Evaluation of Phytoremediation for Management of Chlorinated Solvents in Soil and Groundwater

Prepared by:

The Remediation Technologies Development Forum
Phytoremediation of Organics Action Team,
Chlorinated Solvents Workgroup

RTDF

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Foreword

The Remediation Technologies Development Forum (RTDF) was established in 1992 as a forum for government, industry, and academia to collaborate on the development of cost-effective hazardous waste characterization and treatment technologies. The RTDF is a one of a few government programs designed to foster public-private partnerships for conducting laboratory and field research to develop, test, and evaluate innovative remediation technologies. Through the unprecedented collaboration of the RTDF, companies, government agencies, and universities are voluntarily sharing the knowledge, experience, equipment, facilities, and even proprietary technology to solve mutual remediation problems.

The Phytoremediation of Organics Action Team was established in 1997, as one of a number of RTDF Action Teams to further the RTDF's goals. The team formed specifically to address the development and demonstration of phytoremediation technologies.

The RTDF's website can be accessed at http://www.rtdf.org**.** The Phytoremediation of Organics Action Team's webpage is at http://www.rtdf.org/public/phyto/default.htm.

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Co-Chairs
Robert Tossell, CH2M HILL
Lee Newman, University of South Carolina;
Keith Rose, U.S. Environmental Protection Agency (EPA)

Authors and Reviewers
Frank Beck, U.S. EPA
Joel Burken, University of Missouri-Rolla
Harry Compton, U.S. EPA
Larry Erickson, Kansas State University
Linda Fiedler, U.S. EPA
Milt Gordon, University of Washington
Greg Harvey, USGS
Jim Jordahl, CH2M HILL
Xiujin Qiu, The Dow Chemical Company
Steve McCutcheon, U.S. EPA
Christina Negri, Argonne National Laboratory
Valentine Nzengung, University of Georgia
Steve Rock, U.S. EPA
Ellen Rubin, U.S. EPA
Mike Witt, The Dow Chemical Company

SECTION 1.0 INTRODUCTION

This document is intended to aid regulators, site owners, consultants, neighbors, and other stakeholders in understanding the proper application of planted systems to remediate groundwater contaminated with halogenated solvents. It assumes a familiarity with environmental and regulatory processes, in general, but little knowledge of plant-based, or "phytoremediation," technologies. The document is not intended as regulatory guidance, but as an aid to understanding of the mechanisms of how plants detoxify certain compounds under certain conditions.

Each field application of a phytotechnology has a unique combination of soil, contaminants, and climate. Therefore, each phytotechnology project must be designed, approved, and installed with site-specific conditions in mind. This document is intended to create enough understanding of the science, process, and engineering of phytoremediation systems that site-specific design and regulation can follow.

Specifically this document is designed to:

- Briefly introduce phytotechnologies;
- Identify potential applications of phytoremediation to control, transform, or manage chlorinated volatile organic compounds (CVOCs) in soil and groundwater;
- Show how to conduct a preliminary assessment to determine if a particular site is a good candidate for phytoremediation; and
- Describe monitoring options and show how to assess the effectiveness of phytoremediation at full-scale field implementation.

The remainder of this document is organized as follows:

Section 2.0 Background: Summarizes the mechanisms of phytoremediation and fate and transport of CVOCs;

Section 3.0 Assessment of Applicability of Phytoremediation: Presents general methods for assessing phytoremediation as a remedial technology for CVOCs in soil, surface water, and groundwater;

Section 4.0 Design and Placement: Explains the design and placement information of pilot- and full-scale projects;

Section 5.0 Monitoring and Sampling: Presents methods for monitoring, sampling, and analyzing full-scale phytoremediation;

Section 6.0 Reporting Cost and Performance: Summarizes how to evaluate the cost and performance of phytoremediating CVOCs;

References: Lists references used in the preparation of this document and helpful web resources for obtaining further information; and

Appendix: Provides responses to frequently asked questions about phytoremediation.

SECTION 2.0 BACKGROUND

Phytoremediation is an emerging green technology that uses plants to remove, degrade, or contain toxic chemicals in soils, sediments, groundwater, surface water, and air. It can be used as a stand-alone remediation alternative or as part of a broader site management alternative comprising a number of remediation technologies. Plants have grown naturally at contaminated waste sites and have been planted for aesthetic value or land stabilization. But not until recently has the use of plants gained attention as a viable remedial technology for site contaminants. Currently, phytoremediation is used for treating many classes of contaminants, including petroleum hydrocarbons, pesticides, explosives, heavy metals, and radionuclides, as well as CVOCs (McCutcheon and Schnoor, 2003).

Phytoremediation of organic contaminants primarily occurs by one or more of the following five mechanisms:

- Phytoextraction: the uptake and translocation of dissolved-phase contaminants from groundwater into plant tissue;
- Phytovolatilization: the transfer of the contaminant to air via plant transpiration;
- Rhizosphere degradation: the breakdown of organic contaminants within the microbe-rich rhizosphere (soil surrounding the root);
- Phytodegradation: the breakdown of organic contaminants within plant tissue.
- Hydraulic control: the use of trees to intercept and transpire large quantities of groundwater or surface water in order to contain or control the migration of contaminants.

One of the most important yet least understood topics regarding phytoremediation mechanisms is the fate and transport of contaminants within vegetation and its rhizosphere. Many experiments evaluating the fate and transport of environmental contaminants in vegetation and the rhizosphere are conducted in a laboratory or greenhouse. Due to the use of artificial sunlight, artificial air, and immature vegetation, such experiments are conducted under very different conditions than encountered in the field. Therefore, while laboratory experiments can provide useful data, their results cannot always be replicated in field settings. Other variables yielding different laboratory and field results can include seasons, field settings, vegetation types, growing methods, exposure methods and times, and contaminant concentrations.

The early results of using plants to mitigate the risk of CVOC-contaminated soils and groundwater look promising. However, there is still much work to be done regarding the mechanisms of CVOCs phytoremediation. The following sections further look at the current understanding of the mechanisms of phytoremediation and their effect on the fate and transport of CVOCs.

2.1 Phytoextraction

Phytoextraction is the uptake and translocation of contaminants from groundwater into plant tissue as the plant takes in water and micronutrients from soil through its root system. Plant uptake of chlorinated solvents is influenced by many factors including soil pH, clay content, water content, and organic matter content, as well as the properties of the chlorinated solvent (Ryan et al., 1988). Briggs et al. (1982) quantified plant uptake of a chemical by its octanol-water coefficient (K_{ow}), a measure of the chemical's hydrophobicity. Burken and Schnoor (1998) developed a new relationship—also based on K_{ow}— for organic contaminants and hybrid poplar trees, that demonstrates that trichloroethene (TCE) is readily taken up by hybrid poplar trees.

This relationship, called the "transpiration stream concentration factor" (or TSCF), which represents the translocation of groundwater contaminants to the plants' transpiration, ranges from 0.02 to 0.75 for TCE (Burken and Schnoor 1998; Davis et al. 1999; Orchard et al., 2000; and Ma and Burken, 2002). The TSCF studies were based on hybrid poplar cuttings used in hydroponic experiments. The wide range of measured TSCF values may be due to several variables, such as the initial contaminant concentration, type of vegetation, measurement techniques, and experimental design. The range in values also suggests that there may be other mechanisms in the uptake and transport of CVOCs within plants. Analysis of plant tissue for chlorinated solvents and their degradation products is an important step in determining fate and transport of these chemicals in phytoremediation systems.

CVOCs and their degradation products are usually found in vegetation in contact with soil or groundwater contaminated with CVOCs. It appears that the concentration of CVOCs in the plant tissue is proportional to the level of exposure, although field data are still being collected. Uptake from the atmosphere, via passive binding, should also be considered as plant matter makes up the majority of both surfaces and organic mass in the atmosphere. It is important to factor in plant uptake of airborne solvents as "background" in determining uptake from soil and roots.

2.2 Phytovolatilization

Phytovolatilization is the transfer of a contaminant to air via plant transpiration. Plants normally transpire water as vapor, but volatile compounds can be transpired as well. Phytovolatilization occurs via diffusion from the tree's xylem (a tissue that begins at the root of the tree and continues through the tree to the upper side of the leaf (Kozlowski and Pallardy, 1997)) through its bark or leaves.

Much more research has been conducted on phytovolatilization of contaminants from tree leaves than on the newer concept of volatilization from tree bark. Early hydroponic laboratory experiments involved enclosing the entire subaerial portion of a tree. The TCE measured in the enclosure was presumably transpired through the leaves (Newman et al., 1997, Burken and Schnoor, 1999, Davis et al., 1998), although this was not confirmed in the field (Newman et al., 1999 and Compton et al., 1998). Furthermore, the reported evidence that TCE is taken up and volatilized from the tree, and biodegradation did not play a significant role in TCE reduction. Orchard et al. (2000), who conducted hybrid poplar uptake studies with TCE, detected phytovolatilization in only 12 of the 96 sampling events.

Vroblesky et al. (1999) analyzed tree core samples with the intent of correlating the samples to groundwater plumes. The analysis revealed that TCE concentrations dropped considerably with increasing trunk height. However, the mechanism causing the drop was unexplained. Some of the possible mechanisms include volatilization through the bark of the tree and degradation within the tree. Degradation, however, has been shown to be rather low, and no significant accumulation of metabolites have been detected that could explain the losses observed.

Laboratory research later showed that diffusion from the trunk tissues was indeed a major mechanism for removing CVOCs from the plant following uptake (Ma and Burken, 2003a and Hu et al., 1998). Ma and Burken showed that diffusion from the xylem was linearly related to the concentration of aqueous solution in hydroponics studies. They hypothesized that the difference in experimental arrangements could explain the variable volatilization from leaves and subsequent TSCF calculations (Burken and Schnoor, 1998; Davis et al., 1998; and Orchard et al., 2000).

In other laboratory experiments, partitioning coefficients were determined in order to estimate the *in-vivo* CVOC concentration in transpiration stream within the xylem (Ma and Burken, 2002). The measurement of aqueous concentrations in the xylem also exhibited a concentration gradient between the interior xylem tissue, the outer tissue, and the atmosphere, providing direct theoretical support for diffusion to the atmosphere (Ma and Burken, 2002 and 2003a).

Volatilization of CVOCs from plant tissues to the atmosphere is a major pathway for CVOCs in phytoremediation applications. Although transpiration of chlorinated solvents has been confirmed in studies, researchers predict that transpiration from vegetation will not result in unacceptable levels of airborne CVOCs in the surrounding area (Davis et al., 1998; Narayanan et al., 1999; and McCutcheon and Schnoor, 2003). This hypothesis is supported by earlier studies that could not detect VOCs in the middle of the phytoremediation test plots. Furthermore, calculations show that during the slightest of wind velocities, the flux of VOCs to the atmosphere from a phytoremediation application leads to trivial concentrations in the atmosphere.

2.3 Rhizosphere Degradation

Rhizosphere degradation is the breakdown of organic contaminants within the rhizosphere— a zone of increased microbial activity and biomass at the root-soil interface. Plant roots secrete and slough substances such as carbohydrates, enzymes, and amino acids that microbes can utilize as a substrate. Contaminant degradation in the rhizosphere may also result from the additional oxygen transferred from the root system into the soil causing enhanced aerobic mineralization of organics and stimulation of co-metabolic transformation of chemicals (Anderson et al., 1993).

The fate of TCE was investigated in laboratory settings (Walton and Anderson, 1990) by comparing degradation of TCE in both rhizosphere soil and non-vegetated soil collected from a TCE-contaminated site. The results showed that TCE degrades faster in rhizosphere soils. Anderson and Walton (1995) also reported that TCE mineralization was greater in soil rooted with the Chinese lespedeza, loblolly pine, and soybeans than in non-vegetated soil.

Additional research on CVOC fate in the rhizosphere has shown varying results. Chlorinated pesticides were shown to have enhanced degradation in the rhizosphere (Shann, 1995), and a loss of TCE and 1,1,1-trichloroethane (TCA) was observed in the rhizosphere of alfalfa (Narayanan et al., 1995). Higher numbers of methanotrophic bacteria, which have been shown to degrade TCE, were detected in rhizosphere soils and on roots of *Lespedeza cuneata* and *Pinus taeda* than in unvegetated soils (Brigmon et al., 1999). Orchard et al. (2000) detected TCE metabolites in the roots of hybrid poplar saplings suggesting rhizosphere degradation and concluded that the greatest degradation of TCE occurred in the rhizosphere.

However, Newman et al., (1999) observed no degradation of TCE in the rhizosphere of hybrid poplars. Similarly, Schnabel et al. (1997) observed no degradation of TCE in the rhizosphere of edible garden plants.

Recently, studies have indicated that wetland vegetation and rhizosphere microbial communities can effectively treat chlorinated compounds (Dhanker et al., 1999; Bankston et al., 2002; Nzengung et al., 1999; and Kassenga, 2003).

2.4 Phytodegradation

Phytodegradation is the breakdown of organic contaminants within plant tissue. Although data are limited, it appears that both the plants and the associated microbial communities play a significant role in attenuating chlorinated compounds. Plants produce a large number of enzymes, of which one or more may transform PCE and TCE into daughter products. Although not completely understood, dehalogenase, cytochrome p-450, glutathione-S transferase, methane mono-oxygenase, and monochloroacetic acid are all thought to play a role in chlorinated solvent transformation. Intermediate stable metabolites of these chlorinated compounds include 2,2,2-trichlorethanol, 2,2,2-trichloroacetic acid (TCAA) and 2,2-dichloroacetic acid (DCAA), and have been reportedly found in hybrid poplar (Gordon, 1998; Newman et al., 1997; and Compton et al., 1998), oak, castor bean, and saw palmetto (Doucette et al., 1998).

Some researchers believe that chlorinated solvents are being metabolized within vegetation; however, the exact mechanism has not been determined yet. Bench-scale laboratory TCE uptake tests with poplar cuttings grown in soil were reported to have measurable amounts of TCE transpired to the air (Newman et al., 1997). A three-year study commencing with rooted poplar cuttings in a series of constructed, lined, artificial aquifers evaluated the fate and transport of TCE in the poplar tree. The mature trees were able to remove 99% of the TCE from the groundwater, and less than 9% of the TCE was transpired to the air in the first two years. After two years, TCE was not detected in the air stream. Researchers believe that the mature hybrid poplar tree was dechlorinating the TCE and inferred that degradation in the rhizosphere was not contributing to the loss of TCE (Newman et al., 1999).

In addition, Gordon et al., (1998) detected TCE metabolites in hybrid poplar cutting experiments and suggested that TCE is oxidized as it moves through the cutting. When grown hydroponically in a laboratory, the tropical leguminous tree, *Leuceana leucocephala*, was shown to metabolize TCE as indicated by the formation of one of its degradation products, trichloroethanol (Doty et al., 2003).

An alternate theory about the fate of TCE in poplar trees is that TCE is taken up by suspension cell cultures and is incorporated as a nonvolatile, nonextractable residue (Shang and Gordon, 2002). Another investigation of the fate and transport of TCE in carrot, spinach, and tomato plants showed that TCE was taken up, transformed, and bound to plant tissue (Schnabel et al., 1997). This binding, or “sorption” of organic compounds, has been linked to plant lipid content and tissue chemistry. Mackay and Gschwend (2000) have studied the sorption of chemicals to wood and developed wood-water partitioning equations. Partitioning onto wood was determined to depend predominantly on the water-lignin partitioning of a compound. Lignin is the chief noncarbonhydrate constituent of wood, which binds to cellulose fibers and strengthens the cell walls. Lignin is hydrophobic and shows strong affinity to hydrophobic organic compounds.

Ma and Burken (2002) measured the wood-water partitioning coefficient values for CVOCs binding to poplar tissues. The results ranged from 20.7-59.3 mL/g for the tested compounds (tetrachloromethane, TCE, and 1,1,2,2-tetrachloroethane), which is in agreement with the range of literature values. The fraction of lignin in poplar trees was assumed to be 20%. The lignin content of hardwood is about 18-25%, and the content of softwood is a little higher at 25-30% (Haygreen and Bowyer, 1982). A linear relationship was observed between the partitioning coefficients and vapor pressure and Henry’s law constants.

2.5 Hydraulic Control

A great deal of research has focused on the use of trees─poplar trees, in particular─to intercept shallow groundwater plumes (Wang et al., 1999; Jones et al., 1999; Thomas and Krueger, 1999; Tossell et al., 1998; Gordon, 1997; Newman et al., 1999; Compton et al., 1998; and Quinn et al., 2001). Most of these studies have shown that trees can extract large enough quantities of groundwater to depress the water table, locally inducing flow toward the trees. This depression can be sufficient to create a hydraulic barrier or hydraulic control. Hydraulic control mitigates potential risks by controlling offsite transport of CVOCs and providing more opportunity for the other four mechanisms of phytoremediation to remediate the CVOCs. Proper hydraulic control involves the selection and planting of vegetation to intercept and transpire large quantities of groundwater or surface water.

2.6 Summary

In summary, some researchers believe CVOCs are degraded in the rhizosphere, while others believe that the CVOCs are taken up by plants and phytovolatilized through the leaves or bark. Yet others believe that when CVOCs are taken up by the plant, they are either degraded within the plant or sorbed to its tissues. All five mechanisms have been shown to occur, and research is continuing to further understand how and under what conditions they occur. The varying occurrence of each mechanism may be due to site or laboratory conditions, meteorological conditions, measuring techniques, etc. Through a better understanding of the role of plants, researchers, engineers, and site managers can better manage sites that have been impacted by a broad range of CVOCs. Appropriate field tests and site conceptual models are needed as discussed in the Section 3.

SECTION 3.0 ASSESSMENT OF APPLICABILITY OF PHYTOREDIATION

Screening level assessments are vital to the final remedial selection and often result in a “go” or “no go” decision for a given remedy. This section summarizes the factors to consider when assessing the applicability of phytoremediation for a contaminated site. These factors include site conditions, the phytotoxicity of the contaminants, and regulatory requirements. Figure 1 is an adaptation of the Interstate Technology Regulatory Council’s and the Center for Waste Reduction Technologies’ decision flow chart (developed in 1999), to help decide whether to use phytoremediation.

3.1 Site Conditions

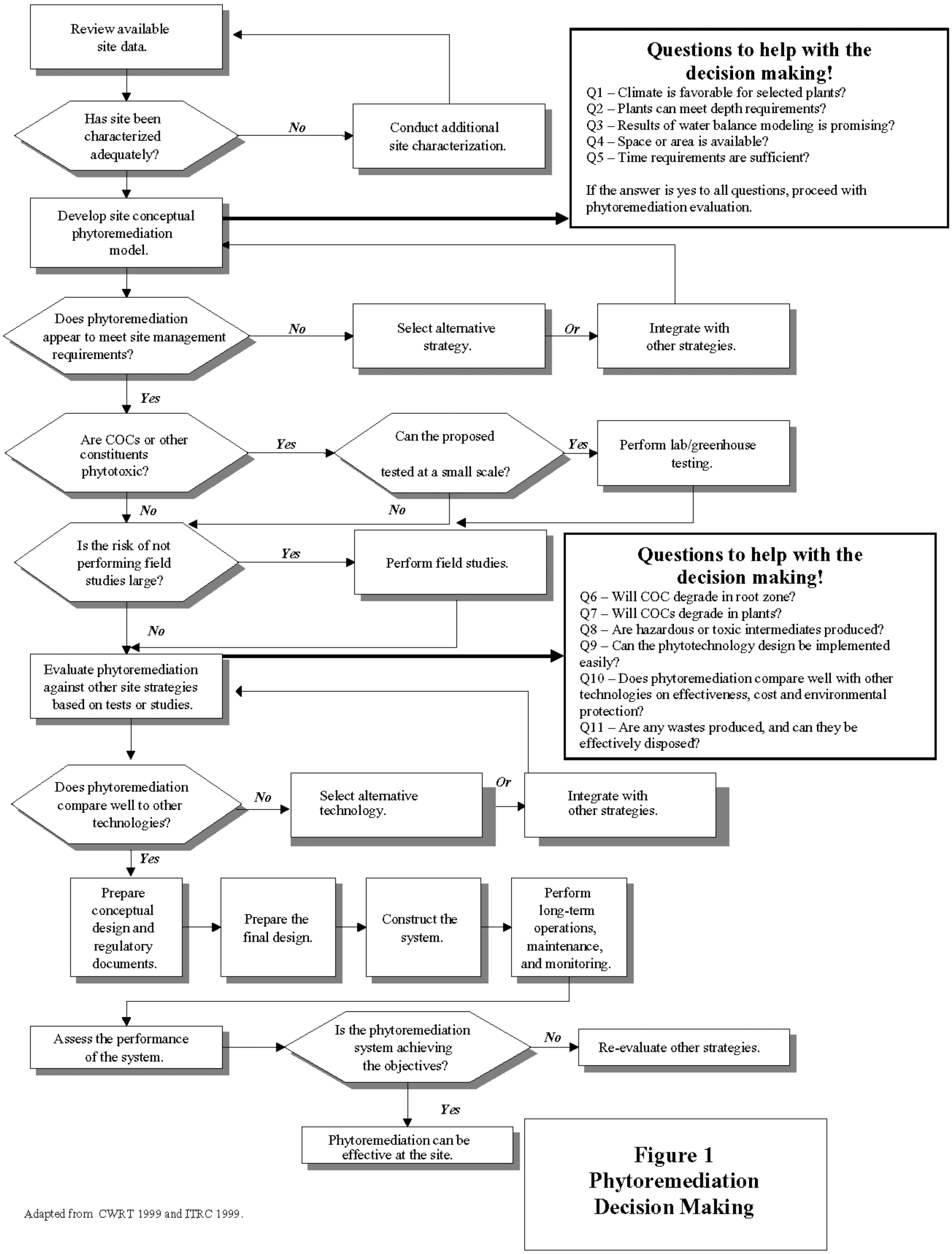
A screening level assessment of phytoremediation as a treatment technology and the ultimate decision to use the technology is partly based on site-specific conditions (e.g., layout, hydrogeologic setting, and distribution of contaminants). The initial assessment begins with a fundamental understanding of site conditions in order to develop of a site conceptual model. The site conceptual model is important since it will form the basis for evaluating the effectiveness of phytoremediation for meeting all or part of the site management objectives. Developing a site conceptual model will include the following steps:

- Review background site data (consistent with project objectives), including but not limited to the project files, including historical documents, the Remedial Investigation/Feasibility Study (RI/FS), draft record of decision (ROD), applicable or relevant and appropriate requirements (ARARs), etc.;
- Develop a geologic cross section to help determine if phytoremediation can achieve hydraulic capture or CVOC sequestering goals;
- Perform basic hydraulic modeling;
- Plot the distribution of CVOCs in the subsurface in both plan view and in cross section;
- Identify and develop approaches to best achieve remedial action objectives for the site, including information on cost and ARARs compliance;
- Review site risks and consider applicability of phytoremediation; and
- Prepare a site-specific phytoremediation conceptual design that meets the site management remedial goals and objectives.

The goal of the site data review, as described below, is to develop a thorough understanding of site conditions, hydrogeological conditions, groundwater capture, contaminant distribution, agronomic conditions, and meteorological conditions.

3.1.1 Site Layout

A review of the site layout could include elements such as property boundary, surrounding features, infrastructure, buried utilities, and other obstacles that would prohibit planting or would have to be removed or altered for planting to occur. Also, the review should determine if there is sufficient land available to plant the amount of vegetation required for a successful remediation project.



Questions to help with the decision making!

Q1 – Climate is favorable for selected plants?
Q2 – Plants can meet depth requirements?
Q3 – Results of water balance modeling is promising?
Q4 – Space or area is available?
Q5 – Time requirements are sufficient?

If the answer is yes to all questions, proceed with phytoremediation evaluation.

Questions to help with the decision making!

Q6 – Will COC degrade in root zone?
Q7 – Will COCs degrade in plants?
Q8 – Are hazardous or toxic intermediates produced?
Q9 – Can the phytotechnology design be implemented easily?
Q10 – Does phytoremediation compare well with other technologies on effectiveness, cost and environmental protection?
Q11 – Are any wastes produced, and can they be effectively disposed?

Figure 1
Phytoremediation Decision Making

Adapted from CWRT 1999 and ITRC 1999.

3.1.2 Hydrogeologic Setting

An understanding of the hydrogeologic setting, such as depth to the water table, the geologic makeup and extent of aquifers and aquitards, groundwater recharge rate, flow velocity and direction, soil porosity, hydraulic conductivity, and seasonal variations is essential.

3.1.3 Groundwater Capture and Water Balance Modeling

Computer modeling can be used to better understand and define the site water balance and to provide a preliminary indication of phytotechnology performance. The purpose of predictive modeling is to assess whether a phytoremediation approach can be used to extract groundwater at rates sufficient to create a water table depression that can alter or contain the migration of CVOCs. As phytoremediation requires time to implement, the retardation of groundwater flow will provide greater opportunity to capture CVOCs. Models also can be useful for evaluating potential risks to human and ecological receptors at the site. Therefore, dual-approach modeling using a plot of trees is suggested. This approach requires:

- Analysis of plant water extraction and transpiration to estimate potential water removal by vegetation; and
- Groundwater capture zone analysis to determine the required water extraction rates to maintain hydraulic control.

Spreadsheet models can be used to simulate plant transpiration using evapotranspiration as the basis for water extraction and flow estimation. Evapotranspiration can be estimated by both meteorological methods and by sap flow measurements. Reference or potential evapotranspiration (ET_o) can be estimated using the Food and Agriculture Organization's (FAO) Penman-Monteith method (http://www.fao.org). This parameterization of the Penman-Monteith equation is the new worldwide standard estimating equation as recommended by the FAO the International Commission for Irrigation and Drainage, and the World Meteorological Organization.

Several computer models, HELP, EPIC, UNSAT-H, and HYDRUS-2D, can be used to estimate evapotranspiration and rainfall infiltration to groundwater. A model validation study indicated that the UNSAT-H and HYDRUS-2D models, which are based upon complex equations for flow, were superior to the HELP and EPIC models, which are based upon simple tracking of the amount of water (Wilson et al., 2001).

MODFLOW^{TM} is traditionally used for capture zone analysis of conventional mechanical groundwater extraction systems, but can be adapted for phytotechnology applications. An alternative groundwater capture zone model is WinFlow (Version 1.07, Copyright 1995, Environmental Simulations, Inc.). For applications involving groundwater remediation, a capture-zone calculation (Domenico and Schwartz, 1990) can be used to estimate whether phytoremediation can effectively capture the plume of contaminants. UNSAT-H, LEACHM, and PRZM, are other available models that can be useful for simulating chemical transport in soil, soil water, soil gas, and groundwater in a dynamic, time-variable fashion. When analyzing the site water balance, the growing season and movement of water during no growth season are important to consider. Also, the proportion of groundwater vs. surface water uptake should be considered (Clinton et al., 2004).

3.1.4 Meteorological Monitoring

To help assess the evapotranspiration rates used in groundwater capture and water balance modeling, information on the following meteorological conditions should be obtained: precipitation, ambient air temperature, soil temperature, wind, solar radiation and relative humidity. These conditions influence the rates of water uptake from by plants. If a weather monitoring station is not set up onsite, local weather stations and NOAA can provide meteorological data. Although meteorological data from local weather stations can provide a good estimate of site meteorological data, the data are not necessarily representative, especially for rainfall events.

3.1.5 CVOC Distribution

Management of CVOCs requires a fundamental understanding of those chemical and physical processes that ultimately affect their fate. Once released to the environment CVOCs are affected by a number of processes including:

- dissolution;
- adsorption;
- advection and dispersion;
- volatilization; and
- biological transformation (microbial attenuation).

These processes will have some role in affect on the nature and distribution of the CVOCs in the subsurface. The relative impact of each process will depend on the nature of the CVOC and site conditions. The geologic and hydrogeologic data should be used to evaluate the rates, directions, and pathways of migration. Evaluation of spatial and temporal trends will help to define the fate and transport of a CVOC and estimate its mobility.

3.1.6 Agronomic Evaluation

The performance of phytoremediation systems is contingent on soil quality, which depends on the physical, chemical, and biological parameters of the soil. Physical parameters are very important and include compactness (bulk density), texture, and permeability. Equally important are chemical parameters, which include fertility, salinity, and presence of phytotoxic elements or compounds (See Section 3.2). Biological factors, including plant and chemical interactions with bacteria, fungi, insects, and burrowing animals, need to be assessed for an effective phytoremediation project.

A list of soil parameters to measure would include:

- available nutrients, including nitrogen, phosphorus, potassium, calcium, sulfur etc.;
- particle size distribution;
- bulk density;
- salinity;
- oxidation/reduction (redox) potential;
- microorganism(s) present for degradation;
- cation exchange capacity;
- pH; and
- organic matter content.

The nature and properties of the soil will govern the type of plant suitable for phytoremediation. If the soil is unsuitable for plant growth, it may require extensive soil amendments to make it useable.

3.2 Phytotoxicity

Certain concentrations of contaminants can be poisonous to plants or “phytotoxic.” Therefore, laboratory testing may be needed to investigate whether site soil and groundwater can be phytotoxic to plants used in phytoremediation. Phytotoxicity studies are recommended when CVOCs and other constituents (e.g., metals, dissolved solids, or other organics) are present in soil or groundwater at concentrations close to published toxicity indices. If there is little concern regarding phytotoxocity, a laboratory test may not be necessary. However, even if contaminant concentrations are below these indices, a properly designed laboratory study is useful for providing data on the performance of the phytoremediation system design. Phytotoxicity studies designed to mimic site conditions can more readily address concerns about potential cumulative effects of multiple chemicals, as most phytotoxicity data available in the literature are for a single chemical or condition. Because the phytotoxicity levels for some compounds can be species-specific, depending on a plant’s inherent enzyme types and levels, the plant species intended for use at the site, can also be tested in the laboratory using site soil and groundwater. And even if the levels of CVOCs are not phytotoxic to a plant, the level dissolved solids or salinity may be phytotoxic.

Laboratory tests should focus on screening species for their ability to tolerate suspected phytotoxic compounds present in site soil and groundwater. The test can be conducted onsite in a greenhouse or at a university or commercial laboratory with experience in conducting treatability studies using site soil. Listed below are some basic guidelines for phytotoxicity screening (ISO 11269-2, 1995; ASTM, 2002; and OECD, 2004):

- A completely randomized block design can reduce environmental bias.
- Toxicity treatment variables (CVOCs or constituents in soil and groundwater that may be toxic) should be tested in triplicate with at least three other different concentrations.
- Controls (uncontaminated soil and water) can be used to assess the baseline performance of plants unaffected by the CVOCs and toxic constituents.
- Controls should be treated the same as toxicity treatments and replicated three to four times.
- Plants need to be propagated in a sufficiently sized container with site soil.
- Soil should be kept at the same moisture level as at the site.
- Controls on CVOC emissions from soils and plant must be made for health and safety purposes.
- Qualitative and quantitative monitoring can be conducted over a period of approximately two months following an acclimation period of one month.
- Site soil should be obtained from both the surface and from a depth 3-5 feet below ground surface. (Even if the surface soil is not contaminated, soil closer to the groundwater may be highly contaminated.)

Qualitative monitoring for phytotoxicity includes visual observation of indicators of plant health such as the percent germination (if plants are grown from seed), leaf yellowing or browning, percent dead plants, and average height of plants per pot (measured from main stem to tip of leader).

Quantitative monitoring for phytotoxicity involves soil and plant tissue analyses. These analyses should be conducted by an accredited analytical laboratory for a range of parameters, including (but not limited to) chloride and nutrients (nitrogen, phosphorous, and potassium). Toxic constituents (CVOCs and other constituents in soil and groundwater that may be toxic) and selected other parameters (e.g., pH and metals) that may affect plant growth may be analyzed periodically, depending on the composition of the soil.

Ferro et al., (1999) assessed the toxicity of certain volatile organic compounds (VOCs)─a mixture of aromatic compounds, chlorinated aliphatics, and alcohols─in poplar trees. The study observed no phytotoxic effects from three different concentrations (42 mg/L, 85 mg/L, and 169 mg/L). Dietz and Schnoor (2001) found hybrid poplar cuttings could be grown hydroponically in concentrations of chlorinated aliphatic compounds ranging from 0.1mM to 5 mM. The cuttings were more susceptible to chlorinated ethenes than to chlorinated ethanes, and growth was restricted mostly by highly chlorinated solvents.

Research has also revealed that hybrid poplars are tolerant to high levels of chlorinated solvents. Ma and Burken (2004) reported that no acute phytotoxicity─in terms of decreased water transpiration or chlorosis (the absence of green pigments)─was observed throughout a short-term experiment at 440 ppm TCE. In an earlier study, no acute phytotoxicity was observed when similar reactors were dosed with 550 ppm TCE (Ma and Burken, 2004). However after 24 days, acute phytotoxicity signs, such as wilting leaves and decreasing water uptake, were reported for one reactor dosed with 820 ppm TCE; one plant died after 36 days.

3.3 Regulatory Considerations

Regulatory consideration for phytoremediation is consistent and equal in evaluation to any other remediation technology. Regulations (40 Code of Federal Regulations [CFR] 300.430) require that a remediation technology be “protective of human health and the environment, maintain protection over time, and minimize untreated waste”.

There are many questions and issues that can be raised by regulators, potentially responsible parties, and the public. One such question is – What is the regulatory driver for the cleanup (e.g., voluntary cleanup, Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA], Resource Conservation and Recovery Act [RCRA], underground storage tank, etc.)?

A variety of permits may be required when using phytoremediation at a site:

- If surface water is treated, a National Pollutant Discharge Elimination System (NPDES) permit may be required.
- If phytovolatilization is the operating mechanism, an air permit may be required.
- If groundwater will be pumped to the ground surface to irrigate the plants or if contaminated soil is excavated or moved from one area to another, a RCRA permit may be required.
- Cities and states may have additional restrictions about using invasive plant species.
- City ordinances may apply.

Other steps to consider when proposing phytoremediation as a remedial technology at a site are:

- Determine whether the anticipated time frame of phytoremediation can fit the regulatory status, the site strategic development plan, and the current or potential risks associated with the groundwater.
- Identify the contaminants of concern, media affected, and cleanup levels. Provide laboratory or field data to the regulator that are consistent with the plants and contaminants of concern at the site.
- Customize monitoring requirements to the site and plants selected. Monitoring the efficacy of an innovative treatment such as phytoremediation may be more extensive than would be required for a more accepted technology.
- Define the fate and transport of the contaminants of concern, including the effects on the food chain and volatilization to the surrounding air. If a contaminant is shown to be bioavailable, an ecological risk assessment should be performed.
- Determine whether the plant material may become hazardous with uptake of contaminants and how it will be disposed.
- Create a contingency plan in the case that phytoremediation does not perform as expected.
- Define the criteria that will determine when remediation is complete and the site closed.
- Assess if there is sufficient containment of contaminated soils, groundwater, and sediments until the phytoremediation plants have established themselves at the site.

Since there are many regulatory issues to be tackled, involvement of regulators and the public is recommended early in the project. Owners and contractors should provide as much data as possible to support the feasibility of phytoremediation at their site. Such data should include laboratory and field studies with the contaminant of concern, the proposed plant species, and similar geologic and climatic conditions. Regulators may accept laboratory studies as evidence that this technology will be appropriate for a site. However, some regulators may require field studies before allowing full-scale phytoremediation to be the chosen remedial technology. Performance standards should be developed so the effectiveness of phytoremediation can be measured against an agreed upon set of criteria. Performance standards may include hydraulic measures, contaminant movement, or contaminant concentration reductions.

Since phytoremediation is a newer technology, it does not have the track record that some other remedial technologies have obtained. However, this is changing. More and more research has been conducted, both in the laboratory and in the field. The research completed in the last decade has been promising and more regulators are open to phytoremediation than in the past.

SECTION 4.0 FIELD PILOT TESTS

A field pilot test can document phytoremediation under real site conditions and, if successful, may generate design and cost data for full-scale application. Pilot testing may consist of planting the appropriate plant species, installing necessary instrumentation, and developing a monitoring plan for chemical fate over time in the soil, groundwater and plant material. The main goal of the pilot test is to assess if the plants will survive and the roots will reach the contamination. In preparation for the pilot-scale test a planning report may include:

- a description of the soil investigation, analytical sampling results, a borehole/well location map, and soil logs, as appropriate;
- field design and layout;
- maps and figures showing details of the proposed field test design;
- the number and type of trees/plants to be used in the pilot (assume some will die);
- the desired spacing of planting to optimize plant water use (400 to 800 trees per acre);
- maintenance requirements including monitoring for diseases;
- institutional controls (e.g., keeping animals and people out of the area);
- the recommended fertilization program; and
- a description of the analytical monitoring program.

Brief summaries of design elements, such as selection of plants, planting techniques, fertilization, soil amendments, and maintenance, are presented in the following sections.

4.1 Plant Selection

Important considerations in selecting a plant species for phytoremediation at a site include the following plant characteristics:

- climatological requirements;
- translocation and uptake capabilities;
- tolerance levels with respect to chemicals known to exist at the site;
- tolerance to drought-prone or poorly-drained conditions;
- tolerance to pH and salinity of the soil and groundwater;
- depth of the root zone;
- growth rate;
- transpiration rate or water use;
- whether it is deciduous or evergreen (affects the period of effectiveness);
- maintenance requirements;
- native vs. non-native species; and
- commercial availability.

Some nurseries or plant propagation companies will propagate some species of plants that are not normally commercially available. This can be very valuable if native species are desirable or even required by other agencies.

4.2 Planting Techniques

The number of trees to plant depends on the size of the space available and the desired plant density. Widely spaced planting has the potential benefit of cost savings if the trees are being installed by augering boreholes, and minimizes or eliminates the cost of thinning. However, greater plant densities will achieve canopy closure more rapidly; therefore, water uptake will also reach a maximum rate more quickly. Greater densities are also appropriate for tree varieties that are more columnar in shape. Very dense plantings should be thinned when trees are about 3-years-old to improve tree vigor and performance. Row spacing is should be at least 10-ft wide to allow mowing equipment between rows during establishment. Digging holes for plantings may be accomplished effectively using techniques such as: 1) augering borehole to the water table or 3 feet below ground surface; 2) trenching rows to the water table or to 3 feet below ground surface; or 3) using a ripper shank-type planter to furrow 1.5 to 2 feet below ground. With each technique, the trees are planted in a mixture of soil and soil amendments, which is backfilled into the holes.

Herbaceous plants used for ground cover and erosion control can be planted using standard agronomic planting techniques such as a seed drill. More information of planting techniques can be found in “Phytoremediation of Groundwater at Air Force Plant 4 – Carswell, Texas” (U.S. EPA, 2003).

4.3 Fertilization

Soil samples can be sent to a laboratory for agriculture analysis to evaluate them for nutrients, grain size, and cation exchange capacity. It is most effective to collect soil samples from the entire rooting depth required to meet remedial goals. Sampling can be stratified based on major changes in soil texture, structure, color, and rooting patterns of existing vegetation.

Nitrogen is likely to be the most limiting nutrient in a soil. Nitrogen application rates are not readily measured from soil tests, and are determined based on estimates of plant uptake and loss mechanisms, such as denitrification. Rapidly growing hybrid poplar plantations may require 200 lb of nitrogen (N) or more per acre per year, although 50 to 150 lb N/acre/year is typically applied (Heilman et al., 1995). Many phytoremediation sites would benefit from at least 100 lb N/acre/year. The actual rates applied can be adjusted based on plant growth, leaf tissue nitrogen (need for fertilization indicated if leaf N less than about 2.7%), and enhanced microbial growth. This is vital for sites impacted by petroleum hydrocarbons or at risk of nitrate groundwater contamination. Nitrogen may be deficient if leaves are small or light green to yellow in color, especially if lower leaves yellow first. Interveinal chlorosis (yellowing of leaves between veins), if present, is due to other nutrient deficiencies or toxicities.

Phosphorus and potassium fertilization also is likely to be required on many sites. In addition, hybrid poplars may respond well to addition of zinc, especially in calcareous soils. Use of zinc in a chelated form is recommended to ensure that the zinc remains mobile and available for plant uptake in the presence of $CaCO_3$. However, caution should be used when using zinc fertilizers since they can be phototoxic at low levels, especially under low pH conditions. Fertilizers applied in slow-release form are recommended.

Required application rates and methods are somewhat site-specific, and should be developed in consultation with a qualified soil scientist or agronomist.

4.4 Soil Amendments

Restoration of soil quality is a prerequisite for successful phytoremediation implementation. In most cases, soils will not require any soil amendments. In cases where soils are of very poor quality or the site has a substantial amount of fill material, soil amendments may help with establishing and maintaining healthy vegetation. It is helpful to contact a local agriculture agency for the amount of amendments needed for the site soil. A soil pH within a range of 6 to 8.5 is best for vegetation. In low pH soils, lime can be used to adjust soil pH, as needed, based on baseline monitoring data. Aged compost or peat moss can be blended with site soil during planting to accomplish the following goals:

- as bulking agent to decrease soil density;
- to obtain a consistent soil structure;
- to improve soil aeration;
- to increase plant nutrient holding capacity and reduce the need for fertilization;
- to increase the moisture holding capacity of the soil; and
- to enhance rhizodegradation of the CVOCs.

4.5 Maintenance Plan

Maintenance of the phytoremediation plot includes routine inspection of groundwater, meterological, and plant monitoring equipment and the plants themselves. Equipment maintenance will be conducted based upon manufacturers' recommendations regarding the level of use. Maintenance of plants and cover vegetation will include:

- mowing ground cover vegetation on a regular basis can greatly enhance growth of trees (Mowing can be difficult with 400 – 800 trees per acre. It may only be recommended when herbaceous plant competition becomes detrimental to trees);
- fertilizing the area based on the soil monitoring results;
- following an animal control plan to keep out deer, voles, beavers, etc.; and
- pruning and replacing trees.

A well thought out maintenance plan can often make the difference between success and failure. Disease or competition can affect a large number of phytoremediation plants especially if the plants are dealing with less than ideal conditions.

SECTION 5.0 MONITORING AND SAMPLING

Monitoring the fate and transport of CVOCs in a phytoremediation application should encompass those mechanisms responsible for solvent attenuation or loss. It is recommended that monitoring include the sampling of soil, groundwater, plants, and air. The approach to sampling these media to track the progress of phytoremediation is discussed in the following sections.

5.1 Soil Sampling

Soil samples should be collected before starting phytoremediation to serve as a baseline for comparison to the mid-point and final sampling results. Sampling locations can be selected based on the site conceptual model. If the hydraulics of the site are well known, the site hydrogeologist can select points that will allow the site manager to be confident that the remediation effects can be documented. The initial soil samples can be collected and analyzed when monitoring wells are installed for groundwater sampling. Soil from all of the monitoring well locations can be sampled, unless there is an overriding reason this cannot be done. Sufficient data must be collected, however. When sampling:

- collect a sufficient number of cores across enough depths so that soil concentrations within the plume can be documented;

- leave space for equipment when the remediation plots are installed so subsequent cores can be collected; and

- when the cores are collected, examine them to be sure that the soil in that area is homogeneous; If the soils are not homogeneous, the number of cores collected will probably have to be increased.

5.2 Groundwater Monitoring and Sampling

Groundwater monitoring should be conducted within the phytoremediation study location and, if possible, both upgradient and downgradient of the test location. Monitoring wells should be installed where groundwater samples will be collected for chemical analysis. Piezometers can be installed in locations where the only data needed are water level measurements for water table contouring and aquifer tests for estimating hydraulic conductivity. A large number of piezometers may be needed to measure small changes in groundwater levels. Use of in-well continuous monitors will give more accurate water level data than periodic measurements by hand because many factors can affect the plant water uptake at a given point in time. Factors such as precipitation, recharge rate, and root locations should also be considered when analyzing water level data.

Groundwater samples collected from monitoring wells should be analyzed for of CVOCs and their microbial daughter product compounds, nutrients; and field parameters such as temperature, oxidation-reduction potential, pH, and specific conductance (which can be measured in a flow-through cell, when practical).

Sampling design and frequency will be based on study objectives; however, it is recommended that groundwater sampling be conducted at least twice per year. Groundwater sampling within the test location and in a control area can provide data for rhizosphere effects and hydraulic control. These data can be used to evaluate whether or not trees are creating a depression in the water table. A single transect may be used for this purpose; however, two or three transects are recommended, to fully evaluate water levels within the planting area and to collect groundwater samples to evaluate the fate of CVOCs.

If the project schedule provides insufficient time for trees to grow large enough to extract groundwater, then sap flow monitoring can be used as an alternative to or in addition to groundwater elevation monitoring. Plant transpiration can be measured with thermal dissipation sap flow sensors that are attached to the trunk of the trees (Dynamax, 1997). A continuous recording datalogger will record sap flow on time weighted basis. Using these data, diurnal fluctuations and daily cumulative values of plant transpiration will be assessed and estimates of total transpiration can be made. These data can be matched against estimates of expected groundwater extraction rates required for hydraulic control.

Over the past ten years, studies have been conducted by the United States Geological Survey (USGS) and United States Air Force (USAF) to quantify the effects of trees on shallow groundwater geochemistry. These studies have shown that cottonwood plantations (5-6 years old) can induce groundwater geochemical changes year round that can initiate in-situ dechlorination of TCE. TCE biodegradation rates at this Texas site were noted to increase and this increase in natural attenuation capacity was associated with a potential decrease in plume-stabilization distance (Harvey, 2004, personal communication).

5.3 Plant Monitoring

Recommended plant monitoring includes qualitative monitoring (i.e., plant health observations), quantitative monitoring (i.e., growth as indicated by leaf area index, girth, and height), and plant tissue sampling for analysis of CVOCs. Randomly selected trees should be used as bench marks for plant monitoring throughout the duration of the phytoremediation project. Monthly qualitative plant monitoring is recommended for a newly planted site, and tissue sample collection is recommended quarterly to semi-annually.

The qualitative health observations are used to assess the overall vigor of the phytotechnology system. Through this process, nutrient deficiencies can be identified and remedied, and diseases can be identified early before they become epidemic and threaten the entire phytotechnology approach. The qualitative assessment will involve observing leaf condition related to nutrient deficiencies, diseases, and pest infestations. Aerial infrared pictures can help reveal health effects such as infestation.

The following quantitative measurements can be conducted throughout the study and at its completion:

- Evapotranspiration can be measured by both meteorological methods (e.g., the Penman-Monteith equation) and sap flow measurement sensors that are attached to the trunk of the trees. These sensors can be linked to a continuous recording datalogger that records sap flow. Using this monitoring approach, diurnal fluctuations and daily cumulative values of plant transpiration can be assessed.

- Leaf area index (LAI) can be assessed in the field using a handheld lux meter that measures light intensity within the canopy relative to light intensity above the canopy. These measurements should be taken monthly or bi-monthly during the growing season to monitor tree canopy development and to correlate plant transpiration measurements with the LAI. The LAI will also be used to assist with estimation of evaporation and transpiration components of the calculated ET_o.

- Monitoring of overall canopy height is recommended at the onset of the study and at the end of the growing season each year. Average canopy height is estimated by measuring the height of several benchmark trees or plants. This is done by vertical distance from the soil surface to the highest point of the vegetation.

- Tree girth (i.e., circumference) of the main stem of the tree is measured at the study onset, and at the end of the growing season each year. Girth can be measured using a soft measuring tape or calipers to determine diameter at breast height and converting to a standard girth.

- Depending on soil characteristics and groundwater depth, it may be worthwhile to evaluate whether the roots have reached the groundwater in the first two to four years of the project by excavating a hole adjacent to a tree.
- Collecting plant and core tissue samples (leaves and stems) from selected benchmark trees or plants and analyzing them to detect chemical uptake is recommended.

5.4 Plant Sampling

A measure of plant interaction with the CVOC in soil or groundwater can be determined by analyzing the presence of the parent compound and metabolites within the plant tissues. Perhaps the ideal sampling approach is to look for the parent compound in tree trunks. The trunk of the tree has been shown to contain the highest concentrations of the original contaminant, before it has a substantial chance of being volatilized out of the bark and leaves. However, the trees must be large enough to be cored without significant harm to the tree, which will limit the approach’s usefulness in young plantations. If the trees are large enough, coring results can help determine if the plant roots have reached the contaminated water. The method for tree coring has been described in detail in Vroblesky et al. (1999) and Ma and Burken (2002). In brief, a core is removed from the tree at breast height, placed into a pre-weighed glass vial with a Teflon® stopper, and stored on ice. The vial is allowed to come to room temperature for two days in the laboratory, and the headspace gases sampled for the presence of the parent compound.

An alternative approach to analyzing plant tissue is to sample the tree branches. This approach does not have the same age or size limitations on the trees that trunk coring has, nor the concerns about harming tree health. Because branch sampling does not harm tree health, it allows for collection of replicate samples. Contaminant concentrations may vary with branch size, however, so the utmost attention needs to be given to optimize sample uniformity during each sampling event. Branches that are closest to the ground may be the best candidates for sampling, as they intercept sap before substantial diffusion losses occur (Negri et al., 2004).

Sampling for the presence of volatile compounds in plants can be complicated by the very nature of the compounds. Volatile compounds are unstable and can dissipate from plant tissues before analysis can be performed. Therefore, it is necessary to collect and ship the samples under conditions that will allow the retention of the compound in the sample. Sample collection and holding also will depend on the method being used for sample analysis. If samples will be examined by head space analysis, samples should be collected in the field in the containers in which analysis will be performed. If samples need to be ground in preparation for analysis, the best method for analyte retention is to grind the samples in a stainless steel bowl under liquid nitrogen, transfer the samples to the analysis containers, and seal the containers as soon as the samples stop off-gassing the liquid nitrogen and are still frozen. Samples can be transported the laboratory on regular ice.

If the samples will be extracted for analysis, additional sample handling protocol is needed. Extraction can be done to detect the parent compound and is necessary to see many of the metabolites that may not be volatile enough to be analyzed for directly from the plant tissues. Many methods are available for extraction and metabolite derivatization, including those presented by Newman et al. (1997 and 1999). For this type of analysis, samples must be frozen immediately on collection─preferably in liquid nitrogen─and stored on dry ice until arrival back in the laboratory. Samples should be stored at -80º until analysis.

Analysis of plant transpiration gases is another way of determining if the plants have reached the contaminant. This analysis may also be required by regulatory agencies to determine the extent of contaminant release into the atmosphere. Transpiration gas samples should be collected from both the leaves and the trunk of the trees. Trunk samples can be collected non-destructively by the methods described by Schumacher et al. (2004). Transpiration gases collected from leaves are more problematic as the volume of water transpired by the leaves is much larger than the volume of contaminant. Since water vapor can foul gas collection systems, care must be taken to avoid fouling or laboratory instruments can be damaged and samples can be invalidated.

The most common way to collect transpiration gases is to enclose a leaf or small group of leaves in a Teflon® bag connected to a vacuum pump via a sample collection tube (carbon or Tenex). The sample collection tube should be wrapped with heat tape to keep the internal temperature above the dew point of water in order to prevent water vapor from fouling the collection material. Air is pulled through the bag at a set flow rate for a set period of time. At the end of this time period, the surface area of the leaf or leaves is measured onsite, or the leaf (leaves) is taken to the laboratory to be scanned for surface area. The surface area used to calculate the amount of compound transpired per unit leaf area per unit time (Newman et al., 1999).

All of these methods have been described in detail in various articles. These sample collection methods have been optimized for conditions encountered by the groups that used them. Therefore, some experimentation will be needed to devise the best methods for a given site. Contacting some of the authors of these studies may be the best way to proceed, as they can provide valuable information about methods that have not succeeded or improved methods they have been developed but not yet published.

5.5 Air Monitoring and Sampling

Monitoring of plant-transpired CVOCs can be conducted using modified, flexible, Tedlar® bags, which are made of non-sorbent plastic. The Tedlar® bags are placed over individual leaves, leafed branches, or around the tree shoot. Samples can be analyzed using sorbent tubes, summa canisters, or solid-phase microextractors (SPMEs). Evaluation of the sample results must account for the CVOC background concentrations in air to determine the levels due to transpiration.

Gaseous emissions from soil surfaces can be characterized using flux chambers. Flux chamber monitoring is particularly useful for distinguishing between the VOCs volatilized from soil and groundwater versus VOC emissions due translocation, transpiration, rhizosphere degradation, sorption, etc. The flux chamber is designed to isolate those emissions that emanate from the soil

without augmentation or suppression of the natural flux emission rate. The frequency of measuring soil mass emissions will be a function of cost, regulatory mandate, and technology design (monitoring may assist with planting location). Quite often, this monitoring effort is used during the first year of planting to establish a baseline level of soil emissions, with subsequent monitoring once the tree's root system is established, such as year three.
The method employed to measure phytovolatilization at Aberdeen Proving Ground in Maryland (http://web.ead.anl.gov/jfield) entailed the use of 100-L, clear, Tedlar® bags. Each bag was split open to envelop a well-leafed branch, temporarily sealed, and allowed to equilibrate anywhere from two to four hours, depending upon incident solar radiation intensity. However, it is recommended to allow air to flow through the bag at all times to prevent the plant from shutting down transpiration due to localized humidity. The best reading is obtained during the first hour of measurement. Transpiration results can be affected by solar radiation intensity (which varies due to sun, shade, and cloud cover), humidity, recent rainfall, time of day, wind speed, and temperature. Temperature and humidity instruments can be incorporated in the Tedlar® bag apparatus for continuous monitoring.

In addition to leaf sampling, research efforts have targeted measurement of CVOCs that diffuse from xylem tissues during transpiration (Ma and Burken, 2002). Activities at the Aberdeen Proving Ground's J-Field site have been documented in detail (Compton et al., 1998 and Schneider et al., 2000), where phytoremediation has been in place since 1996, when 183 hybrid poplars were planted over a contaminant plume. To capture transpired VOCs, an 8-L, Tedlar®, gas-sampling bag was cut open along three seams to yield a Teflon® sheet, measuring roughly 35 cm x 70 cm. The bag was wrapped around the trunk of selected hybrid poplars (*P. deltoides x trichocarpa*) on the site. An activated carbon trap was attached to the valve/hose barb arrangement on the Tedlar® bag. The Teflon® sheet was attached to the tree using adhesive tape, with three 2-inch-long, ¼-inch inner diameter, Teflon® tubes, protruding from the Teflon®-tree connection on the opposite side of the tree. The Teflon® tubes allowed influent air to enter the wrapped section of the tree. The activated carbon trap was connected to a personal air-sampling pump. At the start of a sampling period, the pumps were turned on and adjusted to deliver a constant 1 L/min flow through the wrapped section and the activated carbon trap. Background activated carbon traps were placed roughly within the center of the phytoremediation plot. When using carbon tubes, it is important to heat them to drive off transpired water before analysis.

Upon completion of the last sampling period of the day, the sampling valves in the Tedlar® bag were closed. The next morning, SPME field samplers were inserted in the bags. The SPME fibers were exposed to the air in the wrapped section of the trunk for 20 minutes. The fibers were retracted into the sample holder. Duplicate samples were collected, and trip blanks and background samples also were collected with SPMEs. Trip blanks serve to monitor background contamination picked up in the laboratory or during transport. At the J-field site, samples were taken in the ambient air in the center of the phytoremediation plot. Personnel at Argonne National Laboratory analyzed the SPMEs on a gas chromatograph with an electron capture detector and mass spectrometer. Use of SPME analysis for environmental samples has proven to be accurate and compares favorably with EPA-validated methods for VOC analysis (Llompart et al., 1998). Quantification was not accomplished with the SPME samples, however. Due to the non-linear response curve (Chai and Pawliszyn, 1995), and the non-uniform conditions (e.g., humidity, volume, and geometry) in the sampled media, only qualitative data was obtained.

Similar methods have been undertaken using thermal desorption sampling methods, with similar success.

Samples can be collected every 15-20 minutes throughout the study, or they may be collected at the onset once the apparatus is established for a baseline, then at the end of the study. There is no threshold concentration for action. These are measures of fate and transport of parent VOCs that indicate trees are planted appropriately with respect to plume capture for both area and depth. These measures provide answers for assessing a mass balance.

SECTION 6.0 REPORTING COST AND PERFORMANCE

Accurate and thorough documentation of the cost and performance of phytoremediation projects is important to evaluate its cost efficiency at sites where it is being implemented or considered. The FRTR, has published the *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* (FRTR, 1998). The purpose of the guide is to help encourage, streamline, and standardize data collection and reporting efforts for remediation technologies. The guide describes a standard set of parameters for reporting cost and performance information about treatment technologies. This section summarizes the suggested cost and performance reporting parameters for cleanup treatment technologies, in general, and phytoremediation, in particular.

Performance often is characterized only in terms of a removal percentage or concentration level attained. However, that information alone, in the absence of information about other parameters, may not be adequate to assess the overall performance of a technology. Table 1 summarizes the suggested site and operating parameters to report for applications of groundwater phytoremediation. The parameters to be documented for demonstration-scale projects are similar to those for full-scale projects. Some additional information applicable to demonstrations includes commercialization issues and competing technologies. In addition to the parameters listed in Table 1, documentation should contain all demonstration or cleanup objectives, and whether or not the objectives were met.

Reporting costs of cleanup applications is helpful to others assessing the feasibility of using similar approaches at other sites. The FRTR guide recommends a simplified cost reporting format that is consistent with various ongoing federal programs under which costs are collected. The format is based on conventional capital and operation and maintenance (O&M) components for reporting costs of specific cleanup technologies (i.e., technology-specific costs). In addition to these, most agencies also account for the overall costs of remediation efforts (total project costs), which include such items as management and support activities, site work such as security, access, and utilities; permitting; monitoring; and preparation of various plans.

Table 2 summarizes the recommended technology-specific cost elements. The guide provides more details on each and a sample cost work sheet. The recommended cost format is applicable to full-scale and demonstration-scale projects, and for both ex-situ applications and in-situ projects (such as phytoremediation).

Table 1: Suggested Parameters to Document Phytoremediation Applications

(adapted from FRTR, 1998)

Parameter	Matrix Characteristics	Operating Characteristics
Contaminants and concentrations	X	
Hydrogeology	X	
Cleanup goals and requirements	X	
Soil classification	X	
Clay content and/or particle size distribution	X	
Hydraulic conductivity	X	
pH	X	X
Depth below ground surface or zone of interest	X	
Total organic carbon	X	
Nutrients and other soil amendments		X
Plants per unit area		X
Plant type		X
Climate	X	
Size of site	X	
Plant installation method and depth	X	
Irrigation		X
Required monitoring and reporting		X

Table 2 - Recommended Format for Reporting Technology Costs

(adapted from FRTR, 1998)

Capital Costs
• Technology mobilization, setup, and demobilization
• Planning and preparation
• Site work
• Equipment and appurtenances
• Startup and testing
• Other (including non-process equipment)
Operation and Maintenance Costs
• Labor (including planting, replanting, fertilization, irrigation, pest control, harvesting, etc.)
• Materials
• Utilities and fuel
• Equipment ownership, rental, or lease
• Other (including non-process equipment overhead and health and safety)
Other Technology-Specific Costs
• Patent fee (see http://www.ecolotree.com)
• Compliance testing and analysis
• Soil, sludge, and debris excavation, collection, and control
• Disposal of residues
Other Project Costs

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PHYTOTECHNOLOGY WEB RESOURCES

U.S. Environmental Protection Agency
http://www.cluin.org/techfocus/

Interstate Technology and Regulatory Council
Phytoremediation Decision Tree
http://www.itrcweb.org/phyto_1.pdf

Phytotechnology technical and regulatory guidance document
http://www.itrcweb.org/PHYTO2.pdf

International Journal of Phytoremediation
http://www.aehs.com/journals/phytoremediation/

International Phytoremediation Electronic Network (U. Parma, Italy)
http://www.dsa.unipr.it/phytonet

Remediation Technologies Development Forum
http://www.rtdf.org/public/phyto/default.htm

U.S. Department of Agriculture PLANTS National Database
http://plants.usda.gov

Wildlife Habitat Council
http://www.wildlifehc.org

APPENDIX FREQUENTLY ASKED QUESTIONS

The answer to most questions about phytoremediation begins, “It depends….” Because the use of plants as tools for remediation relies on the organisms of the plants and the associated rhizosphere microbes, the site conditions are always unique and every project must be custom designed and installed. This section is intended to give brief answers to some commonly asked questions, and to direct the reader to the relevant sections of the document for further information.

MECHANISMS

How does phytoremediation work?
The use of plants, in general, and trees, in particular, to remove, degrade, or contain toxic chemicals located in soils, sediments, ground or surface water, and air.
Section 2.0

What happens in winter when the plants are dormant?
Water consumption essentially stops when plants are dormant. Degradation by microbes and the rhizosphere effect continues, but at a reduced rate.
Section 2.3, 2.4, 2.5

What happens if there is a catastrophic windstorm, fire, disease, beaver, or insect infestation that kills the plants?
If the plants die or are damaged, the beneficial effects are lost or greatly diminished.

TREES

Which trees should be used and how do you decide?
Some trees have been studied for phytoremediation of groundwater. Various varieties have been studied in various conditions and climates, and all plant selection must be made based on site specific conditions. Climate, altitude, soil salinity, position and concentration of contaminant are some of the determining elements.
Section 4.1

How are plants selected for a remediation?
Based on site data and published information about trees, a list of candidate plants can be developed. Plants from that list can be tested to see if they survive under the site conditions. Using a variety of plants decreases problems of monoculture.
Section 3.2

How fast do they grow? How long do they live?
Tree growth depends on species, soil, and climate. For example, Hybrid Poplars can grow 3 meters per year. In general, those trees that grow rapidly tend to be shorter lived and to be more easily damaged in storm events.
(Dickmann et al., 2001; Dickmann and Stuart, 1983)

What do you have to do for operations and maintenance (O & M)? How much does O & M cost?

A new planting may require irrigation, weed control (mowing, mulching, or spraying), pest control, and some percentage of replanting. Agricultural and silvacultural practices and costs vary greatly from region to region.
Section 4.5

Costs would include the labor, materials, utilities, and equipment costs for irrigation, weed control, pest control and replanting. At some point, after the vegetation is well established, O&M costs are expected to be minimal.
Section 6.0

EFFICACY

Will phytoremediation work on my site?

It depends.....
Figure 1

How much groundwater can be cleaned? How many gallons? How deep?

It depends on groundwater flow, soil characteristics, and the type of plant used for the remediation, as well as climate, altitude, and type of planting.
Section 3.0

Depth to groundwater is often variable from season to season, or from year to year, and that influences the efficacy of trees to impact water quality. It is reasonably easy to plant trees to influence groundwater that is 15 feet below ground surface. The deepest phytoremediation impacted aquifer is at 40 feet below ground surface.
U.S. EPA, 2003; Hirsh et al., 2003; and Negri et al., 2004

How do you know it is working?

Monitoring the stabilization or decrease in concentration of the contaminant of concern (COC) in water/soil, formation of metabolites for degradable compounds and detection of the COC and their metabolites in the plant tissues will allow evaluation of phytoremediation.
Section 5.0

How long from planting until the groundwater is affected? How long until the groundwater is clean?

The depth to groundwater and the method of planting determines how long before the trees impact groundwater. Complete restoration of the groundwater will depend on the site, the type of contaminant, the extent of contamination, and the phytoremediation technologies enhanced in the design. The mass of contaminant starts decreasing once the trees impact groundwater. The plants may have to be in place for the foreseeable future as they are only cleaning the soluble contaminants that are passing the roots and not the source area that will continue to add the contaminant to the aquifer.
U.S. EPA, 2003 and 2000

SAFETY

Do the plants become contaminated in this process?
According to the current research, there is little or no accumulation of volatile contaminants in plant roots, wood, leaves, or fruit. Plants may accumulate metals or other toxic materials, but finding volatiles in plants is rare.
Section 2.0, Newman et al., 1999, and Hirsh et al., 2003 (29).

Are fruit and nuts from these plants safe for humans and animals?
Probably not, but test them to be sure.

Is the wood usable?
Yes.

How can one tell if a plant is safe or not?
Analysis of plant and core tissue sampling (leaves and stems) will determine if the plant is safe.
Section 5.3

Do plants release contaminants into the air? If so, how much, and how often?
Possibly. Extensive sampling in the field shows minimal amounts of VOC can come from plant leaves and bark.
Section 2.2

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