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Term Paper

Phytoremediation: A General Overview

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Abstract

Phytoremediation is the use of specific species of plants for the remediation of site contaminants. Attention has been drawn to this idea with the indication of cost savings when compared to conventional treatment technologies. This overview is designed to supply an analysis of the technology of phytoremediation today by providing an understanding of the basic concepts in the use of plants for treatment of soils and waters: degradation, extraction, and containment. Along with these three pillars of phytoremediation are experimental limitations preventing successful remediation. Examples of all three types of phytoremediation are explored and one case study is shown. By comparing documation, it was resolved that phytoremediation is still in its infancy and that more laboratory and field studies are needed before industrial application can begin to take hold. Understanding of the subject has increased exponentially since the incept of the idea, and new tools in the analysis of biochemistry and chemical mechanisms are achieving an unprecedented look into the mechanisms occurring within plants and the possibilities they hold for contaminant control.

Keywords

Phytoremediation, Phytoextraction, Phytodegredation, Phytostabalization, Chelating agent, Hyperaccumulate, Rhizodegredation, Phytotoxic, evapotranspirate

Introduction to Phytoremediation

Plants have long been adapting to survive in a variety of stressful environments. This uncanny ability to live in areas of high salinity, extreme heat, drought, or freezing temperatures, exemplifies the tolerance various plant species can have. Phytoremediation is a term coined in 1991 (EPA, 2000). Basic information came from previous research in constructed wetlands, oil spills, and heavy metal accumulation. Research methods can be categorized into to areas: exploration of mechanisms and evaluation of claims. Laboratory experiments are primarily used to understand observations in the field and to gain knowledge on the biochemistry occurring. With recent advancements in genetic modification, scientists have been able to create plants for specific environmental uses. Plants can be enhanced with qualities that allow them to be used in the effort to relieve environmental stresses and assist in the restoration of polluted soils. There are four characteristics preferred in a plant for phytoremediation techniques. The first is that the plant should be able to accumulate the pollutants to be extracted. Second, the plants should have enough tolerance to be able to not only survive in polluted soils, but to carry pollutants within their shoots. Third, the species should be fast growing with an amplified ability to accumulate toxins. Lastly, the plant should be easily harvestable for simple disposal (Kärenlampi et al., 2000). The three general techniques used in phytoremediation are degradation, extraction, and stabalization. These methods, used in conjunction with recent advancements in biochemistry, are improving the appeal and overall ability of phytoremediation to treat current issues.

Experimental Factors

Climate/Soil. Climate plays a significant role when it comes to phytoremediation. Although there are over 400 species of plants known to date which could be used for site cleanup, only a small fraction would be able to survive in the temperate zone of the specific region needing remediation. Not only would the plant have to be compatible with local weather and seasonal patterns, but also be able to adapt to the local ground soil composition. This includes porosity, pH, and moisture content among others. Most research focus has been on the ability for a plant to hyperaccumulate contaminants under specific and constant surroundings. Experimentally this allows for an accurate analysis of the plants peak capability, but if used in the field, results would tend to vary, but by how much? Yu (et al., 2005) performed an experiment to attempt to quantify the effect temperature has on phytoremediation efforts. Using fresh leaf samples from a weeping willow (*Salix babylonica*) and Chinese elder (*Sambucus chinensis*), Yu and his colleagues placed the leaves in containers with 0.95 g/L potassium cyanide solution for up to twenty eight hours using temperatures from 11°C to 32°C and monitored the disappearance of cyanide (CN) (Yu et al., 2005). The graph in Figure 1 shows the individual plant results. It is clear from this that increasing the temperature also increased the overall metabolism of CN.

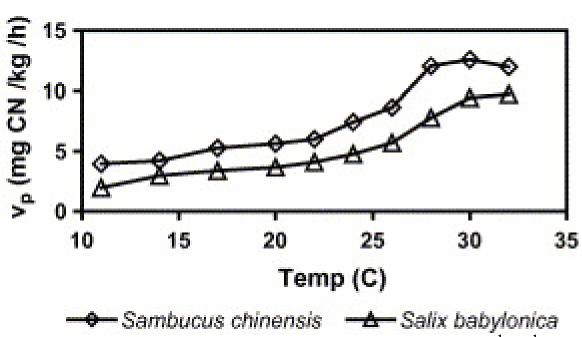

Figure 1: The rate of CN disappearance v_p (mg kg^{-1} h^{-1}) of Chinese elder and weeping willow leaves as a function of temperature (Yu et al., 2005).

Although this experiment showed higher conversion associated with higher temperatures, other phytoremediation efforts may differ. The toxin CN is metabolized in vascular plants which possess the enzymes necessary to convert CN into asparagine by a reaction that obeys the Michaelis-Menten enzymatic kinetics. Under more complex reactions with various intermediates and larger contaminant compounds, the relationships become harder to generalize and model (Sung et al., 2001).

Root depth. A limiting factor in the containment, degradation, or extraction of pollutants is root depth. Since the actual processes can only take place within a specified distance from the root structure, it is important to consider the extent of the pollution in choosing which species of plants to use. Soil carries the complexity of different contaminant concentrations and environmental properties at various depths (Sung et al., 2001). The plant chosen for the project has to be able to reach and tolerate the chemical in its various concentrations throughout the soil.

Contaminant uptake/growth factor. Another aspect of phytoremediation is the ability for the plant to grow and take in contaminants. The speed at which a plant is able to develop new leaves and roots is directly related to the amount of contaminants that a plant is able to metabolize within a specific time period. Therefore, quick growth is a desirable characteristic if a plant is to be used for phytoremediation. In fact, a plant with accelerated growth is more desirable even if it may metabolize contaminants at a slower rate than a plant that could metabolize more but grew slower because the ability to harvest on a more frequent basis and a quicker plant-recovery make the contamination remediation process quicker in most cases.

The appeal of plants, which can grow fast and uptake more, is becoming more of a reality today due to genetic engineering (Kärenlampi et al., 2000). For instance, Kärenlampi and his colleagues placed an MT gene from metal-tolerant yeast and transferred it into several metal-sensitive yeast types. The MT gene had been shown in previous experiments to increase the ability to tolerate metals. What they found was that cadmiun and copper tolerance of the previously metal-sensitive yeasts increased. This, however, had no effect on the ability to accumulate metals (Kärenlampi et al., 2000).

Contaminant Concentration. The difficulty with plants in the case of phytoremediation is that their tolerance for the contaminant is based on their genetics. Species of plants that are accustomed to growing in soils laden with chemicals like arsenic or lead among others have been adapting to the conditions for hundreds of years. There is a point where the plant just cannot survive if the concentration of contaminants is too high. This effect is deemed phytotoxic. Phytotoxicity is where a plant can no longer be unaffected by the contaminants surrounding or building within its tissues.

Types of Phytoremediation

Degredation. Degradation is the process by which a chemical compound is broken down into defined products. Assuming a chemical was volatile or toxic, it would be ideal for its degraded products to be environmentally neutral. This is the principle behind using phytoremediation for a degradation process (EPA, 2000). There are two possible mechanisms for degradation in plants. The first involves the root zone, or the rhizosphere and the second is by metabolism within the plant.

A combination of microbes living around the roots or enzymes exuded by the roots themselves assist in the breakdown of specific chemicals (Sung et al., 2001). Knowledge on this technique of rhizodegradation is limited due to the complex relationship displayed between various microbes and the nutrients and enzymes excreted by the root structure required for degradation of chemicals (Ellen at al., 2005). It is tested for experimentally in two ways: (1) studies of soil metabolism, and (2) isolation and culturing of microbe species (Ellen et al., 2005). The most notable relationship between plants and microbes are between bacteria that fixate nitrogen for plant use, while nutrients are provided by the plant to the bacteria (Ellen at al., 2005). An attempt to model the relationship in the rhizosphere was tested by Sung (2001 referenced by Sung unpublished 2000 work). The complexity of the model is easily seen in the water-phase mass balance equation shown in Equation 1 that includes biodegradation by microorganisms in the soil along with sorption into soil and roots.

$$\frac{\partial \theta_{rhw} C_{rhw}}{\partial t} = -\frac{\partial}{\partial z}\left(q_w C_{rhw} - D_{Hw}\frac{\partial \theta_{rhw} C_{rhw}}{\partial z}\right) - a_s p_b \left(k_1 C_{rhw} - C_{rhs}\right)$$
$$- k_m C_m \left(\frac{C_{rhw}}{K_{rhw} + C_{rhw} + K_i C_{rhw}^2}\right)\left(\frac{C_{rhp}}{K_{rhp} + C_{rhp}}\right) - \sigma_r K_{nrw}\left(K_{rw} C_{rhw} - C_r\right) - U_w T_{scf} C_{rhw} \quad (1)$$

Equation 1: Equation for the water-phase mass balance in the soil, which includes contaminant advection and dispersion, sorption onto soil and roots, and degradation by microorganisms in the soil (Sung et al., 2001). "θ_{rhw} is the water content ($cm^3\ cm^{-3}$), q_w is water flux ($cm^3\ cm^{-2}\ h^{-1}$), D_{Hw} is the hydrodynamic dispersion coefficient ($cm^2\ h^{-1}$), C_{rhw} is the mass concentration of contaminant dissolved in pore water ($g\ cm^{-3}$), a_s is the first-order kinetic rate coefficient (h^{-1}), ρ_b is bulk density ($g\ cm^{-3}$), k_1 is the distribution coefficient ($g\ cm^{-3}$), C_{rhs} is the sorbed concentration ($g\ g^{-1}$), k_m is the nongrowth substrate utilization rate ($g\ g^{-1}\ h^{-1}$), C_{rb} is the microorganism concentration in soil ($g\ cm^{-3}$), C_{rhp} is the primary substrate concentration in the soil ($g\ cm^{-3}$), K_{rhw} is the half saturation constant for contaminant ($g\ cm^{-3}$), K_{rhp} is the half-saturation constant for primary substrate based on soil water phase ($g\ cm^{-3}$), and K_i is the inhibition coefficient ($cm^3\ g^{-1}$)" (Sung et al., 2001).

Johnsongrass was used to evaluate this model among others in Sung's experiment (2001). TNT and chrysene were control contaminants in liquid phase used in varied concentrations to test the model based on actual data collected by tissue samples versus that of the model's solution. Results showed that the ability for the plants to uptake toxins were most dependent on microbial concentrations and bioavailability of liquid phase contaminants (Sung et al., 2001).

The other mechanism is by metabolism within the plant. This involves the substance being taken into the plant and then broken down by metabolic processes within the plant, thereby detoxifying the chemical (Sung et al., 2001). A recent research project attempted to alter plants to assist in pollution control (Morikawa and Erkin, 2003). Inorganic compounds like nitrogen oxides and sulfur oxides can be transformed just as well as organic chemical compounds such as PAHs, TPHs, and PCBs. The focus of Morikawa and Erkin's research was to look for and exemplify qualities in plants that carried the potential to remediate nitrogen dioxide. By genetically engineering plants to produce the enzymes necessary for metabolism of nitrate in greater quantities, it would be theoretically possible to create a plant that 'cleans the air' of this pollutant known to be a key compound in the greenhouse effect (Morikawa and Erkin, 2003). Morikawa and Erkin (2003) used *Arabidopsis* plant to quantitatively show that genetic engineering improves a plant's ability to use nitrogen dioxide for metabolism. Research on this 'wonder plant' idea is still going on today in the form of inserting a gene into plants by a bacteriophage to produce an enzyme that can reduce the nitrogen dioxide complex into nitrogen gas and water (Morikawa and Erkin, 2003).

Though these experiments show promise, it is important to note the numerous other variables directly affecting the degradation process. These include soil temperature, moisture content, pH, aeration, and organic matter. All of these can rapidly change the balance of microbes within the soil or the ability for the plant species to grow, thereby altering the capability of plants to uptake contaminants. Some options to curtail this effect are to add chemicals to the soil to alter soil quality, increasing the bioavailability of contaminants. This will be discussed further in the extraction section.

Extraction. Extraction involves using a plant that is known to accumulate contaminants in its tissues and then harvesting the plant for proper disposal. This accumulated volume is much smaller and more cost effective to dispose of then typical excavation of soil or sediment (EPA, 2000). Mostly, this technique is applied to heavy metals and radionuclides in soil, sediment, and sludges (White, 2001). The pollutants are ideally concentrated in the shoots or the leaves, but experiments in root harvesting have also shown promise. This is a less desirable situation though, as the whole plant must be harvested and then new ones planted and established before further extraction can take place (EPA, 2000).

Rhizofiltration (root extraction) is also useful for separating unwanted metals from a water source. An experiment was performed by Mathias Ebel (et al. 2006) surveying the use of free floating plants called water hyacinths (*Eichhornia crassipes)* for remediation of cyanide (CN) from a water source. Metals such as silver and gold are commonly extracted by use of CN, from which the industrial effluent containing CN is then released into tailing ponds or sometimes directly into rivers. The care taken to dispose of contaminants can be directly associated with the policies of the government where the mining is located. Annual production of cyanide hydrogen (HCN), according to Mudder and Botz (2001), has been calculated to be 1.4 million tons. The chemical HCN is highly toxic, and more then 100,000 tons of CN enter the environment annually (Yu et al., 2005 as referenced by Mudder and Botz, 2001). In January 2000, a gold-leaching dam burst in Romania releasing around 100,000 kg of CN into the local watershed (Ebel et al. 2006 as referenced by UNEP/OCHA, 2000). This exemplifies the danger associated with use of toxic chemicals and the necessity for a way to remediate them.

In Ebel's experiment (et al., 2006), Water hyacinths were placed into control tubs that contained a soluble, known concentration of CN simulating tailing ponds. Results showed a high tolerance for HCN, the soluble form of CN and a feasible extraction as shown in Figure 2.

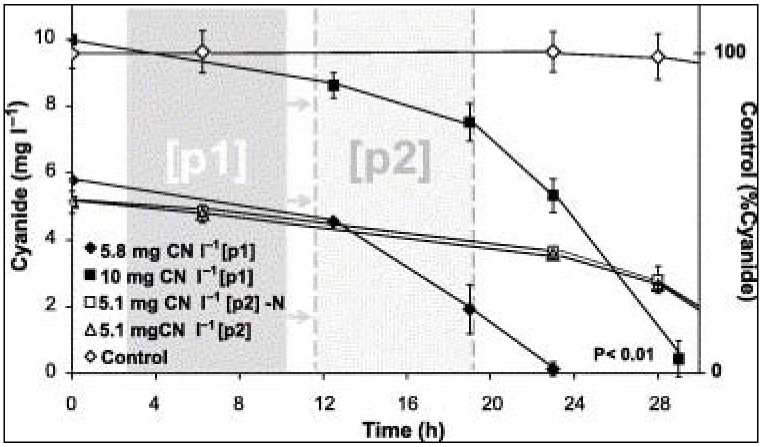

Figure 2: Cyanide removal by water hyacinth plants as a function of time." p1 (filled symbols): dark/light period 1 (27 °C; 3 h light, 8 h dark, 16 h light); p2 (open symbols): dark/light period 2 (16 °C; 11.5 h light, 8 h dark, 16 h light); –N: cyanide as only N source (right *y*-axis: the cyanide concentration of the control lacking plants is expressed in % relative to the initial CN concentration). Error bars denote standard deviation (n = 3)" (Ebel et al., 2006).

Water hyacinth's attributes: low maintenance, ready availability, quick spread, significant root mass, make it an excellent choice for use in tropical regions. Climate, however, limits its use. Also, socially it may not be acceptable to use this plant in areas where it is not native due to its multiplication capability by rhizomes (Ebel et al., 2006). Although it was not used in this experiment, while the plant chosen to extract the contaminant is growing, various amendments may be added to the growing medium to increase the availability of metals to the plants. When the plants mature, chemicals may then be dosed to induce a greater accumulation of contaminants from the soil into the plants. The plants would then be harvested and disposed of appropriately (White, 2001). This method is used mainly for remediation of metals. The three factors of metal uptake are: the bioavailability of contaminants, the concentration and overall activity of the metals, and the reaction rate of the plant uptake process (Schmidt, 2003).

Studies by E. Lombi et al. (2001) and Ulrich Schmidt (2003) focused on the effect soil additives have on plant accumulation. The research done in 2001 by E. Lombi et al. used EDTA treatment and maze (*Zea mays*) while monitoring the uptake of cadmium (Cd) and zinc (Zn). They found that although EDTA did increase the solubility of heavy metals, it did not directly effect plant accumulation of the metals (Lombi et al., 2001). In the comprehensive study by Schmidt (2003), a general overview was opposite of E. Lombi's conclusion. The references and results shown in Table 1 from past experiments show that using chelating agents, such as EDTA increased the concentration of contaminant in the plant tissues.

Table 1: Lead (Pb) concentration in plants compared with and without using chelating agents (Schmidt, 2003).

Concentration in the plant tissue

Plant	Chelate added	Without chelate	After chelate addition	Total Pb	Reference
		mg kg-1 dry matter		mg kg-1	
Perennial French ryegrass	4g EDTA kg-1	96	24000	6750	Deram et al., 2000
Pea	2g HEDTA kg-1	90	10600	2450	Huang et al., 1997a
Corn	2g HEDTA kg-1	60	10200	2450	Huang et al., 1997a
Cabbage	0.9g EDTA kg-1	125	5010	10600	Shen et al., 2002
Sunflower	5.8g CDTA kg-1	67	5200	4000	Cooper et al., 1999
Indian mustard	2.9g EDTA kg-1	313	5000	600	Blaylock et al., 1997
Redtop	5.8g CDTA kg-1	25	3000	4000	Cooper et al., 1999
Corn	5.8g CDTA kg-1	36	2600	4000	Cooper et al., 1999
Corn	0.44g EDTA kg-1	90	500	2500	Wu et al., 1999
Perennial ryegrass	1g EDTA kg-1	50	330	110	Albasel and Cottenie, 1985
Cabbage	2.9g EDTA kg-1	3	90	1100	Grcman et al., 2001

An important note here is that the chemicals being researched between the two products were different; Pb versus Zn and Cd. Also, the addition of chelating agents stunted the growth of all plants when dosing reached a certain point. In the case of ryegrass, corn, and pea plants the chelating agent stopped and killed plants less than a week after addition (Schmidt, 2003).

If the plants accumulation is specific enough it may also be possible to recycle contaminants for reuse; an idea that makes phytoextraction especially appealing. For example, recent research by G.S Bañuelos (2006) has shown the marketing potential of selenium polluted sites. Here, phytoremediation was chosen as a low-cost environmentally friendly approach for managing the concentration of soluble selenium (Se) in soil and water environments. At the time, U.S. Food and Drug Administration (FDA) recommended approximately 200μg Se be taken on a daily basis as research had shown it was an antioxidant capable of depressing anticancer activity (Bañuelos, 2006). As a result, commercial value could be placed on using phytoremediation to extract Se by using plant species, such as Canola, that would be grazed upon by animals to accumulate selenium in small quantities. The animals would therefore provide Se enriched meat for the dinner table. A provocative idea to say the least, but if this method became socially acceptable then phytoremediation would become an even more cost effective and useful way for treating some sites (Bañuelos, 2006).

Containment. This is the least practiced out of the three, but quite effective with metal contaminants. Typically a tree or other long-lived plant will accumulate metals around the roots, binding them to a specific area either naturally or with use of soil additives. Although this does not dispose of the contaminant, it effectively prevents leaching into groundwater and overall dispersal (Kärenlampi et al., 2000). Another name for this is phytostabalization. Due to the long-term nature of this method, and the lack of actual remediation, this scheme is not typically used.

Technical Considerations. There are several steps to determining whether phytoremediation is the best choice for a site cleanup; the most important if the plants to be used are capable of doing the job (EPA, 2000). Laboratory studies and past results are relied heavily upon for this initial step. If there is a suitable plant species for the climate, contaminant, and concentration of toxins, then the next step to consider is protectiveness. What protective measures will ensure containment of the pollutant within the area? As an example, fences may need to be constructed to prevent animal grazing. The next question that needs to be asked is if the cleanup with be completed within a suitable time frame? Phytoremediation techniques often take years to complete. Finally, is there a backup plan in the case that the remediation choice does not accomplish its goals? Often this backup plan is to revert to conventional techniques.

Economical Considerations. Standard cost information is generally not available due to the current state of knowledge. Each site has different parameters that need to be accounted for such as size, type or types of contaminants, and potential plant species used. Although a definite financial value cannot be placed on phytoremediation as a whole, it is generally accepted that the cost would be significantly less than conventional methods. "It had been estimated that the market for just the phytoextraction of metals in 2005 would be $70-100 million (Lombi et al., 2001 as referenced by Glass, 2000)." Morikawa and Erkin (2003) stated that phytoremediation as a whole was 60-80% less costly than conventional methods. Price estimates in 2004 for remediation of full-scale commercial sites began at $200,000 plus an additional $40 to $70 per cubic yard of soil (Ellen et al., 2005 as referenced by Business Publishers Inc., 2004). A rough comparison is made in Table 1, showing estimated costs and savings of using phytoremediation vs. more conventional techniques.

Table 1: Shows a comparison between phytoremediation and conventional contaminant removal techniques for three different problems (EPA, 2000).

Problem	**Phytoremediation Type**	**Cost (in thousands)**	**Conventional Choice**	**Cost (in thousands)**	**Projected Savings**
Lead in soil, 1 acre	Extraction, harvest disposal	$150-250	Excavate and landfill	$500	50-65%
Solvents in Groundwater, 2.5 acres	Degradation and hydraulic control	$200 to install plus some maintenance	Pump and Treat	$700 annual running cost	50% cost savings by 3rd year
TPH in soil, 1 acre	In situ degradation	$50-100	Excavate and landfill incinerate	$500	80%

Social Considerations. A part of phytoremediation that must be assessed when considering its application includes social factors. The most important of these is the potential to harm human health and the environment. Currently, the predictability of the technology is low as our understanding of the molecular, biological, and physiological processes involved is still being refined (Khan et al., 2000). Today phytoremediation still remains highly in research and development laboratory stages with few field demonstration studies (Wolfe and Bjornstad, 2002). The uncertainty in the use of phytoremediation stems from the lack of consistent data along with the variations within the objectives from site to site.

Research has shown that phytoremediation is most effective in a low to moderate concentration of contaminants in toxic sites. Since every contamination site is different, it makes it hard for decision makers to decide on a technology that has not been proven in their specific situation. They wouldn't be able to predict problems or the reliability of a phytoremediation process in terms of feasibility or cost estimates without previous history to look at. Current technologies for disposal, although expensive, work the same in almost every situation (Bjornstad, 2002). The process for soil washing and soil excavation, for example, are well defined.

The genetic engineering of plants for use also has social uncertainties. Among the bias held by many against genetic manipulation of resources, the biodiversity impact of introducing these altered plants into an ecosystem adds to the concern. Planting non-native species that could potentially out-compete native plants and become invasive could change the ecological system of the area. Considering that the phytoremediation efforts at best would still take years requires a sense of liability and a need for long-term monitoring and funding. Also, if the organization attempting to use this questionable technology has a history of not being able to be trusted, social acceptance could be damaged. The one important question pertaining to these issues must be asked: Is it better to worry about human health/potential problems and clean up sites quickly or save money and remedy the situation over a longer time period through phytoremediation (Bjornstad, 2002)?

Drawbacks. Root contact is the primary limiting factor when it comes to phytoremediation. Plants require the contaminant to be within reach in order to degrade, extract, or contain the pollutant. The effectiveness of remediation therefore is highly dependent on the plant species' individual root type and depth. Although it is possible to deep plow soil to the surface, volatile compounds and potential emission risks would need to be evaluated.

Another limit is growth rate. Metal hyperaccumularors, for instance, are generally slow-growing with a small biomass along with a shallow root system. Phytoremediation of sites may take up to several years making conventional disposal, though expensive, an appealing choice. It is necessary to compare the risk of leaving a potentially harmful contaminant in the ground for that amount of time or paying the extra money for more conventional disposal.

A third limit is contaminant concentration. Although genetic engineering of plants has assisted the ability of plants to live in and around contaminants, plants still have a limit. If the concentration of a contaminant is too great, there is a risk that plants used in phytoremediation may become phytotoxic; this limits the growth of plants and can potentially kill them. As a result, sites with low to medium levels of contaminants are the best choices for using phytoremediation techniques.

Many other limits exist, and are specific to certain applications and the remediation technique used. Continued developments in research are attempting to reduce the significance of these limitations and success has been documented.

Case Study. In 1996, at a former Carswell Air Force Plant in Fort Worth, Texas, 1 acre of *Populus deltoids* (Eastern Cottonwood) was planted to remediate TCE from a shallow aerobic aquifer. There were 660 total cottonwoods planted in two sizes: whips that were ¾" diameter and 5-gallon bucket trees 1" in diameter. There was also a 19-year-old cottonwood of the same species living nearby that was sampled along with the other trees. Seventeen months after the trees were planted trenches were dug to determine root depth; they found that the roots had indeed reached the aquifer. Laboratory tests initially indicated that the whips were capable of evapotranspirating TCE after one growing season. Root sample testing revealed increased amounts of vinyl chloride. The disappearance of PCE in the presence of a willow tree investigated near the site was also found. It was therefore concluded that cottonwoods and willows are able to degrade PCE and TCE. Another interesting statistic found was that TCE from the groundwater underneath the 19-year-old was 80% less than those concentrations found underneath the newly planted trees and the cis-1,2 DCE byproduct of TCE degradation was present in greater amounts as a result. There are over 900 Air Force sites with TCE contamination that could potentially use this treatment.

Conclusion. Phytoremediation is a promising technology, but one that needs continual refinement to serve the duties required of it. With the advent of new technologies and the constant pursuit of knowledge, in time, phytoremediation may become what so many scientist hope—an effective, greener way of treating chemical waste. Countless experiments have shown potential, but too many variables remain. The time and monitoring it takes for a site to be remediated by plants is immense. Resources may not be available to support a long project on a commercial scale. The potential drawbacks and variables must also be taken into account. The technology has not built an extensive portfolio of success. Despite this though, hopes remain high. Knowledge on plant biochemistry and mechanisms are improving. Genetics could assist in creating super-remediation plants that can tolerate contaminant concentrations more-so than plants available today. Though this technology is still a fledgling, research will continue to help it grow wings.

Acronyms

TCE	Trichloroethylene
TNT	Trinitrotoluene
TPH	Total Petroleum Hydrocarbons
PAH	Polynuclear Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PCE	Perchloroethylene

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