars, amino acids, carbohydrates, and essential vitamins that may act as growth and energy-yielding substrates for the microbial consortia in the root zone (Figure 10.1). Exudates may also include compounds such as acetates, esters, benzene derivatives, and enzymes. This process enriches the *in situ* microbial populations present in the rhizosphere for enhanced degradation of organics by the provision of appropriate beneficial primary substrates for cometabolic transformations of the target contaminants. It was also reported that wherever significant transformation of contaminants was evident, the following enzyme systems were present: dehalogenase, nitroreductase, peroxidase, laccase, nitylase, and oxygenase.

In addition to the plant exudates, the rapid decay of fine-root biomass can become an important addition of organic carbon to soils. The additional organic carbon, in turn, may increase microbial mineralization rates. The increase in organic carbon levels also serves to retard the contaminant migration into groundwater.

Roots also harbor mycorrhizae fungi, which metabolize organic contaminants. These fungi, growing in symbiotic association with the plant, have unique enzymatic pathways,
similar to white rot fungus enzymes, that help to degrade organics that could not be transformed solely by bacteria.

In summary, plants provide exudates that provide an excellent habitat for increased microbial populations and pump oxygen to roots, a process that ensures aerobic transformations near the root that otherwise may not occur in the bulk soil. Due to the presence of certain primary substrates in the exudate system, anaerobic cometabolic transformations may also take place in the rhizosphere. A typical microbial population in the rhizosphere comprises $5 \times 10^6$ bacteria, $9 \times 10^5$ actinomycetes, and $2 \times 10^3$ fungi per gram of air-dried soil.

### 10.3 PHYTOREMEDIATION MECHANISMS OF HEAVY METALS

Most heavy metals have multiple chemical and physical forms in the soil environment. All forms are not equally hazardous, nor are all forms equally amenable to uptake by plants. The chemistry of the metal and its mobility will inherently impact the toxicity in the environment.

Metal fractionation or sequential extraction schemes (such as TCLP) sometimes are used to describe metal behavior in soils. Most metals interact with the inorganic and organic matter that is present in the root-soil environment. Potential forms of metals include those dissolved in the soil solution, adsorbed to the vegetation’s root system, adsorbed to insoluble organic matter, bonded to ion exchange sites on inorganic soil constituents, precipitated or coprecipitated as solids, and attached to or inside the soil biomass.

Phytoremediation of heavy metal contaminated soils can be divided into phytostabilization and phytoextraction approaches.

#### 10.3.1 Phytostabilization of Heavy Metals

Implementation of phytostabilization involves the reduction in the mobility of heavy metals by minimizing soil erodibility, decreasing the potential for wind-blown dust, and reduction in contaminant solubility by the addition of soil amendments.

Erosion leads to the concentration of heavy metals because of the selective sorting and deposition of different size fractions of the soil. Eroded material is often transported over long distances, thus selectively extending the effects of contamination and increasing the risk to the environment. Erosion can, therefore, cause the buildup of concentrations of normally nontoxic contaminants to toxic levels at locations where transported material is deposited.

Planting of vegetation at contaminated sites will significantly reduce the erodibility of the soils both by water and wind. Density of vegetation will effectively hold the soil and provide a stable cover against erosion.

Another element of phytostabilization is to supplement the system with a variety of alkalizing agents, phosphates, organic matter, and biosolids to render the metals insoluble and unavailable to leaching. Materials with a calcareous character or a high pH can be added to influence the acidity: compounds such as lime and gypsum. Specific binding conditions can be influenced by adding concentrated Fe, Mn, or Al compounds. To maintain or raise the organic matter content in the soils, various materials such as humus or peat materials, manure or mulch can be added.

This chemical alteration should be quickly followed by establishing a plant cover and maximizing plant growth. The amendments sequester the metals into the soil matrix and plants keep the stabilized matrix in place, minimizing wind and water erosion.

#### 10.3.2 Phytoextraction of Heavy Metals

The use of unusual plants that have the ability to accumulate very high (2 to 5%) concentrations of metals from contaminated soils in their biomass provides the basis for this phytoremediation technique. The metals are translocated to the shoot and tissue via the
roots. These plants are called hyperaccumulator plants and they exhibit the ability to tolerate high concentrations of toxic metals in above-ground plant tissues; these species contain toxic element levels in the leaf and stalk biomass (LSB) of about 100 times those of nonaccumulator plants growing in the same soil, with some species and metal combinations exceeding conventional plant levels by a factor of more than a thousand.9

Many hyperaccumulator plants that are nonwoody (not a tree) have been identified to have the capacity to accumulate metals. *Thlaspi caerulescens* was found to accumulate Zn up to 2000 to 4000 mg/kg.10 The Indian mustard plant *Brassica juncea*, grown throughout the world for its oil seed, was found to accumulate a significant amount of lead.11 One planting of mustard in a hectare of contaminated land was found to soak up 2 t of lead. If three plantings could be squeezed in per year, 6 t of lead per hectare can be extracted. Both hemp dogbane (*Apocynum* sp.) and common ragweed also have been observed to accumulate significant levels of lead. *Aeollanthus subcaulis* var. *lineris* and *Paspalum notatum* are other hyperaccumulator plants known to accumulate Cu and Cs, respectively. Hyperaccumulator plants can address contamination in the shallow soils only up to 24 in. in depth. If contamination is deeper, 6 to 10 ft, deep-rooted poplar trees can be used for phytoextraction of heavy metals. These trees can accumulate the heavy metals by sequestration. However, there are concerns specifically for trees that leaf litter and associated toxic residues will be blown off site. This concern may be tested in the laboratory to see whether uptake and translocation of the metals into the leaves exceed the standards.

Hyperaccumulators have the metal-accumulating characteristics that are desirable, but lack the biomass production, adaptation to current agronomic techniques, and physiological adaptations to the climatic conditions at many contaminated sites. It has been reported that harvesting done at different seasons in a year had pronounced differences in accumulation levels.10 In the future, genetic manipulation techniques may provide better hyperaccumulator species. The success of phytoextraction depends on the use of an integrated approach to soil and plant management. The disciplines of soil chemistry, soil fertility, agronomy, plant physiology, and plant genetic engineering are currently being used to increase both the rate and efficiency of heavy metal phytoextraction.

The schematic of the process involved in heavy metal phytoextraction is shown in Figure 10.2. Translocation from the root to the shoot must occur efficiently for the ease of harvesting. After harvesting, a biomass processing step or disposal method that meets regulatory requirements should be implemented.

### 10.3.3 Phytosorption and Phytofiltration of Heavy Metals

Aquatic plants and algae are known to accumulate metals and other toxic elements from solution.12 There are large differences in bioremoval rates due to species and strain differences, cultivation methodology, and process control techniques. In the past, commercial systems have used immobilized algal biomass for removing radionuclides and other heavy metals in the aqueous phase.13

Plants that are naturally immobilized, such as attached algae and rooted plants, and those that could be easily separated from suspension, such as filamentous microalgae, macroalgae, and floating plants, have been found to have high adsorption capacities. In a recent study, one blue-green filamentous algae of the genus *Phormidium* and one aquatic rooted plant, water milfoil (*Myriophyllum spicatum*) exhibited high specific adsorption for Cd, Zn, Ph, Ni, and Cu.12

It has been reported that porous beads containing immobilized biological materials such as sphagnum peat moss can be used for extracting metals dissolved in the aqueous phase.14 The beads designated as BIO-FIX beads readily adsorbed Cd, Pb, and other toxic metals from dilute waters.

In a recent study, it was reported that *Saccharomyces cerevisiae* yeast biomass, when treated with a hot alkali, exhibited an increase in its biosorption capacity for heavy metals.15

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It was also reported that caustic treated yeast immobilized in alginate gel could be reactivated and reused to remove Cu, Cd, and Zn in a manner similar to the ion exchange resin.

10.4 PHYTOREMEDIATION OF NITROGEN COMPOUNDS

Nitrogen is an important nutrient for plant growth. When nitrates or other inorganic nitrogen species are present above the allowable limits in groundwater, phytoremediation is a viable remediation alternative under shallow water table conditions. Corn and deep-rooted poplar trees have been found to be very effective in reducing nitrate concentrations in groundwater.\textsuperscript{16,17} Poplar trees were most effective at reducing the nitrate concentrations, and the perennial nature of the trees ensures prolonged protection throughout the year. Deeper planting of the trees, closer to the water table, resulted in better growth and greater nitrogen accumulation in leaves.\textsuperscript{17}

Munitions wastes such as 2,4,6-trinitrotoluene are of considerable interest as candidates for phytoremediation.\textsuperscript{5} An excreted nitroreductase activity in the root zone has been identified as the catalyst for degradation of this compound.

10.5 FIELD APPLICATIONS OF PHYTOREMEDIATION

Many successful field-scale applications of phytoremediation have been reported in the literature. Each successful application reported has site-specific conditions unique to that particular site as well as different remediation objectives. Although phytoremediation is not a panacea for hazardous waste problems, it has proven effective in several applications for remediation of shallow contaminated sites. Before the technology can mature, we need a better understanding of the role of metabolites, enzymes, and the selection of plant and tree systems for various wastes and hydrogeologic conditions.

Trees potentially are the lowest-cost plant type to be used for phytoremediation. A number of trees can grow on land of marginal quality, and this will allow establishment of trees on
sites with low fertility and poor soil structure, thus keeping costs low for plant establishment. Since trees are perennial plants with long life spans, site remediation can continue for decades with little or no maintenance costs. Trees of the Salicaceae family (willow and poplar) have been planted at several locations because of their flood tolerance and fast growth. Various grass species such as prairie grass, crested wheat grass, and cattails have been used in phytoremediation. Alfalfa has been used widely for its deep rooting and root zone metabolic activity. Parrot feather and Eurasian water milfoil have been applied to break down ammunition wastes.

A proprietary technique call TreeMediation™ has been developed with a specific deep root system. Such root systems are known to facilitate the uptake of contaminated groundwater by hybrid poplar trees up to 30 ft below land surface. In addition, the hybrid poplar trees can transpire a quantity of water sufficient to impact the flow of groundwater when planted in sufficient density. Such hydraulic control in shallow groundwater conditions is valuable in that the migration of the contaminant plume can be reduced or eliminated.

One recent study demonstrated that poplar trees, which possess cytochrome P-450s analogous to the oxygenases responsible for transformation of compounds such as TCE in the mammalian liver, exposed to 100 mg/l of TCE did uptake and chemically alter this contaminant. TCE and its metabolites were found in the roots and tissue of the study trees, but not in control trees or in the soil used for potting the trees. In a subsequent study, popular seedlings exposed to 14C-labeled TCE were found to generate 14C-labeled carbon dioxide. Intermediate compounds generated during oxidation are thought to be 2,2,2-trichloroethanol, and di- and trichloroacetic acid. Similar studies have shown positive results for toluene and benzene.

Poplars are phreatophytic, capable of extending their roots into aerobic water tables. For example, the roots of poplars growing alongside streams can easily be observed intertwined in the stream bottom. The degree to which poplar roots would penetrate the saturated zone cannot be easily estimated. However, if their access to soil moisture from precipitation is limited, poplars will draw large amounts of water from the top of the saturated aquifer. Evapotranspiration will draw down the water table below the trees similar to a pump and treat system. Under optimal conditions, a hybrid poplar occupying 4 m² of ground can cycle 100 l of groundwater per day; this translates to approximately 30,000 gal of water per acre of trees per day. Poplar trees have been reported to grow 6 to 8 ft per year. Figure 10.3 shows the development of the root zone with time. Predicted impact on groundwater flow at a shallow water table site is shown in Figure 10.4. Simulations of a proposed design can be carried out based on extent of contamination, hydrogeological data, and past precipitation and infiltration records.

A big advantage of phytoremediation over conventional pump and treat systems is the ability of the roots to penetrate the microscopic scale pores in the soil matrix. Contaminants adsorbed or trapped in these micropores are minimally or not impacted by the pump and treat system. In the case of phytoremediation, the roots can penetrate these micropores for contaminant removal.

Another reported application of phytoremediation is the planting of 10,000 poplar trees per hectare as the final cap on a landfill in Oregon. Treatment of organic wastes is not the main goal at this site, but rather to keep the site natural and free from infiltration. This proprietary technique is known as Ecolotree™ cap, and installation involves the placement of a thick cover with soil amendments for storage of water within the root zone. Densely planted poplar trees uptake water through their extensive root systems as a pump and transpire the water back to the atmosphere. Advanced moisture control systems using time domain reflectometry (TDR) technique have been installed at this site. Although hybrid poplars seem to tolerate organic chemicals quite well, high concentrations of metals, salts, and ammonia are toxic.

For long-term closure of landfills in temperate climates, it might be desirable to use higher value hardwood trees such as walnut or pecan, in addition to fast-growing poplars,
unless there is a ready market for poplar products. Walnuts or pecans under good fertility conditions use large amounts of water and produce both nuts and wood. In subtropical regions, eucalyptus would be more appropriate than poplars. One would use alfalfa only in a situation where a short-lived perennial is satisfactory. Replanting would be necessary after a few years, if the remediation was not completed in that time. It is essential to choose climatically adapted species from among those with desired growth characteristics.

Degradation of petroleum contaminants in the rhizosphere has been reported in the literature. Microbial numbers were substantially greater in soil with plants when compared to soil containing no plants, indicating that plant roots enhance microbial populations in contaminated soil for enhanced biodegradation of contaminant.20

Another reported study investigated the uptake of two pesticides, alachlor and atrazine, present in the soils.21 It was found that plant uptake is an influential process on the fate of alachlor and atrazine.

A recent report considers some strategies for engineering plants to improve bioremediation in the root zone.22 One of the simpler approaches is to make use of the organism Agrobacterium rhizogenes to induce a state called hairy root disease. Depending on the
virulence of the strain used, the extent of root production is variable, but generally infection leads to a significant enhancement of rooting without obvious detrimental effects on the host plant. Increased root mass has the apparent advantage of increasing the surface area available for microbial colonization. Root exudation may be increased in proportion to increase in root area. Such rhizosphere enhancements could improve bioremediation potential of the plant–microbial system. It is suggested that when water is not freely available in unlimited quantities, increased root mass could lead to greater water uptake, and hence greater contaminant mobilization and potential degradation.

Genetic engineering of plants by insertion of genes for chlorinated phenolics catabolism is in progress.22 These enzymes may also allow metabolism of TCE. A number of companies have introduced genes for degradation of herbicides into crop plants.22 Some of these approaches could prove useful for remediation of other contaminants.

10.6 LIMITATIONS AND KNOWLEDGE GAP

- Phytoremediation is most effective only at sites with shallow contamination in the soils and/or sites with shallow water table.
- Can be applied only under warmer climates for 12 months per year remediation.
- This technique may not be applicable for highly hydrophobic contaminants due to the tendency of the contaminants to remain adsorbed to the soil particles.
- The question as to whether the contaminants can accumulate in leaves and be released as litter or accumulate in the wood and mulch has not been resolved from a regulatory point of view.
- The possibility of binding or complexation of some of the contaminants with the exudates and subsequent transport by the groundwater.
- Evaluation and development of proper handling and disposal methods for the harvested hyperaccumulator plants. The feasibility of cost-effective metal recovery techniques should be evaluated further.
- Enhancement of tree root mass, via genetic engineering techniques, for increased rhizosphere detoxification and contaminant translocation.
- Enhancement of detoxification in the plant by cloning the plant with bacterial genes.

REFERENCES