Technology
Overview Report

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GWRTAC O SERIES

Phytoremediation

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FOREWORD

About GWRTAC

The Ground-Water Remediation Technologies Analysis Center (GWRTAC) is a national environmental technology transfer center that provides information on the use of innovative technologies to clean-up contaminated groundwater.

Established in 1995, GWRTAC is operated by the National Environmental Technology Applications Center (NETAC) in association with the University of Pittsburgh's Environmental Engineering Program through a Cooperative Agreement with the U.S. Environmental Protection Agency's (EPA) Technology Innovation Office (TIO). NETAC is an operating unit of the Center for Hazardous Materials Research and focuses on accelerating the development and commercial use of new environmental technologies.

GWRTAC wishes to acknowledge the support and encouragement received for the completion of this report from the EPA TIO.

About "O" Series Reports

This report is one of the GWRTAC "O" Series of reports developed by GWRTAC to provide a general overview and introduction to a groundwater-related remediation technology. These overview reports are intended to provide a basic orientation to the technology. They contain information gathered from a range of currently available sources, including project documents, reports, periodicals, Internet searches, and personal communication with involved parties. No attempts are made to independently confirm or peer review the resources used.

Disclaimer

GWRTAC makes no warranties, express or implied, including without limitation, warranty for completeness, accuracy, or usefulness of the information, warranties as to the merchantability, or fitness for a particular purpose. Moreover, the listing of any technology, corporation, company, person, of facility in this report does not constitute endorsement, approval, or recommendation by GWRTAC, NETAC, or the EPA.

ABSTRACT

This technology summary report provides a brief overview of an environmental remediation technology, including an introduction to its general principles, reported applicability and utilization, and cited advantages/disadvantages. Also provided are locations of, and information about, organizations conducting research related to phytoremediation (Appendix A) and other references compiled during preparation of this report (Appendix B). This report is provided for informational purposes only and is not intended as a state-of-the-art peer reviewed analysis of this technology. Information used in the preparation of this report was gathered from periodicals, through Internet searches, and in some cases, from personal communications with involved parties. No attempt was made to confirm the veracity of interpretations and/or representations made in any information resource used. In addition, listing of any technology, corporation, company, person, or facility does not constitute endorsement, approval, or recommendation by the National Environmental Technology Applications Center (NETAC).

Phytoremediation uses plants to cleanup contaminated soil and groundwater, taking advantage of plants' natural abilities to take up, accumulate, and/or degrade constituents of their soil and water environments. Results of research and development into phytoremediation processes and techniques report it to be applicable to a broad range of contaminants including numerous metals and radionuclides, various organic compounds (such as chlorinated solvents, BTEX, PCBs, PAHs, pesticides/insecticides, explosives, nutrients, and surfactants. According to information reviewed, general site conditions best suited for potential use of phytoremediation include large areas of low to moderate surface soil (0 to 3 feet) contamination or large volumes of water with low-level contamination subject to low (stringent) treatment standards. Depth to groundwater for *in situ* treatment is limited to about 10 feet, but *ex situ* treatment in constructed troughs or wetlands has also been investigated.

There are five basic types of phytoremediation techniques: 1) *rhizofiltration*, a water remediation technique involving the uptake of contaminants by plant roots; 2) *phytoextraction*, a soil technique involving uptake from soil, 3) *phytotransformation*, applicable to both soil and water, involving the degradation of contaminants through plant metabolism, 4) *phyto-stimulation* or *plant-assisted bioremediation*, also used for both soil and water, which involves the stimulation of microbial biodegradation through the activities of plants in the root zone, and 5) *phytostabilization*, using plants to reduce the mobility and migration potential of contaminants in soil.

Major advantages reported for phytoremediation as compared to traditional remediation technologies include the possibility of generating less secondary wastes, minimal associated environmental disturbance, and the ability to leave soils in place and in a usable condition following treatment. Cited disadvantages include the long lengths of time required (usually several growing seasons), depth limitations (3 feet for soil and 10 feet for groundwater), and the possibility of contaminant entrance into the food chain through animal consumption of plant material.

This document was prepared for distribution by the Ground-water Remediation Technologies Analysis Center (GWRTAC). GWRTAC is being operated by NETAC, under a Cooperative Agreement with the United States Environmental Protection Agency's (EPA) Technology Innovation Office (TIO).

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1.0 INTRODUCTION

Phytoremediation, the use of plants to remediate environmental media, is being pursued as a new approach for the cleanup of contaminated soils and waters, including groundwater. Plant-*assisted* bioremediation, sometimes referred to as a type of phytoremediation, involves the interaction of plant roots and the microorganisms associated with these root systems to remediate soils containing elevated concentrations of organic compounds. These techniques could provide cost-effective methods of remediating soils and groundwater contaminated with metals, radionuclides, and various types of organics, with fewer secondary wastes and less environmental impact than would be generated using traditional remediation methods.

All plants extract necessary nutrients, including metals, from their soil and water environments. Some plants, called hyperaccumulators, have the ability to store large amounts of metals, even some metals that do not appear to be required for plant functioning. In addition, plants can take up various organic chemicals from environmental media and degrade or otherwise process them for use in their physiological processes.

Phytoremediation technologies are in the early stages of development, with laboratory research and limited field trials being conducted to determine processes and refine methods. Additional research, including genetic engineering, is being conducted to improve the natural capabilities of plants to perform remediation functions and to investigate other plants with potential phytoremediation applications (2, 3, 11, 17).

2.0 APPLICABILITY

2.1 CONTAMINANTS

Contaminants that have been remediated in laboratory and/or field studies using phytoremediation or plant-assisted bioremediation include:

- Heavy metals (Cd, Cr(VI), Pb, Co, Cu, Pb, Ni, Se, Zn)
- Radionuclides (Cs, Sr, Ur)
- Chlorinated solvents (TCE, PCE)
- Petroleum hydrocarbons (BTEX)
- Polychlorinated biphenyls (PCBs)
- Polynuclear aromatic hydrocarbons (PAHs)
- Chlorinated pesticides
- Organophosphate insecticides (e.g., parathion)
- Explosives (TNT, DNT, TNB, RDX, HMX)
- Nutrients (nitrate, ammonium, phosphate)
- Surfactants.

2.2 SITE CONDITIONS

Phytoremediation and plant-assisted bioremediation are most effective if *soil contamination is limited to within 3 feet of the surface*, and if *groundwater is within 10 feet of the surface* (4, 17). These technologies are applicable to sites with low to moderate soil contamination over large areas, and to sites with large volumes of groundwater with low levels of contamination that have to be cleaned to low (strict) standards (3, 6, 15).

3.0 METHODOLOGY

3.1 PROCESSES OF PHYTOREMEDIATION

Phytoremediation is based on certain natural processes carried out by plants including:

- Uptake of metals and certain organic compounds (i.e., moderately water soluble, log K_{ow}=0.5 to 3, such as BTEX) from soil and water;
- Accumulation or processing of these chemicals via lignification, volatilization, metabolization, mineralization (transformation into CO_2 and water);
- Use of enzymes to breakdown complex organic molecules into simpler molecules (ultimately CO_2 and water);
- Increasing the carbon and oxygen content of soil around roots (and so promoting microbial/ fungal activity) through release of chemicals (exudates) and decay of root tissue;
- Capture of groundwater (even contaminated groundwater) and utilization for plant processes (17, 19, 20).

3.2 TYPES OF PHYTOREMEDIATION

Several classification schemes were found relating to the types of phytoremediation, the most common of which is presented below.

- ***Rhizofiltration***, the absorption, concentration, and precipitation of heavy metals by plant roots;
- ***Phytoextraction**,* the extraction and accumulation of contaminants in harvestable plant tissues including roots and surface shoots;
- ***Phytotransformation***, the degradation of complex organic molecules to simple molecules and the incorporation of these molecules into plant tissues;
- ***Phytostimulation*** or ***plant-assisted bioremediation***, the stimulation of microbial and fungal degradation by release of exudates/enzymes into the root zone (rhizosphere);
- ***Phytostabilization***, involving absorption and precipitation of contaminants, principally metals, by plants, reducing their mobility and preventing their migration to groundwater (leaching) or air (wind transport), or entry into the food chain (4, 16, 19).

In addition, ***groundwater migration*** can be affected through the use of deep-rooted trees such as poplars to capture groundwater and retard contaminant migration. The trees utilize the water and then transpire it, potentially depressing the local water table. If enough trees are utilizing groundwater in a limited area, the water table maybe be depressed "up to the equivalent of 3 feet of rainfall per year" in semiarid areas. Through the capturing process of trees, contaminated groundwater that would have migrated downgradient is held in the root zone of the poplars, where degradation can occur through plant processes (phytoremediation) and plant-assisted bioremediation (phytostimulation) (4, 20).

3.3 HARVESTING/DISPOSAL OF PLANT MATERIAL

Once plants have accumulated waste materials, plant shoots can be harvested and roots removed, with disposal or subsequent processing methods dependent on the toxicity of the end products of in-plant organic chemical processing and the storage locations and relative concentrations of contaminants within plant tissue.

If organic contaminants are degraded to harmless compounds, disposal may not be required. If significant accumulation takes place only in roots, then only these tissues must be disposed of or processed. The most commonly mentioned process for dealing with metals-enriched plant material is *controlled incineration*, which results in ash with a high metals content. It is hoped that an economically feasible method of metals recovery from this ash will be developed, further reducing the environmental impacts of this technology. Radiologically-contaminated plant material could be vitrified as with other radioactive wastes. Conventional disposal methods such as landfilling may also be possible in some instances. Preliminary information indicates that wood from trees that have taken up/degraded TCE, and contain metabolites of TCE, can be used for pulp (7).

Other methods of plant tissue treatment currently under investigation include:

- Sun, heat, and air drying
- Composting
- Pressing and compacting
- Leaching (6, 9, 14, 16).

3.4 IMPLEMENTATION

Phytoremediation techniques are still being tested, in stages ranging from lab- to field-scale. Current research includes:

- Lab studies to investigate the processes behind phytoremediation;
- Screening studies to find suitable plants for further investigation;
- Bench- and pilot-scale testing of promising plant species;
- Limited and full-scale field trials.

3.5 GROUNDWATER REMEDIATION METHODS

3.5.1 Rhizofiltration

Surface water rhizofiltration may be conducted *in situ*, with plants being grown directly in the contaminated water body. If groundwater is located within the rhizosphere (root zone), rhizofiltration of groundwater can also be *in situ*. Alternately, rhizofiltration may involve the pumping of contaminated groundwater into troughs filled with the large root systems of appropriate plant species. The large surface areas provided by these root systems allow for efficient absorption of metals from the contaminated groundwater into root tissues.

In addition to removal through absorption, metals are also removed from groundwater through precipitation caused by exudates (liquids released from plant tissues). These precipitates are filtered from the groundwater after it passes through the plant troughs and before treated water is removed from the process loop. Roots are harvested, and depending on the species of plant used, shoots may be transplanted to grow new roots. Plants can be replaced in the system to ensure constant operation results.

Rhizofiltration using sunflowers has been used in the remediation of radionuclides from surface water near Chernobyl (strontium and cesium) and in water using a rhizofiltration system, as described above, at a DOE facility in Ohio (3, 6, 9, 16, 20).

3.5.2 Phytotransformation

Surface water remediation via phytotransformation can be accomplished *in situ* in ponds or wetlands. In addition, groundwater can be remediated using phytotransformation *in situ* if the water table is within the zone tapped by deep-rooted plants such as poplars or *ex situ* by pumping water to troughs or constructed wetlands containing appropriate plants. In the phytotransformation process, plants take up organic contaminants and degrade them to less toxic or non-toxic compounds (2, 3, 15, 17, 19, 20) .

This technique is being tested on explosives-contaminated groundwater (TNT and RDX) at Milan Army Ammunition Plant in Tennessee by the U. S. Army Corps of Engineers Waterways Experimental Station (WES) (2, 3, 16, 17). In addition, an Environmental Security Technology Certification Program (ESTCP) project is testing the ability of trees with roots tapping groundwater to degrade TCE and hydrazine present in the aquifer (8). The U.S. Air Force is planning to evaluate phytoremediation through field studies followed by cell cultures and bio-chamber studies (7).

3.5.3 Plant-Assisted Bioremediation

This technique involves the installation of appropriate plants in areas in which near-surface bioremediation is being conducted. The plants provide carbonaceous material from liquids released from roots and through the decay of root tissue. In addition, oxygen released from the root systems of these plants increases the oxygen content in the bioremediation area. These additions to the soil as a result of plant activity increase the rates of microbial activity and thus the rates of contaminant degradation. The above-mentioned ESTCP project also involves study of the beneficial effects of plant roots on the rate on *in situ* bioremediation by microorganisms (2, 4, 8, 10, 17, 19, 20).

3.6 SOIL REMEDIATION METHODS

3.6.1 Phytoextraction

This process involves the removal of metals, radionuclides, and certain organic compounds (i.e., petroleum hydrocarbons) by direct uptake into plant tissue. Implementation of a phytoextraction program involves the planting of one or more species that are hyperaccumulators of the contaminants of concern. Amendments (i.e., fertilizer, water, etc.) may be required, as determined from preliminary field testing, to ensure successful plant growth. Lengths of time before harvesting the plants are also determined from preliminary testing, and after this period of time, plant tissue is removed and, if necessary, a new crop of plants are planted. Although testing has focused on single plants, several species may be used at a site, either at the same time or subsequently, to remove more than one contaminant (11, 14, 16, 17).

Characteristics of plants able to perform phytoextraction include:

- Ability to accumulate and tolerate high concentrations of metals in harvestable tissue;
- Rapid growth rate;
- High biomass production (This results in more metal removed per planting) (2, 11, 16).

DOE field trials involving phytoextraction of metals and radionuclides from soils are being conducted in association with Cornell University, at sites in Montana and Idaho (3). Also, a study is being conducted by the University of Iowa and Kansas State University, in association with the Hazardous Substance Research Center (HSRC) at Kansas State, to determine the efficiency of poplars to take up and accumulate arsenic and cadmium in soils (17).

3.6.2 Phytostabilization

Phytostabilization, as stated above, is the use of certain plant species to absorb and precipitate contaminants, generally metals, reducing their bioavailablity, and so reducing the potential for human exposure to these contaminants. This technique can be used to re-establish a vegetative cover at sites where natural vegetation is lacking due to high metals concentrations in surface soils or physical disturbances to surficial materials. Metal-tolerant species can be used to restore vegetation to the sites, thereby decreasing the potential migration of contamination through wind erosion and transport of exposed surface soils and leaching of soil contamination to groundwater (erosion and leaching are common in unvegetated areas).

Characteristics of plants appropriate for phytostabilization at a particular site include:

- Tolerance to high levels of the contaminant(s) of concern;
- High production of root biomass able to immobilize these contaminants through uptake, precipitation, or reduction;
- Retention of applicable contaminants in roots, as opposed to transfer to shoots, to avoid special handling and disposal of shoots (2, 3, 13, 15, 17).

Phytostabilization field studies are being conducted at the University of Iowa and Kansas State University, in conjunction with the HSRC at Kansas State. These tests involve the revegetation of a mine tailings site in Kansas containing, elevated levels of cadmium, lead, and zinc, to reduce wind and water erosion (1).

3.6.3 Plant-Assisted Bioremediation

Techniques for soil remediation using plant-assisted bioremediation are the same for the groundwater application described above. This technique is being tested at a Chevron site in Ogden, Utah using alfalfa to address fuel contamination (4) and at the University of Iowa using poplar trees to address atrazine contamination (12).

4.0 TECHNOLOGY PERFORMANCE

4.1 GENERAL

Use of phytoremediation is currently limited to research activities and limited field testing. While several recent and on-going applications have reportedly been successful in lowering contaminant concentrations, full-scale remediation projects have not been completed and regulatory approval is not yet in place. Reported results show some potential for practical applications of these techniques to achieve remedial objectives and regulatory approval; however "at least two or three more years of field tests are necessary to validate the initial, small-scale field tests." (2).

Specific methodologies for application to contaminated sites have standardized, but general principles have been established. The general steps followed in the design and implementation of a phytoremediation project, for any of the techniques, include:

- Site characterization, including determination of soil and water chemistry/conditions, climate, and contaminant distribution;
- Treatability studies to determine rates of remediation and appropriate plant species, density of planting, location, etc.;
- Preliminary field testing at the site to monitor results and refine design parameters;
- Full-scale remediation;
- Disposition of resulting affected plant material (15).

4.2 COST INFORMATION

Current estimates of costs for phytoremediation vary widely, and little information was found as to the conditions on which the estimates were based. A cost estimate for phytoextraction included $10,000 per acre for planting, with total remediation costs, including maintenance, monitoring, verification testing, etc. estimated at $60,000 to $100,000 per acre (17, 20). Another estimate placed costs at approximately $80 per cubic yard of contaminated soil (2). Removing radionuclide contamination from water using sunflowers was estimated to cost "from $2 to $6 per thousand gallons of water treated, including waste disposal and capital costs" (5).

5.0 TECHNOLOGY ADVANTAGES

The advantages of the various types of phytoremediation are outlined in Table 1 below.

TABLE 1. ADVANTAGES OF TYPES OF PHYTOREMEDIATION

ADVANTAGE	RHIZO-FILTRATION	PHYTO-EXTRACTION	PHYTO-STABILIZATION	MIGRATION CONTROL
Can be performed with minimal envirnomental disturbance	X	X	X	X
Applicable to broad range of contaminants, including many metals with limited alternative options	X	X	X	X
Possibly less secondary air and/or water wastes generated than traditional methods	X	X	X	X
Organic pollutants may be degraded to CO_2 and H_2O, removing, as opposed to transferring, environmental toxicity	X	X		
Cost-effective for large volumes of water having low concentrations of contaminants to low (stringent) standards	X			
Topsoil is left in a usable condition and may be reclaimed for agricultural use		X		
Soil can be left at site after contaminants are removed, rather than having to be disposed or isolated		X		
Cost-effective for large areas having low to moerately contaminated surface soils		X		
Reduces volume of contaminated material to be landfilled or incinerated*		X		
Can achieve remediation goals without using toxic chemicals		X		
Reduce the risk of exposure (during clean-up) by limiting direct contac with contaminated soils			X	
Plant uptake of contaminated ground-water can prevent off-site migration				

*Example: "Removing heavy-metal contaminated soil from two and a half acres to a depth of about 18 inches creates about 5,000 tons of soil that must be disposed of in a hazardous waste landfill. In contrast, plants that take up the metal are burned and leave a residue of between 25 and 30 tons of ash to be disposed of."

6.0 TECHNOLOGY LIMITATIONS

Possible disadvantages associated with all phytoremediation/plant-assisted remediation techniques include:

- Long length of time required for remediation (usually more than one growing season);
- Treatment is generally limited to soils at less than 3 feet from the surface and groundwater within 10 feet of the surface;
- Climatic or hydrologic conditions (e.g., flooding, drought) may restrict the rate of growth of types of plants that can be utilized;
- Ground surface at the site may have to be modified to prevent flooding or erosion;
- Contaminants may still enter the food chain through animals/insects that eat plant material containing contaminants;
- Soil amendments may be required, including chelating agents to facilitate plant uptake by breaking bonds binding contaminants to soil particles.

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APPENDIX A

RESEARCH LOCATIONS/INFORMATION

Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL, 60439. Dr. Ray Hinchman, (708) 252-3391, Fax: (708) 252-6407, E-mail: hinchman@anl.gov, Christina Negri, (708) 252-9662, Fax: (708) 252-9281, E-mail:negri@qmgate.anl.gov

"Biomining" the Soil to Remove Heavy Metals, Research at Argonne is focused on enhancing phytoremediation rates through irrigation, fertilization, alteration of chemical/physical soil conditions, and/or use of non-toxic chelating agents. The use of electrokinetics to deliver chelating agents and control metals movement in soil is also being studied at Argonne. (Project brief: http://www.anl.gov/LabDB/Current/Ext/H603-text.002.html)

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Treating Produced Water by Imitating Natural Ecosystems, Additional research at Argonne involves phytoremediation of salty wastewater produced during natural gas production ("produced water"). Pilot and field studies are being conducted to investigate the salt-removing abilities of various plant species. (Project summary: http://www.es.anl.gov/htmls/treat.html)

Battelle Memorial Institute

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Environmental Security Technology Certification Program (ESTCP)

Two ESTCP FY95 projects involve phytoremediation. One involves the use of plants to remove munitions contamination from groundwater using an *ex situ* (constructed wetland) application of phytoremediation at Milan Army Ammunitions Plant, Tennessee. Also, a project using deep-rooted trees to degrade TCE and hydrazine in groundwater and to prevent off-site migration of these contaminants is being conducted through ESTCP. (Project summary: http://www.acq.osd.mil/ens/ESTCPProjSum.html)

Great Plains/Rocky Mountain Regional Center, Hazardous Substance Research Center (HSRC)

The following research briefs from HSRC's Great Plains/Rocky Mountain Center can be found at http://www.engg.ksu.edu/HSRC/Annual.Research.html#92-05:

- The Use of Poplar Trees in Remediating Heavy Metal Contaminated Sites
- Metals Soil Pollution and Vegetative Remediation
- Acid Processing Metalliferous Waste Reclamation by Material Reprocessing and Vegetative Stabilization
- Fate and Transport of Heavy Metals and Radionuclides in Soil: The Impacts of Vegetation
- Vegetative Interceptor Zones for Containment of Heavy Metal Pollutants
- Riparian Poplar Tree Buffer Impact on Non-point Source Surface Water Contamination: A Paired Agricultural Watershed Study
- The Use of Vegetation to Enhance Bioremediation of Surface Soils Contaminated with Pesticide Wastes
- Uptake of BTEX Compounds and Metabolites by Hybrid Poplar Trees in Hazardous Waste Remediation
- Plant Assisted Remediation of Soil and Ground Water Contaminated by Hazardous Organic Substances: Experimental and Modeling Studies
- Development of a Systematic Methodology for Optimally Designing Vegetative Systems for Remediating Contaminated Soil and Ground Water

The following citations for documents from HSRC's Great Plains/Rocky Mountain Center can be found at: http://www.engg.ksu.edu/HSRC/Annual.Bibliography.html

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This consortium is conducting research to advance phytoremediation techniques for use in soils, sediments, and groundwater contaminated with munitions (TNT, DNT, TNB, RDX, and HMX) and chlorinated solvents (TCE and PCE). Filed experiments, conducted with Auburn University and the Air Force Armstrong Lab at Tyndall AFB, have shown phytoremediation to reduce TNT levels in soils to acceptable cleanup levels. (Newsletter entries: http://www.wes.army.mil.serdp/newsletter/95oct.html and http://wwel.wes.army.neal/el/newsfeb96.html)

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APPENDIX B

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