THE FEASIBILITY OF POPLARS FOR PHYTOREMEDIATION OF TCE CONTAMINATED GROUNDWATER: A Cost-Effective And Natural Alternative Means Of Groundwater Treatment

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ABSTRACT

THE FEASIBILITY OF POPLARS
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Trichloroethylene (TCE) is a chlorinated solvent that has been extensively used for metal degreasing, among other industrial uses, leading TCE to be one of the most common groundwater contaminants. This widespread contamination presents a threat to human health and the environment given that trichloroethylene is a known laboratory animal carcinogen and a potential human carcinogen. Since the late 1990's poplar trees have proven in laboratory, greenhouse, and field scale projects to effectively phytoremediate TCE contaminated groundwater. Three poplar phytoremediation field studies were analyzed and indicated that hydraulic control of the groundwater plume and degradation of trichloroethylene within plant tissue were prominent methods for contamination containment and removal. Volatilization and microbial degradation in the rhizosphere were not major contaminant reduction mechanisms in these case studies and other field scale projects reviewed.

Pump-and-treat remediation of groundwater, utilizing air stripping towers has been implemented at trichloroethylene contaminated sites since the 1980's. Three Superfund sites with TCE contaminated groundwater utilizing pump-and-treat remediation with air stripping towers were analyzed in an effort to examine this method's efficiency at reducing groundwater contamination. Field scale projects have indicated that air stripping towers can remove up to 99% of TCE from influent water, which can lead to decreasing aquifer concentrations. However, the studies also showed aquifer concentrations reaching asymptotic levels over time, prior to reaching cleanup goals.

A comparison of air stripping and poplar phytoremediation suggested that poplars may be better for treating TCE contaminated groundwater if energy consumption, public perception, ecological restoration, and cost are concerns. But when contamination is high (ppm range) or contaminant mass reduction is desired in a short period of time, air strippers may be more effective. Air strippers may also be more effective at sites where there is not a large land base where trees could be planted or in.

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List of Abbreviations

bgs	Below ground surface
CRWQCB	California Regional Water Quality Control Board
DCE	cis or trans-1,2-Dichloroethene
DCAA	Dichloroacetic Acid
DNAPL	Dense Nonaqueous Phase Liquid
EPA	Environmental Protection Agency
gpm	Gallons per minute
kg	Kilograms
MCL	Maximum Contaminant Level
mM	Millimols
NAPL	Nonaqueous Phase Liquid
PCBs	Polychlorinated Biphenyls
PCE	Tetrachloroethylene (a.k.a Perchlorethylene)
ppb	Parts per billion (1 ppb = .001 ppm; 1 ppb = 1 µg/L)
ppm	Parts per million (1 ppm = 1000 ppb; 1 ppm = 1 mg/L)
TCA	1,1,1-Trichloroethane
TCAA	Trichloroacetic Acid
TCE	Trichloroethylene
VOC	Volatile Organic Compounds

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INTRODUCTION

Contamination of the world's aquifers is a widespread issue reaching a critical point. In theory, cleanup of groundwater to drinking water standards is possible but there are a multitude of variables that complicate the issue. Chlorinated solvents, including trichloroethylene (TCE), are a common source of groundwater contamination given their widespread use across many industries nation wide. A common problem faced by property owners and environmental consultants is making a decision of what type of remediation system is best to use to treat the contaminated groundwater to meet regulatory thresholds. Cost and method effectiveness are among the factors affecting the choice of method for treatment.

Phytoremediation, the use of plants to absorb chemicals from soil and water, is an up-and-coming treatment method that is an aesthetically pleasing, less invasive and natural way to cleanup contaminated sites. Under certain conditions, phytoremediation can effectively remove TCE from contaminated groundwater potentially meeting regulatory or site specific clean-up levels. This thesis focuses on TCE specifically because of its prevalence in the environment and the body of literature that is available on this subject. Phytoremediation has been effective in many laboratory and greenhouse studies and its practicality and effectiveness has been observed in field studies as well. **The goal of this thesis is to determine if using poplars (*Populus sp.)* to remediate trichloroethylene contaminated groundwater in practical field applications is an effective phytoremediation method and whether phytovolatilization from the poplars contributes significantly to the remediation of TCE. If so, are there are inherent risks of volatilizing TCE from poplars to the atmosphere?** This will be accomplished by examining scientific literature, analytical data, and case studies on the subject. **This thesis further provides a comparative analysis of phytoremediation using poplars and the classic remediation method of pump-and-treat technology for the treatment of TCE contaminated groundwater in an effort to identify if, why, and when phytoremediation is a superior treatment method.** This will be accomplished by comparing the two remediation methods and evaluating their cost, benefit, ease of use, site characteristic requirements, limitations, contaminant requirements, and other variables. Furthermore, the efficiency and practicality of the pump-and-treat method will be evaluated by examining data from Superfund Sites and NPL sites overseen by the EPA.

The following is a summary of the chapters contained within this thesis. Chapter 1, entitled *Chlorinated Solvents & Trichloroethylene* briefly discusses the definition, chemical properties, toxicity, and environmental prevalence of TCE and why it is an important constituent to cleanup. Chapter 2, *Phytoremediation*, discusses the various forms of phytoremediation and their applicability to environmental remediation. Chapter 3 is titled *Common Remediation Technique- Pump-and-Treat*. This chapter discusses what pump-and-treat remediation entails and focuses on the use of air stripping towers to remove TCE from groundwater. Chapter 4, entitled *Phytoremediation of Trichloroethylene*, discusses in detail how and why poplars can be used to clean TCE contaminated groundwater; the various phytoremediation mechanisms that are involved; and the efficiency of poplars. Case studies of practical field applications of this remediation method are analyzed at the end of this chapter. Chapter 5, *Comparative Evaluation of Groundwater Treatment Methods*, includes a thorough discussion on the comparison of poplar phytoremediation and pump-and-treat remediation. Chapter 6 is the conclusion of the thesis.

1.0 CHLORINATED SOLVENTS & TRICHLOROETHYLENE

1.1 Definition of Chlorinated Solvents

Chlorinated solvents, also known as halogenated volatiles or volatile organic compounds, are organic compounds that are created by at least one chlorine atom bound to a carbon atom that shares electrons with another chlorine atom. This type of electron sharing is known as covalent bonding. One organochloride subset is chlorinated hydrocarbons, which include hydrocarbons that have at least one hydrogen atom replaced by a chlorine atom [1]. Trichloroethylene, dichloroethene, and chloroform are some examples of chlorinated hydrocarbons. Given the molecular properties of make-up of these chlorinated hydrocarbons they are known as effective industrial solvents, hence the name chlorinated solvents. Chlorinated solvents are so effective because of their polar nature, making it easy for them to dissolve a multitude of other chemical compounds.

1.2 Trichloroethylene

Trichloroethylene (TCE) is a colorless, non-flammable, non-corrosive liquid with a sweet odor [2]. TCE was first developed by E. Fischer in 1864. TCE production in mass began in the 1920s when it was used in the food industry to extract oils from plants, including soy, coconut, and palm and was also used to decaffeinate coffee [3]. TCE's main use has been as an industrial degreasing solvent because it is extremely efficient at instantly stripping paint, degreasing metal parts, and can even dissolve some plastics [4, 5]. In the late 1950s TCE popularity began to decline as 1,1,1-trichloroethane was beginning to be utilized more frequently because of its less toxic nature. Nevertheless, with the implementation of the Montreal Protocol (signed in 1987 but enforced in 1989), the use of 1,1,1-trichloroethane was phased out along with other substances, including halogenated hydrocarbons, believed to be aiding in ozone depletion [6]. With the phase-out of 1,1,1-trichloroethane, TCE use began to increase once again in the 1990s. TCE production increased from 118,000 kilograms* (260,000 pounds) in 1981 to an astounding 145,150,000 kg (320 million pounds) in 1991 [4].

* kg

Over the years, TCE has also been used for other practical purposes such as a medical anesthetic, as a dry cleaning solvent, for production of ethanol, and as an extraction solvent for greases, oils, fats, waxes, and tars. TCE has also been used as an ingredient for many products including paints, cosmetics, cleaning fluids, typewriter correction fluid, removers/strippers, adhesives, spot removers, and rug-cleaning fluids [5]. TCE was used regularly as a dry cleaning solvent until the 1950s when it was generally replaced by tetrachloroethylene.

In Europe and North America from the 1930s through the 1960s TCE was used as a medical anesthetic, replacing chloroform and ether because of its cost effectiveness and quick acting nature. TCE was even used as a pain medication for women during labor in the form of an inhaler. Typical doses of TCE that were given were up to 1% (v/v) vapor.

Because of the known irreversible human health effects and environmental impacts, use of TCE as an industrial solvent has decreased significantly. Several major manufacturers ceased TCE manufacturing in the early 1980s leaving only Dow and PPG Industries as producers [7]. According to the Chemical Economics Handbook, 30,000 metric tons of TCE were used for metal cleaning and other emission sources in 2000 [8]. Because of TCE's widespread use and prolific contamination, it is an extensively researched compound [9].

1.3 Characteristics

TCE is one of the prominent chlorinated solvents because of its widespread uses. Other names that TCE is known as are trichloroethene, Trike, Tri, and a variety of trade names [4, 10]. TCE is a sweet smelling, non-flammable liquid that is typically clear in color [4, 11]. TCE structure is formed by two carbon atoms that share a double bond and three chlorine atoms [12]. Figure 1-1 depicts the chemical structure.

TCE is moderately soluble in water [11, 13]. TCE has a high vapor pressure and a low adsorption coefficient to soil [10]. As such, when TCE is released to soil, it has the potential to readily migrate through soil into groundwater. High vapor pressure is also associated with greater volatilization [14]. A high Henry's Law Constant causes TCE to readily volatilize from surface water to air [12]. TCE has moderate hydrophobicity (log k_{ow}), indicating that it is readily taken up by plant tissue [13].

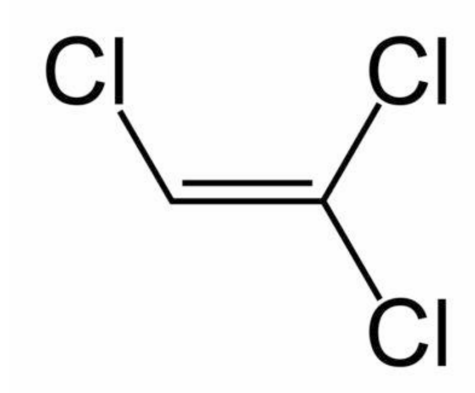

Figure 1-1 Chemical formula for trichloroethylene. Source: Wikipedia (2007)

TCE is photo-oxidized in air by sunlight (half-life of five days) giving off phosgene and dichloroacetyl chloride as byproducts [15].

Table 1-1
Physical Properties of TCE

Property	Value
Chemical Formula	$ClCH{=}CCl_2$
Molecular Weight	131.39 g/mol
Density	1460 kg/m^3
Specific Gravity	1.4642 at 20^{o}C
Solubility in water	1,000 mg/L or 2.04 mol/L at 25^{o}C
Water Partitioning coefficient	2.29
Vapor Pressure	60 mm Hg at 20^{o}C
Vapor Density	4.53
Henry's Law Constant	0.4370
Hydrophobicity (log k_{ow})	2.33

Sources: ATSDR 2003, Schnoor (1997), and Chappell (1998).

1.3.1 Half-life and Residence Time

Environmental Media Transport - TCE naturally volatilizes according to its relatively short residence time, but its half-life depends upon the medium it is within (soil, air, surface water, or groundwater). Other variables that affect the half-life of TCE are temperature, water movement, water depth, and air movement [16]. Because of its short half-life, global transport of TCE is relatively unlikely [16]; however, with the constant volatilization of TCE from emission sources and surface waters, there is a constant flux of TCE to the atmosphere. Nonetheless, TCE is maintained in the environment due to is constant use and release and because it is a breakdown product of tetrachloroethylene (PCE), which is used extensively in the dry cleaning industry and also in metal degreasing and as a chemical intermediate.

When TCE is released to surface water, it quickly evaporates and is released as vapor in the air because of the Henry's law constant. Based on the Henry's law constant, a half-life for a water depth of one meter is calculated to be 3.4 hours [17]. Although, some report that the evaporation half-life of TCE in water at room temperature is 20 minutes [12]. The main route for removal of TCE from water is through volatilization. In groundwater, TCE sticks to particles in the water and can settle to the bottom of an aquifer and thereby decreases its likelihood for volatilization (see the DNAPL section). TCE is very stable in aquifers [5].

When a dense non-aqueous phase liquid (DNAPL) is introduced to the subsurface (in the unsaturated zone), it can be distributed into four different phases: air phase (vapors), solid phase, water phase, and the immiscible phase [18]. For example, if TCE was introduced to the subsurface, it could adsorb to the soil (solid phase), volatilized into the soil gas (air phase), solubilize in the groundwater (water phase), and be present as a DNAPL (immiscible phase), thereby contaminating all four phases. This creates four different treatment issues that all must be understood and addressed. The contaminant has the ability to change phases over time, so the characteristics of the onsite contamination now may not be the same in five years. The mobility in the four phases in the unsaturated zone is extremely complex and is not discussed in this thesis.

TCE evaporates less quickly from soil and can bind with organic materials in soil because of its polar nature. The type of soil does not necessarily affect TCE's residence time. TCE does not chemically transform or undergo covalent bonding with soil particles.

Degradation - In air, TCE reacts with photochemically produced hydroxyl radicals and is photodegraded [11]. Experiments have shown that at 25ºC the half-life was 6.8 days. Other studies have derived similar results ranging from 5 to 8 days [17]. During cold months, the half-life can extend to 14 days [16]. This characteristic occurs in other mediums as well. Degradation in air showed to be temperature and season dependent.

Photodegradation in air occurs as the TCE is photo-oxidized in air by sunlight (with a half-life of five days), which gives off dichloroacetyl chloride and phosgene as byproducts [15].

A study on the aerobic degradation of TCE in seawater showed that 80% of the TCE was degraded in eight days [19]. This study indicated that the time required for degradation increases in the presence of oxygen. Another study looked at microbial degradation of TCE in domestic wastewater and reported a half-life of 7 days. During microbial anaerobic degradation in water, TCE degrades to dichloroethylene (cis-, and trans-1,2) and vinyl chloride.

Anaerobic degradation products of TCE are dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and 2,2,2-trichloroethanol (TCEt).

Toxicity of degradation products – Phosgene gas and liquid are toxic and are known as pulmonary irritants [20]. Dichloroacetyl chloride may cause autoimmune responses because of its acylating ability and may be more toxic than TCE [21, 22]. Vinyl chloride can be produced as a degradation byproduct in soil and groundwater during the anaerobic degradation of TCE. This is one of the reasons why TCE contamination of aquifers is of critical importance because of the production of the human toxicant vinyl chloride as TCE degrades under anaerobic conditions. TCAA can be phytotoxic and can be toxic to humans in large doses. TCAA and DCAA have been used as pharmacological ingredients for humans including some cancer applications [23, 24]. DCAA is not known to be carcinogenic to humans but it can be in other species (EPA IRIS, 2007). TCEt is also used for medicinal purposes in humans.

1.4 Behavior as a Contaminant in Groundwater

TCE is known as dense non-aqueous phase liquid (DNAPL) because its specific gravity is greater than water and does not easily dissolve or mix with water [25]. Specifically, TCE can migrate to the bottom of the body of water (whether it be surface water or groundwater). TCE will continue its downward migration until its volume is depleted through the saturation process or its migration is prevented by contact with an impermeable (or low permeable) layer [18]. Once the impermeable layer is reached, the

DNAPL can also migrate horizontally. DNAPL pools can serve as long-term sources of contamination because of these behaviors, even when the original source of the contamination (such as a metal degreasing facility) has been remediated. This is one of the complicated aspects of TCE as a groundwater contaminant. The principal method that groundwater becomes contaminated with DNAPL is as it flows through and around the DNAPL contaminated area. TCE's behavior is in contrast to compounds such as petroleum hydrocarbons that are less dense than water and typically float on the surface of a body of water and are termed LNAPL (light non-aqueous phase liquids).

An effective remediation technology for DNAPLs addresses the removal of or in situ treatment of the plume at the bottom of the aquifer. DNAPLs are a problematic issue to deal with because they are extremely hard to identify and locate and they are a significant limiting factor in site remediation projects [18].

1.5 Prevalence in the Environment

The potential for human exposure to TCE is potentially great due to the widespread contamination of soil and water across the country [26]. This contamination is due to the prevalent use of TCE as an industrial degreasing agent, the manufacturing of TCE, and its disposal. TCE is common in landfill leachate.

1.5.1 Water

TCE was first discovered as a groundwater contaminant in 1977. The Agency for Toxic Substances and Disease Registry (ATSDR) reported that TCE is the most frequently identified contaminant in groundwater and is present in the highest concentrations than all other groundwater contaminants [5, 11]. It has been estimated that between 9% and 34% of the drinking water supply has at least trace levels of TCE contamination, although most drinking water supplies have levels of TCE that meet drinking water standards (less than 5μg/L). The actual percentage of drinking water supplies that have levels of TCE above the drinking water standard is unknown [3, 5]. A study on California drinking water supplies identified TCE in 10-12% of the 9,331 water sources that were sampled [27]. Average detected concentrations in the California study ranged from 14.2 μg/L to 21.6 μg/L. According to the Environmental Protection Agency (EPA), 852 of the nation's 1,430 National Priority List Superfund sites have TCE as a contaminant of concern [11]. TCE has also been detected in rain water in Portland, Oregon as well as in snow in Alaska, and the open ocean [11]. These detected levels do not mean that the TCE is at levels that are hazardous levels to human health or the environment, it simply means that TCE is present, indicating a release. TCE is released to water through industrial wastewater discharge (from metal finishing, paint and ink manufacturing, electronic component manufacturing, and rubber processing) and landfill leachate [4, 11]. TCE's physical and chemical properties are what make it prevalent in the environment [12].

1.5.2 Air

Air emissions of TCE have steadily declined from 1987 through 1994 from approximately 24.7 million kg (54.5 million pounds) down to approximately 13.5 million kg (29.7 million pounds) [28]. More current air emissions data was difficult to retrieve. The major source of air releases is through industrial degreasing operations.

1.5.3 Food Stuff

TCE has also been detected in dairy products, meat, oils and fats, and vegetables [29]. Detections of TCE in food can be attributed to the use of contaminated water or absorption of TCE from the atmosphere. Concentrations of TCE was identified in British food including beef steak (3.0 μg/kg), beef fat (6.0 μg/kg), pork liver (4.0 μg/kg), and fresh bread (2.0 μg/kg) [30].

1.5.4 Disposal

The recommended disposal method for TCE waste is incineration, although in order to incinerate TCE you must first mix it with a combustible fuel [31]. TCE waste can also be disposed of in landfills. The EPA regulates the amount of halogenated volatile organic compounds that are allowed to be disposed of in landfills at no more than 1,000 mg/kg for the halogenated volatile organic compounds (HVOCs).

1.5.5 Bioaccumulation

Limited to moderate bioaccumulation of TCE in wildlife has been observed in the bluegill sunfish (bioconcentration factor of 17) and rainbow trout (bioconcentration factor of 39) [10, 17]. Bioaccumulation in plants and animals is limited because of the physical and chemical properties of TCE [17]. Typically, TCE does not bioaccumulate because it has a low octanol-water partition coefficient (a high coefficient is required, among other traits for bioaccumulation to occur) [32].

1.6 Toxicity

According to the EPA Air Toxics department, most of the TCE that is used in the United States is released into the indoor air during industrial degreasing activities [5]. Indoor air in these facilities reaches higher concentrations and is associated with the occupational exposure [5]. Most of the information on human effects of TCE exposure was derived from documented occupational exposures [3]. Occupational exposure can be decreased by the use of personal protective equipment (PPE), engineering controls, and proper workplace practices [31]. People living around factories that use or make TCE may also be exposed to ambient airborne TCE, albeit at lower concentrations due to dilution. Exposure to the general public is typically through contaminated drinking water; indoor air exposure through inhalation of vapors intruding into buildings that are located above areas of soil and groundwater contamination; exposure from anesthesia; exposure to consumer products containing TCE; and exposure to hazardous waste disposal sites containing TCE [5].

Ingestion and inhalation are the two main exposure routes. Dermal absorption of TCE is not seen as an important route of exposure, but it is still important to use protective clothing. During inhalation exposure, most of the TCE that is inhaled is immediately exhaled. The ATSDR notes that at 100 to 200 ppm of TCE humans inhale about 50% of the dose in 30 minutes [16]. The dermal permeability coefficient for humans exposed to TCE has been estimated at 0.015 ± 0.003 cm per hour, but vary based on whether the exposure is through soil or water [33]. Pulmonary and gastrointestinal absorption of TCE is rapid. Most of the TCE that enters the body is metabolized, primarily in the liver, and much is excreted from the body. In one human study, volunteers were exposed to acute doses between 54 to 140 ppm TCE and approximately 90% of the inhaled dose was metabolized within a short time frame (though the amount of time was not stated) [16]. Inhalation exposure to 100 to 200 ppm, approximately 30% to 50% of the absorbed dose was excreted in urine as trichloroethanol and 10% to 30% was excreted as TCAA. The approximate biological half-life for trichloroethanol is approximately 10 hours, while the biological half-life for trichloracetic acide is 52 hours [16].

The remaining dose of TCE that is not immediately metabolized or exhaled is spread throughout the body via the circulatory system where it circulates until it is metabolized or excreted. One key characteristic of TCE activity is that the products of TCE metabolism are the primary source of TCE toxicity [34]. The common metabolic products of TCE are chloral hydrate, trichloroethanol, TCAA, and dichloracetic acid [35]. TCE is first oxidized to chloral hydrate which is then oxidized to TCAA or to trichloroethanol. DCAA forms when TCAA is dechlorinated or from trichloroethanol [30]. Figure 1-2 illustrates the metabolic process in humans.

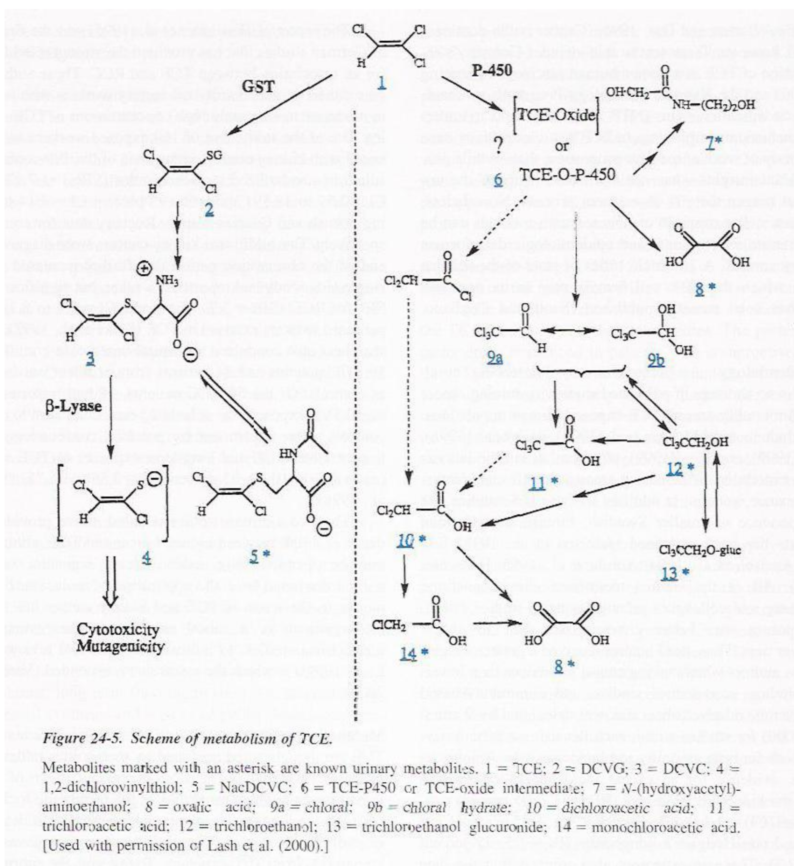

Figure 1-2 Depiction of the metabolic process of TCE in the human body. Source: Adopted from Figure 24-5 from *Toxicology* by Casarett et al. (2001).

The following paragraphs describe the various health effects that TCE has, based on the dose and duration of exposure. One cautionary note is that there seems to be quite a bit of variability in the outcome of TCE studies conducted on animals.

1.6.1 Acute Effects

The primary impact of acute inhalation exposure to TCE in in the central nervous system from exposure levels greater than 50 ppm [2]. Symptoms include burning skin and eyes, sleepiness, fatigue, headache, confusion, unconsciousness, visual disturbances, nausea, vomiting, and euphoria [5, 36]. Liver and kidney damage, as well as effects on the gastrointestinal system and skin have also been reported in acute toxicity from occupational exposure. Respiratory and circulatory system depression and even death may occur if exposure is acute. Central nervous system depression is the foremost noted effect of acute TCE exposure [16]. Acute exposure to laboratory animals has resulted in neurological, lung, kidney, and heart damage [5]. Death has occurred in workers when extremely high levels of vapors were inhaled during degreasing operations or dry cleaning operations [31]. In these cases death was due to ventricular fibrillation or central nervous system depression.

1.6.2 Chronic Effects

When TCE is inhaled it depresses the central nervous system during both acute and chronic exposure, hence its former use as an anesthetic. Symptoms occurring after chronic exposure include headaches, dizziness, sleepiness, nausea, confusion, euphoria, facial numbness, and confusion, leading to unconsciousness [5]. Some studies reviewed by the American Conference of Industrial Hygienists (ACGIH) indicated that chronic occupational exposure to less than 100 ppm of TCE resulted in a variety of nervous system disturbances [2]. As with acute exposure, chronic exposure can lead to liver, kidney, immune and endocrine system damage in humans. The EPA identifies liver damage as the predominant health effect from a lifetime of chronic exposure to levels above the MCL of 5 ppb [10]. This damage has been identified in people that have suffered an occupational exposure (over 50 ppm for 4 to 5 weeks) and in people that have consumed contaminated drinking water [5, 34]). Other health complications TCE has been linked to in laboratory studies are heart defects and fertility impairment as observed in laboratory animals. Neurological effects from chronic exposure include impaired trigeminal nerve function (blink reflex). Laboratory animals chronically exposed to 1,000 to 3,000 ppm have experienced histologic changes [16]. No increased risk of reproductive and developmental effects has been detected in human babies born to mothers exposed to TCE, but animal studies do not support this.

1.6.3 Risk to Human Health

The human carcinogenic risk posed by TCE is a highly contested subject because of the ambiguous strength of evidence that has been compiled thus far and the applicability of laboratory animal biologic data to humans. Controversy has arisen within the last five years which spurred an independent review of laboratory animal and human exposure data by the National Academy of Science. In 1999, the EPA produced a draft report summarizing a review of exposure data on TCE that concluded that TCE posed a greater risk to human health that previous studies have indicated. The Department of Defense, Department of Energy, and the National Aeronautics and Space Administration argued, in response to this draft report, that the EPA exaggerated the risk, did not use best available science to make its determinations, and ignored any data indicating that TCE was not as harmful as other studies had made it seem. Part of this reaction may have had to do with the fact that the Department of Defense owns approximately 1,400 military properties that are contaminated by TCE, while the Department of Energy owns 23 nuclear weapons complexes that are contaminated with TCE, as well as some National Aeronautics and Space Administration centers [34]. These government agencies have a vested interest in “down playing” the risk that TCE poses because of the number of contaminated properties each organization owns.

It is difficult to predict whether humans are more or less susceptible to cancer caused by TCE exposure than laboratory animals because the difference in species formation of S-(1,2-dichlorovinyl)-L-cycteine has not been adequately defined [34]. The ATSDR notes that some epidemiological studies on humans have shown carcinogenic effects with an increased incidence of stomach, liver, prostate, kidney, and non-Hodgkin lymphoma; whereas other studies did not indicate an increased incidence [16]. The EPA recognizes that there is some evidence indicating that TCE has the potential to cause cancer in people that are chronically exposed to levels above the MCL of 5 ppb [10]. The studies citing an increased risk in cancer in humans is consistent with laboratory animal study results that also noted liver and kidney cancer in rats [34] and an increase in cancer of the cervix, lungs, testes, and lymphatic systems in other animals [5].

The International Agency for Research on Cancer (IARC) lists TCE as “probably carcinogenic to humans” and the National Toxicology Program lists it as “reasonably anticipated to be a human carcinogen” [11, 37]. National Institute for Occupation Safety and Health (NIOSH) recognizes TCE as a potential occupational carcinogen. The EPA concludes that TCE is highly likely to cause cancer in humans. This tentative conclusion is supported by increased risk in workers to cancer of the kidney, liver, lymphatic system, prostate and cervix [38]. The EPA’s official carcinogen assessment for TCE has been withdrawn pending further scientific review [39].

The EPA’s inhalation Reference Concentration for chronic TCE exposure in air is 40 $\mu g/m^3$ of air and the inhalation Reference Dose (chronic) is 0.011 $\mu g/m^3$ of air; however this data has not been published on the EPA’s Integrated Risk Information System (IRIS) database [38, 40]. The dermal Reference Dose (chronic) is $4.5x10^{-5}$ ppm/day and the oral Reference Dose (chronic) is $3.0x10^{-4}$ ppm/day [40]. A reference dose refers to an estimation of the dose that a human can be exposed to that likely will not increase the risk of health effects over a lifetime. The ATSDR has calculated the minimal risk level (non-cancerous) for inhalation of TCE as 0.1 ppm or 0.5 mg/m^3, based on studies showing the chronic neurological effects in laboratory rats [5]. The minimal risk level is a calculation of the daily allowable level of exposure to humans that will likely not result in a non-cancer health impairment over a specified period of exposure. The permissible exposure limit is the legal amount of a toxicant that an employee can be exposed to during an 8 hour work day. For carcinogenicity risk, the EPA has reported that drinking water with 1 ppm of TCE over a lifetime will cause 32 humans out of 100,000 to be at risk for cancer [41]. All of the reference doses are much lower than this concentration and thus are adequately protective.

The fate of TCE in the environment is of great concern because one of its anaerobic breakdown products, vinyl chloride, is more toxic than the parent compound and is a more potent human carcinogen. For example, the EPA drinking water standard for vinyl chloride is 2 ppb (TCE is 5 ppb). The EPA has reported that drinking water with 1 ppm of vinyl chloride over a lifetime will cause 9,570 cases of cancer out of 100,000 people [41].

1.7 Regulations

Because of the health effects of TCE exposure, strict worker exposure regulations are in place. OSHA has put into effect a limit for worker exposure at 100 ppm in the air for an 8-hour workday, 200 ppm not to be exceeded during any 15 minutes during the work day, and 300 ppm for any five minutes in any 2-hour work period [42]. NIOSH recommends airborne exposure not to exceed 25 ppm in any 10-hour work period. The American Conference for Industrial Hygienists (ACGIH) recommends airborne exposure not to exceed 50 ppm in an 8-hour work period and 100 ppm as their short-term limit [36]. The legal worker exposure limit is regulated by OSHA and the limits provided by other entities are recommendations. According to the Scorecard.org (2005) TCE is listed on a number of federal regulatory databases including the following:

- Air Contaminants (Occupational Safety and Health Administration)
- Hazardous Air Pollutants (Clean Air Act)
- Hazardous Constituents (Resource Conservation and Recovery Act)
- Hazardous Substances (Superfund)
- Maximum Contaminant Level (Safe Drinking Water Act)
- Priority Pollutants (Clean Water Act)
- Registered Pesticides (Federal Insecticide, Fungicide, and Rodenticide Act)
- Toxic Release Inventory Chemicals

The Safe Drinking Water Act was created in 1974 in an effort for the EPA to set safe levels for chemicals in drinking water. Most of the "safe" levels are based on information about the possible health risks that are associated with each chemical and are called Maximum Contaminant Levels (MCL). The MCL for TCE is 5 parts per billion (ppb). However this is based on the lowest level of TCE the EPA feels that municipal water systems can achieve using current technology, and not on the fact that this level is considered safe [4].

The Clean Air Act (amended in 1990) is a guideline for air pollution control and sets emission limits for some substances deemed as hazardous air pollutants. TCE is one of those substances [43]. Amendments in the Clean Air Act require specific industries that emit TCE to implement emission controls to greatly reduce their total emissions.

The Resource Conservation and Recovery Act (RCRA) has regulated TCE as a spent solvent process waste and as a characteristically toxic waste [44]. This means that sites that have TCE contamination must adhere to specific regulations about how to dispose of TCE and TCE contaminated media. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) has regulations requiring the reporting of spills and leaks of TCE greater than 45 kg (100 pounds), which equals approximately 8 gallons [44].

2.0 PHYTOREMEDIATION

Phytoremediation is a relatively new term that was coined in 1991, which literally means plant (phyto) cure (remedy) [45]. The term phytoremediation refers to a set of mechanisms used by plants to remove contaminants from soil and water [46]. Certain aspects of phytoremediation have been practiced in Europe and the Middle East for centuries as a means to buffer streams from agricultural contamination, but the principles didn't gain popularity in the United States until the mid to late 1990s [47]. Phytoremediation is a remediation technique that specializes in removing, degrading, immobilizing, or stabilizing contamination in soil, sediment, sludge, groundwater, or surface water by using living plants [45, 47-49]. The remediation can be conducted in situ or ex situ, although most of the phytoremediation techniques deal with in situ remediation [49].

Since the 1990s considerable research and method development has occurred in the general phytoremediation field that draws upon technical knowledge from the environmental, agricultural, silviculture, and horticulture fields [45]. Nevertheless, it is a relatively new remediation technique as compared to other techniques that have been used for multiple decades at a multitude of contaminated sites. Phytoremediation has shown to be effective in laboratory and greenhouse studies, at numerous brownfields, a site at Chernobyl, as well as some military installations, just to name a few [13]. Phytoremediation is unlike other remediation techniques because it can not used in an "off the shelf" manner, rather the phytoremediation system is tailored to specific site conditions such as the types and levels of contaminants, the media that is contaminated, site soils, remediation goals, and groundwater characteristic [47]. Furthermore, phytoremediation is an aesthetically pleasing, less invasive and natural way to cleanup contaminated sites [9, 14, 46]. Phytoremediation is also seen as a viable alternative because of the cost savings that are involved [46, 50, 51].

The types of contaminants that can be treated include petroleum hydrocarbons, pesticides, explosives, heavy metals, radionuclides, solvents, polycyclic aromatic hydrocarbons, landfill leachates, and chlorinated volatile organic compounds (like TCE)

[48, 49]. More contaminants that can be treated by phytoremediation may exist, but the current body of evidence is limited to those listed above. As research progresses in this subject, the extent of its use in relation to contaminants will expand.

2.1 Phytoremediation Methods

The general process of phytoremediation includes the uptake of contaminants from soil or groundwater; the transformation of the contaminant by the plant; and the physical control over migration of the contaminant by the plant [13]. The type of contaminant that is present on a site and the medium(s) that is contaminated are the driving force for the type of phytoremediation that is preferred. Organic contaminants can be phytoremediated using phytostabilization, phytoextraction, phytovolatilization, rhizosphere degradation, rhizofiltration, phytodegradation, and hydraulic control [46, 49, 52]. Inorganic contaminants can be phytoremediated using phytoaccumulation, phytoextraction, rhizofiltration, phytovolatilization, phytostabilization, and hydraulic control [49]. The mechanisms involved in the remediation process include up-taking contaminants into plant tissue, adsorbing or absorbing contaminants to plant roots, degrading contaminants with microbes or enzymes, transpiring volatile contaminants, immobilizing contaminants in soil, or controlling the migration of contaminants in groundwater. Table 2-1 lists all of the phytoremediation processes, the types of contaminants they have successfully remediated, and the medium in which they work.

The following sections include a brief description of how each particular process of remediation works, the medium in which it works, and the types of contaminants it can effectively[†] remediate based on laboratory studies, the types of plants that can perform the process, and the specific advantages and disadvantages related to the process. Some of the phytoremediation processes sound similar (for example rhizofiltration and phytostabilization) and involve similar concepts but there are differences between them, thus the independent categorization.

[†] Most contaminants have been shown to be effectively remediated in laboratory studies while a few have been shown in field studies. Accordingly, it is not safe to assume that laboratory studies have proven effectiveness as some laboratory results have not been successfully replicated in the field.

Table 2-1 Phytoremediation Processes

Removal Process	Contaminant	Medium
Phytoextraction	Metals	Soil, Sediment, Sludges, Water (occasionally)
Phytodegradation	VOCs[‡], Pesticides, Petroleum Hydrocarbons, Explosives	Soil, Water, Sediment, Sludges
Rhizosphere Biodegradation	Pesticides, Petroleum Hydrocarbons, Polyaromatic Hydrocarbons, Polychlorinated Biphenols	Soil, Sediment
Rhizofiltration	Metals, Hydrophobic organic chemicals, Radionuclides	Water
Phytovolatilization	VOCs, mercury, selenium, arsenic	Water, possibly for soil, sediment, sludge
Phytostabilization	Metals, Hydrophobic organic chemicals, Phenol, VOCs	Soil
Hydraulic Control	VOCs, Petroleum Hydrocarbons, Metals, Landfill Leachate, Pesticides	Water
Vegetative Cover	All	Soil, Water
Riparian Corridor	Nutrients, Pesticides, Water soluble organics, inorganics	Water

2.1.1 Degradation Mechanisms

The following are processes of phytoremediation that have to do with the degradation of the contaminant due to specific characteristics of the plant. The degradation can occur within the plant tissue or within the root zone of the plant.

2.1.1.1 Phytodegradation

Phytodegradation, also known as phytotransformation, is the degradation of contaminants through metabolism within plant tissue or external to the plant by the excretion of enzymes by the plant (exudates) [45, 48, 49]. This process does not include the breakdown of contaminants by microorganisms (see rhizosphere biodegradation).

[‡] VOC stands for volatile organic compound.

Phytodegradation also includes the mineralization of contaminants [46]. The metabolic activity is identified when known metabolites of specific contaminants are found within the plant tissue. The break down products of the pollutants are incorporated by the plant tissue and used as nutrients, or are re-released into the environment [45, 49] which may cause secondary contamination. Phytodegradation has been shown to be effective in removing contaminants from sediment, sludges, soil, groundwater and surface water [45].

Phytodegradation (Figure 2-1) is most effective in large land areas that have relatively shallow contamination. Groundwater that is within reach of tree roots can be effectively remediated as well as groundwater that is mechanically pumped to the surface and used for irrigation. Phytodegradation is not necessarily climate dependent as it has shown to be effective in a variety of climatic conditions, as long as the plants that are used are appropriate for the site's climate.

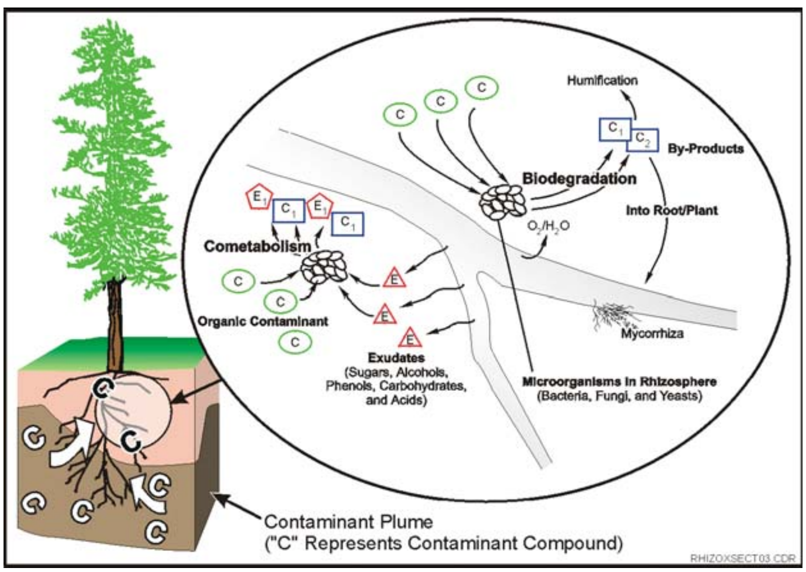

Figure 2-1 Phytodegradation Process. This figure depicts the phytodegradation process in trees. Source: ITRC (2001)

The uptake of contaminants by the plant is necessary for degradation to occur and is dependent upon the hydrophobicity, solubility, polarity, and concentration of the contaminant as well as the uptake efficiency and transpiration[§] rate of the plant [13, 45]. Those organic contaminants with moderate hydrophobicity (log k_{ow} between 0.5 and 3.0) are most readily taken up by plant tissue and are efficiently removed. Moderate

[§] Transpiration is defined as the movement of water by plants to the atmosphere (Ma and Burken, 2002).

hydrophobic contaminants that can be phytodegraded are BTEX (benzene, toluene, ethylbenzene, and xylenes), chlorinated solvents, and aliphatic chemicals [13]. Hydrophobic contaminants that are also lipophilic can sorb to plant roots but can not be taken in by plant tissues. Very hydrophobic chemicals (log k_{ow} >3.5) tend to bind so strongly to root surfaces that they can not be translocated within the plant tissue [13]. Very soluble contaminants (log k_{ow} <1) tend to have low sorption and tend not to sorb to plant roots or be taken within the plant tissue. And finally, polar contaminants can be taken in by plant tissue whereas non polar (those with molecular weights less than 500) will only sorb to root surfaces [45].

Other conditions affecting the relative uptake of a contaminant are the type of plant being used, the depth of the roots and the properties of the exudates from the roots, the age of the contamination, and other physical and chemical characteristics of the soil. Unfortunately, the uptake and translocation of contamination into the aboveground portions of plants is highly variable. Both aquatic and terrestrial plants can be used for phytodegradation [49].

Organic contaminants are the main targets for phytodegradation. One study identified over 70 organic contaminants that were absorbed by and accumulated in plant tissue by 88 plant species (Paterson et al. 1990 in Adams et al. 2000). Organic contaminants include explosives, pesticides, halogenated compounds and chlorinated solvents (TCE), phenols, and nitrites. Metabolism of contaminants within plant tissue has been identified with atrazine, TCE, trinitrotoluene (TNT), dichloro-diphenyl-trichloroethane (DDT), hexachlorobenzene, pentachlorophenol (PCP), polychlorinated biphenyls (PCBs), and diethylhexylphthalate [49]. Of inorganic compounds, only nitrate was identified as being able to be phytodegraded. Nitrate can be taken up by plants and metabolized as proteins and volatilized as nitrogen gas [45].

Examples of phytodegradation include the following: Alfalfa degradation of TCE and TCA through exudates that stimulated bacteria; legumes, Loblolly pine, and soybeans mineralization of TCE; minced horseradish roots "successfully" treatment of 2,4-dichloophenol contaminated wastewater (850 ppm); reduction of chlorinated phenols in wastewater because of the plant exuded enzyme oxidoreductase, into the water; poplar metabolism of atrazine; and parrot feather decrease of TNT in soil from 128 to 10 ppm, partially through the plant exuded enzyme nitroreductase [45].

The bulk of research and field studies have been conducted at Army Ammunition Plants. Research has been concentrated in the laboratory and greenhouse and very few field applications have been documented [13].

2.1.1.2 Rhizosphere Biodegradation

Rhizosphere biodegradation (also referred to as rhizodegradation, phytostimulation, and plant-assisted bioremediation) is the process of degradation of organic contaminants in rhizosphere soil through microbial activity caused by the presence of the plant roots [45, 49]. The rhizosphere is the zone at the root-soil interface where there is an increase in microbial activity [48]. The degradation results in the formation of byproducts or the mineralization of the parent product [53]. The degradation is due to the increased microbial activity of yeast, fungi, and/or bacteria propagated by the addition of organic material, the release of enzymes, and other nutrients provided by the plant roots [13, 49, 54]. The relationship between rhizosphere microbes and plant roots is symbiotic in that they each provide life-sustaining properties to one another [54]. Microbial activity in the rhizosphere soil has been measured at one to two orders of magnitude greater than in non-rhizosphere soil [45]. Even in soil contaminated with BTEX, propanil herbicide, PCBs, and 2,4-D herbicide, greater numbers of degrading bacteria were found in the rhizosphere than non-rhizosphere soil. Bioremediation, a distinctly different process often confused with phytoremediation, refers to remediation of a contaminant by microbes (whether naturally occurring or artificially introduced) and does not necessarily involve the presence of plants.

Organic material from the plant includes old roots as well as substances released by the roots (exudates) such as sugars, sterols, nucleotides, flavanones, enzymes, alcohols, and acids [45, 49]. The buildup of organic material in the rhizosphere slows organic chemical transport since the chemicals are attracted to organic material [13] and provides habitat for microbes, oxygen and water to the rhizosphere which in turn increase aerobic degradation of the organic contaminant and microbial mineralization rates. Fungi provide an additional pathway for degradation of organics that can not be done by bacteria in the absence of fungi [13]. Rhizosphere biodegradation has been studied in laboratories, greenhouses, and several field studies [45].

Soil properties must allow for root penetration and growth. Rhizosphere biodegradation can be successful in humid, arid, to cold conditions as long as the plants that are chosen appropriately [45].

Contaminants that can effectively be treated through rhizosphere biodegradation include petroleum hydrocarbons, some solvents, polyaromatic hydrocarbons (PAHs), BTEX, perchlorate, atrazine, alachlor, polychlorinated biphenyl, and other organic compounds [45, 49] to break-down products that are less harmful to humans and the environment. Pesticide contaminated agricultural soils were the first type of soils where rhizosphere biodegradation was studied [45]. In order to evaluate rhizosphere biodegradation several field studies compared vegetated soil spiked with various contaminants to degradation in un-vegetated soil and showed that greater numbers of degrading bacteria in the rhizosphere than non-rhizosphere soil indicating that in the root zone of plants, biodegradation increased. Mineralization rates of pyrene, TCE, PCP, surfactants, parathion and diazinon were also greater in rhizosphere soil than in non-rhizosphere soil. Microbial population enhancement in contaminated soil that is planted with vegetation versus contaminated soil that was un-vegetated was also shown in the following cases: rice (*Oryza sativa L.)*, through increased production of rhizosphere bacteria, readily transformed propanil. Cattails (*Typha latifolia)* and hybrid poplar trees also aided in rhizosphere bacteria proliferation because of exudates excreted by the plants [55]. Legumes (*Lespedeza cuneata (Dumont))*, Loblolly pine (*Pinus taeda (L.))*, and soybeans (*Glycine max (L.))* mineralized TCE more than in non-vegetated soil.

2.1.2 Extraction Mechanisms

Extraction mechanisms are those involving plants that sequester the contaminant from a contaminated medium, but it does not involve the break-down of the contaminant.

2.1.2.1 Phytoextraction

Phytoextraction (Figure 2-2), also known as phytoaccumulation or phytomining, involves the uptake of predominantly metal contaminants by plant roots and the translocation in the above-ground portions of the plant, its shoots and leaves [13, 45, 46, 48, 49, 56]. Phytoextraction is typically used to remediate soil, sediment, or sludges, but can sometimes be used with contaminated water as well [45].

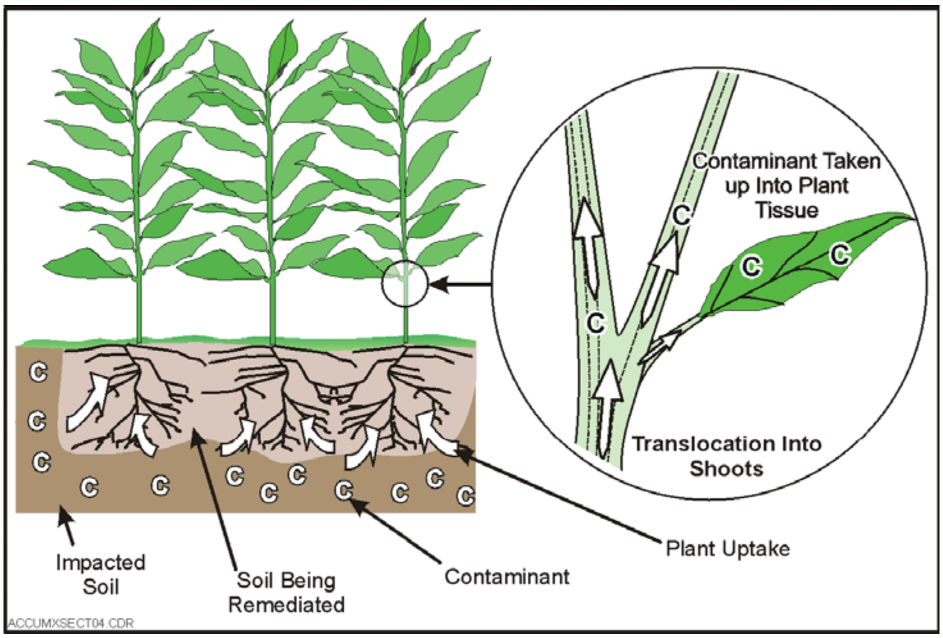

Figure 2-2 Phytoextraction Process. This figure depicts the phytoextraction process in plants. Source: ITRC (2001)

The depth in soil that is most readily affected by phytoextraction is often the top one foot, or the immediate zone that is influenced by roots [45]. The zone of immediate influence is so shallow because often the metal accumulating non-woody plants do not have deep roots.

The plants are harvested periodically (weeks or months) and must be disposed of because contaminants build up in their tissue and because of a diminishing up-take rate [46]. The cycle of planting and harvesting plants may need to be repeated several times in order to bring down the contaminant concentrations in the soil. This method of phytoremediation creates waste, but this is lower compared to remediation by excavating contaminated soils.

Typical disposal methods are landfilling, incineration, or composting but when the metals can be recycled, the biomass used for firewood or mulch [49]. Plants involved in phytoextraction and rhizofiltration may require further treatment before disposal to prevent leaching and secondary contamination [45]. Testing of the plant for levels of contamination prior to disposal must occur in order to determine whether the plant is considered hazardous waste (which is a regulatory determination) and whether the contaminants are likely to leach from the plant [49]. These factors will influence the type, location, and cost of disposal.

Phytoextraction has been more effective at remediating inorganic compounds that are readily bioavailable[**] such as nickel, zinc, cadmium, arsenic, copper, and selenium [13] than for less bioavailable metals such as lead, chromium, and radionuclides [45, 49]. The level of metal accumulation depends both on the metal type and the plant. Metals accumulated in the plant can occasionally be re-used. For example, plants containing selenium have been sent to areas that are selenium deficient and used for animal fodder [45].

Hyperaccumulating[††] plants are typically found in the Brassicaceae (Indian mustard), Euphorbiaceae, Asteraceae, Lamiaceae, or Scrophulariaceae families [45]. Fast growing crop plants with larger biomass such as corn, sorghum, and alfalfa (*Medicago sativa)* may even be more effective than hyperaccumulators at removing a larger amount of metals. More effective hyperaccumulators are plants that accumulate the metals in the aboveground, harvestable portion of the plant rather than in the roots so that the metal containing portion of the plant can be easily removed during harvesting [13]. In order to achieve cleanup levels within three to five years, the plant must accumulate up to ten times the amount in the soil [13].

Phytoextraction has proven effective at a Brownfield site in Trenton, New Jersey that had lead contaminated shallow soils. After one year, approximately 50% of the lead had been removed from the soil reaching cleanup standards of 400 mg/kg. This site used *Brassica*

[**] Bioavailability is the degree of ability of something to be absorbed and ready to interact in organism metabolism.
[††] Hyperaccumulation refers to plants that accumulate high levels of metals to a specified concentration or to a specified multiple of the concentration found in other adjacent plants.

juncea, a plant in the mustard family [13]. In comparison, excavation of contaminated soils for disposal at a landfill can take weeks or months to complete, depending upon the size of the area and the depth of contamination.

2.1.2.2 Rhizofiltration

Rhizofiltration occurs when contaminants that are in solution in groundwater adsorb or precipitate onto plant roots or are absorbed into the plant roots [13, 46, 49]. Some metals may precipitate on roots because of exudates from the plant [45]. Algae and bacteria on the plants can sorb contaminants as well. Rather than being planted in soil, plants used for rhizofiltration are raised hydroponically[‡‡]. Contaminated water is either pumped passed the roots of the plants or the plants are floated on top of pools of contaminated water. As with phytoextraction, plants used for rhizofiltration may need to be harvested and disposed of after accumulating contaminants from the water [45].

The Root Concentration Factor, the ratio of contaminant in roots to the concentration dissolved in soil water (µg/kg root per µg/L), is important in estimating the amount of the contaminant that can be sorbed to plant roots [13] and how effective the current phytoremediation system is. Each contaminant has its own Root Concentration Factor, which can be compared to values measured in the field.

The contaminants that can effectively be remediated by this process are hydrophobic organic chemicals, heavy metals (lead, cadmium, copper, nickel, zinc, and chromium), and radionuclides [49]. This method is not effective in soil because the contaminants must be in solution [45]. According to Adams et al. (2000) rhizofiltration has successfully been used at U.S. Department of Energy sites for remediation of radionuclide contaminated water.

2.1.2.3 Phytovolatilization

Phytovolatilization (Figure 2-3) is the uptake of a volatile contaminant from water into a plant's transpiration stream (which is the pathway that water moves through) and

[‡‡] Hydroponic plants are grown with their roots in water, in the absence of soil.

transmission of the contaminant or its degradation products into the air through plant transpiration [13, 45, 46, 48, 49]. In the case of volatile metals such as mercury and selenium, the metal is taken-up, speciated into organic or inorganic forms, and then transpired [49]. Transpiration is a component of a tree's natural growing process of taking in water and nutrients from the soil and groundwater and emitting water vapor to the atmosphere. Transpiration is key in determining the rate of contaminant uptake and it depends upon plant type, leaf area, nutrients, soil moisture, temperature, wind, and relative humidity [13, 56]. Transpiration is also influenced by climate and the availability of water [50]. Typically, transpiration of water vapor (and contaminants) is through the stomata in leaves, but sometimes it occurs through the stem or trunk as well. Compounds with vapor pressure of greater than 0.01 atmospheres (atm) are volatilized and the amount that is volatilized is directly proportional to increasing vapor pressure [9]. Phytovolatilization often occurs along with phytodegradation. Thus far, phytovolatilization has been used primarily for the treatment of contaminated groundwater, but may be applicable to soil, sediment, and sludge as well [45].

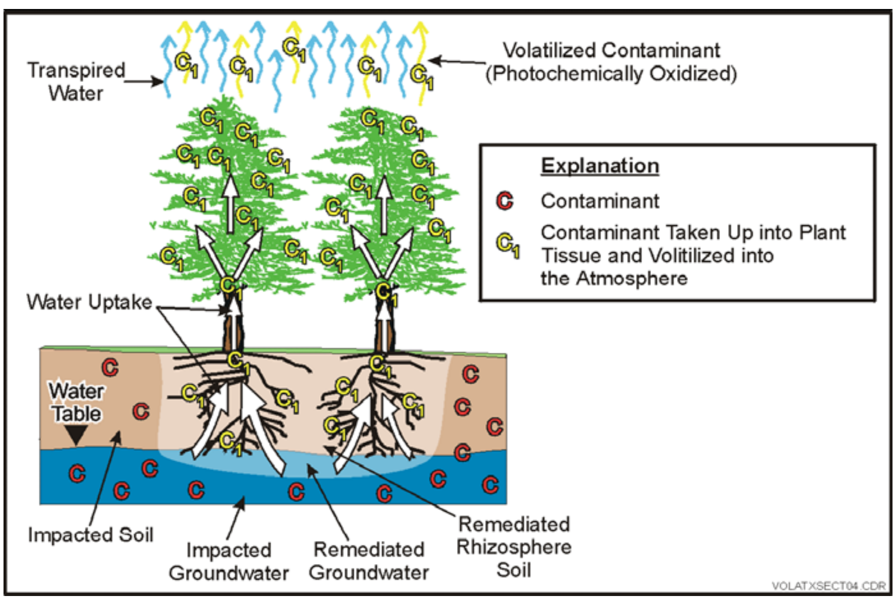

Figure 2-3 Phytovolatilization Process. This figure depicts the phytovolatilization process in trees. Source: ITRC (2001).

Site conditions that are most desirable include soil that is able to readily transmit water to the plant roots; contaminated groundwater located within the zone of influence by the plant roots; and climatic conditions that favor high transpiration rates [45]. Unlike other phytoremediation methods, the contamination does not have to be within the rhizosphere because trees can cause groundwater to flow into the root zone of influence in effect creating a larger zone of influence around each tree. This is also why trees are sometimes referred to as solar powered water pumps.

Phytovolatilization has been effective with such volatile organic compounds as chlorinated solvents (TCE, TCE and carbon tetrachloride), BTEX, methyl tert-butyl ether (MTBE), as well as mercury, selenium [45, 49, 52] and arsenic. The problem with using phytovolatilization with these metals is the formation of volatile methylated species that can be more toxic than the original form [45].

One field study investigating the remedial properties of canola in selenium contaminated water with concentrations ranging from 100 to 500 ppb indicated that phytovolatilization was one of the successful phytoremediation techniques [45]. Some plants have even been genetically engineered to be more effective at phytoremediation. Banuelos et al. (1997, cited in [45]) showed that engineered plants were able to withstand mercuric ion contamination up to 20 ppm and were able to change the mercuric ion to metallic mercury which was then volatilized from the plant. An interesting side note, when reproduced and grown naturally, the plants used in the above study experienced phytotoxicity (death of the plant when exposed to extremely high doses of contaminants) when exposed to levels of mercuric ion between 5 and 20 ppm; whereas the genetically engineered forms of these plants were able to tolerate higher concentrations.

2.1.3 Containment and Immobilization Mechanisms

Containment and immobilization involves processes that bind the contaminant to the soil, interrupt the contaminants transport mechanisms, or causes the contaminant to no longer be bioavailable [45].

2.1.3.1 Phytostabilization

Phytostabilization refers to the process of immobilizing contaminants within soil by plant roots, thereby decreasing or preventing contaminant migration via wind, water, leaching, and soil dispersal [45, 46, 49]. The immobilization can be achieved in a variety of ways including absorption of the contaminant into the root; adsorption onto the outside of the roots; precipitation of the contaminant in the root zone; and by the roots mechanically stabilizing the soil [45, 49]. The main difference between phytostabilization and rhizofiltration is the contaminated media that is being remediated.

The containment of the contaminant in the root greatly reduces its impact on human health and the environment. Part of the immobilization process is how plants can affect pH, soil gases, and redox conditions and thereby change the contaminant chemistry [45, 49] such as metal solubility and the up-take ability of the contaminant.

The mere presence of live plant roots in the soil aids in the prevention of soil erosion by physically holding the soil grains together and prevent erosion that can cause the contamination to spread to other areas, depending upon whether the soil is eroded by surface water, by wind, or by mass movements of soil (landslides)[46]. This method also prevents leaching to groundwater. In order for phytostabilization to be effective the soil must be heavy-textured and high in organic matter, and contain enough water for growing the desired plants [45]. Growing the appropriate plants requires specific climatic conditions including adequate precipitation that support those plants.

This method has been effective during remediation of heavy metals, phenols, chlorinated solvents (trichloromethane and tetrachloromethane), and hydrophobic organic compounds [49]. This is an ideal method for metal contaminated soil where typically the best form of remediation is just to keep the contaminants in place and has been used in many mining applications [13]. Typically, hydrophobic contaminants are bonded too strongly to soil and roots to actually be absorbed by the plant into tissue. Mercury has been the optimum metal for phytostabilization, while arsenic and cadmium tend to be taken in by the plant tissue (which is to be avoided during phytostabilization) because of their similarity to plant nutrients phosphate, calcium, and zinc. As an exception, poplar leaves tend not to accumulate the metals.

2.1.3.2 Hydraulic Control

The process of hydraulic control involves the use of trees to contain or control the migration of contaminant plumes in groundwater by removing the groundwater and contaminants through their roots for consumption [45, 48, 49, 57]. Research has indicated that phreatophytic trees can draw in enough water to create a localized cone of depression in the aquifer. The cone of depression causes the water to flow toward the tree, thereby hydraulically controlling the spread of the contaminant plume in the water [48, 49].

A basic concept for phytoremediation of groundwater is that plant uptake must be as fast as the groundwater movement in order to prevent the contaminated water to migrate past the zone of plants. Along the same lines, it has been documented that the faster the groundwater flow, the larger the plants need to be, and the denser the plants should be planted [45]. Other names for hydraulic control include phytohydraulics or hydraulic plume control [45]. Hydraulic control is often used in concert with other phytoremediation methods. Hydraulic control a critical component to phytoremediation of groundwater because it helps contain a plume of contamination, and prevents it from migrating down gradient, thus protecting further groundwater resources, and most importantly drinking water, from getting contaminated. Even though trees consume the water they return it back to the hydrologic cycle when they emit it through their leaves as water vapor. In theory this closes the loop for aquifer recharge.

The zone of influence around roots is the groundwater below and up-gradient from the plant roots, as well as water that is drawn upward above the water table in the capillary fringe. The depth of roots depends upon the type of plant that is used (trees have deeper roots than herbaceous plants) and how deep the root ball is placed in relation to the elevation of shallow groundwater [45].

The effectiveness of hydraulic control depends on groundwater depth and concentration of contaminants; soil texture and degree of saturation at the site; hydraulic conductivity and transmissivity[§§]; planting materials and techniques that extend the depth that roots can reach; and transpiration rates that in turn depend on the size of the tree and its maturity, precipitation rates, temperature, density of plants, and wind [45].

The types of contaminants that can effectively be contained are water-soluble, leachable organic and inorganic compounds such as chlorinated solvents, petroleum hydrocarbons, landfill leachate, heavy metals, nutrients, and pesticides [45]. Poplars, cottonwoods, willows and other phreatophyte trees have been used for this application [45, 48] because their roots have the ability to reach through the soil into the upper reaches of aquifers into shallow regions of contaminated groundwater, and because of the large volumes of water they transpire. Phreatophytes are also native throughout most of the country [13]. Other plants that have been used include alfalfa and some grasses [45].

Water uptake rates reported in the literature were highly variable likely because of seasonal, climate, species, age, and site specific variations or even the difference between laboratory, greenhouse, or field studies. Therefore, it should be noted that it is difficult to determine average uptake rates. Estimates varied from 2 liters per day per tree up to 100-200 liters per tree per day for young trees [45]. Transpiration rates for mature trees range from 750 liters up to 1,500 liters per tree per day or up to approximately 3,750 liters per year per tree (600 to 1,000 gallons of water per tree per year). Another estimate for mature trees was36-60 inches of water per year for an area planted with 1500 trees per acre [13] In contrast, hardwoods use approximately half the amount of water that phreatophytes do [13] and thus are not as desirable for hydraulic control. According to Schnoor (1997), the practical maximum for uptake in a phytoremediation system with complete canopy cover is two meters of water per year.

In order to determine the fate or transport of the contaminant in groundwater, one must determine groundwater flow direction and flow velocity. A capture zone calculation determines if the hydraulic control will effectively arrest the plume of contaminants, and takes into account that organic contaminants are taken-up at different concentrations than other contaminants in the soil or groundwater ("transpiration stream concentration factor"

[§§] The capability for the thickness of an aquifer to transmit water.

[TSCF]]) due to membrane barriers at the root surface. The capture zone calculation determines the uptake rate of the contaminant in milligrams per day [13, 56], and requires the following variables[58]:

- U represents the uptake rate of the contaminant (mg/day);
- Transpiration stream concentration factor (TSCF) also known as the efficiency of uptake;
- Transpiration rate of vegetation (T) in liters per day (L/day); and
- Aqueous phase concentration in soil water or groundwater (C) in milligrams per liter (mg/L).

$$U = (TSCF)\ (T)\ (C)$$

If the plume is not entirely taken-up by the vegetation, the plume that emerges on the other side of the vegetation will be evapoconcentrated, meaning that the mass of contaminant inside of the plume will be smaller due to the uptake of water by the vegetation but the concentration will be greater (because water volume is lower) [13].

2.1.3.3 Vegetative Cover

Hydraulic control of water also includes using vegetation as a cap for soil. This method relies on the evapotranspiration[***] and phytoremediation properties of plants as well as utilizing the plants to minimize the amount of surface water infiltration that can leach contaminants from the soil into groundwater [45]. A vegetative cover typically requires minimal maintenance. Some landfills and other waste disposal units may use vegetative cover, but not all. They can be used for prevention of surface water infiltration as well as the treatment of soil, sediment, and sludge. Vegetative cover is of two different types: Evapotranspiration Cover and Phytoremediation Cover.

Evapotranspiration cover utilizes the water storage capacity of soil and the evapotranspiration process in plants to minimize water infiltration through the vegetative

[***] The evaporation and transpiration properties of plants.

cover. The cover essentially acts as a cap to keep in place any contaminants that are below and prevents any precipitation or surface water from infiltrating through the soil and potentially mobilizing contaminants. In order to be effective, evapotranspiration cover relies on a thick, monolithic unit of soil that can efficiently trap water from downward migration until it can be drawn out of the soil by the plant for transpiration [45].

Phytoremediation cover is one that is similar to the evapotranspiration cover, except that another goal is to simultaneously degrade the underlying contaminants. The mechanisms that are involved in the phytoremediation cover process are water uptake, microbial degradation, and plant metabolism. Phytoremediation cover integrates aspects of hydraulic control, phytodegradation, rhizosphere biodegradation, phytovolatilization and phytoextraction.

In general, the goals of vegetative cover systems are to prevent exposure of contaminants to humans or wildlife; prevent infiltration of water into the contamination below; minimize maintenance; and prevent gas that is generated in the subsurface to migrate to the surface [45].

Vegetative cover is more effective with poplar trees and grasses; soil of high water storage capacity, such as a mixture of clays and silts, and soil thickness; and with a water table that is not as high as to reduce the soil's water holding capacity. Soil layers may need to be thicker in arid and semi-arid regions. High precipitation at a site requires more soil water storage capacity [45].

2.2 Duration for Cleanup

A calculation may be completed in order to estimate the uptake rate of the contaminants (shown in section 2.1.3.2) and another calculation can determine how long it may take to achieve cleanup of a known action level. The full equations can be found in Schnoor (1997). These equations are just estimates and should only be used as approximations since the true cleanup time is highly variable based upon site specific conditions and their interaction with contaminants. The equations require data on the contaminant uptake rate, the initial mass of the contaminant, time, and the mass of the contaminant at its cleanup level.

2.3 When is Phytoremediation Appropriate?

In order to determine whether phytoremediation is an appropriate means for remediation, the site characteristics must be evaluated. In general, it has been determined that phytoremediation is most appropriate at sites that have the ability for plant growth that encompass a large land area that have widespread low to moderate levels of contamination at depths within the root zone [41, 45]. Phytoremediation is not appropriate for sites that have discrete pockets of contamination or areas with high contamination. In these cases, more traditional remediation methods should be employed. General site conditions, contaminant profile, soil characteristics, groundwater characteristics, and the local regulatory requirements must be determined in order to identify which phytoremediation method can be used [48].

The following conditions set the conceptual framework for determining whether phytoremediation is possible, and allow landscape architects to tailor the phytoremediation project to fit the exact site conditions.

Site layout - allows an understanding of what is currently developed on the site, where the contaminant boundaries are in reference to site features, property boundaries, and whether there is enough land available for planting.

Hydrogeological data - allows a conceptual idea of subsurface water conditions such as the type of aquifer present (confined or unconfined), groundwater recharge rate, groundwater flow direction and velocity, and seasonal fluctuation of the groundwater levels.

Meteorological/climatological data - allows the determination of plant types will survive the weather experienced at the site and the potential evapotranspiration rates for the plants. Precipitation, air temperature, soil temperature, wind, solar radiation, and relative humidity all factor into the evapotranspiration rates of the plants [48].

Structure and condition of site soils - determine which plants can be used and which phytoremediation technique should be employed. For example, silt and clay soils are excellent for vegetative cover and for phytostabilization you need heavy-textured and highly organic soils [48]. The soil pH must be monitored throughout the remediation process [48] because it will affect the contaminant absorption as well as the plant's ability to grow. If soil pH or nutrients are not adequate for plant growth, soil amendments may be necessary. The water content and holding capacity of the soil determine how much water can infiltrate the soil and be stored before being taken in by plants [48]. The content of the water in soil will also affect the rate of phytoremediation [45].

Contaminant profile - allows for an understanding of the type of contaminant(s) that are present and how they behave in the environment. The most important determination is whether the contaminant is organic or inorganic because some of the phytoremediation methods are fairly specific as to whether they can remediate both types of contaminants or just one. It is also beneficial to know how the contaminant degrades, if degradation byproducts are created, and whether or not those byproducts are more toxic than the parent contaminant. If a byproduct is considered more toxic than the parent contaminant, than it may be required to monitor and/or control the release of the byproduct.

Depth and degree of contamination - are also critical defining factors. If contaminant levels are too high, phytotoxicity can occur thereby causing plants to die and costs of the remediation to rise if planting must be re-done. It is important to identify if site soil and groundwater will be too toxic to plants proposed to be used in the project. Simple lab tests can determine this, such as greenhouse dose-response test. Signs of phytotoxicity are leaf yellowing/browning, percentage of dead plants, growth of the plant, tissue analyses.

2.4 Plant Choices

Native plants that take root on contaminated properties may have some measurable impact on the contaminant concentrations, but the idea of phytoremediation is to harness or select for those plant characteristics that will have the greatest impact on contaminant removal or degradation [50]. An example of this would be choosing plants that are known to accumulate large quantities of metals in their tissue. Table 2-2 shows a list of plants that are typically used for phytoremediation. There are specific characteristics that are most desirable in plants that are used for phytoremediation and there are certain site characteristics that must be considered when choosing plants.

Table 2-2 Phytoremediation Plant List

Removal Method – Rhizosphere Biodegradation	Removal Method - Phytodegradation	Removal Method - Phytoextraction
Red Mulberry	Parrot feather	Euphorbiacae family
Crab apple	Stonewort	Asteraceae family
Osage orange	Black willow	Lamiaceae family
Spearmint	Bald cypress	Scrophulariaceae family
Rice	River birch	Corn
Cattails	Cherry bark oak	Sorghum
Legumes	Live oak	Pennycress
Loblolly pine	Poplars	Indian mustard
Bush bean		Alfalfa
Grasses		
Alfalfa		
Soybeans		

Removal Method - Rhizofiltration	Removal Method - Phytovolatilization	Removal Method- Phytostabilization
Sunflowers	Black locusts	Tall fescue
Milfoil	Kenaf	Colonial bentgrass
Water hyacinth	Canola	Big bluestern
Pennyworth	Red fescus	Indian mustard
Duckweed	Tall fescue	Grasses
Water velvet	Indian mustard	Soybeans
Colonial bentgrass	Alfalfa	
Indian mustard	Poplars	

Site considerations - the climate at the remediation site must be well understood and the appropriate plants should be chosen accordingly. Choosing plants for inappropriate climates is one of the reasons why phytoremediation sites can fail. In temperate climates, the typical trees that are chosen are those that are fast growing, deeply rooted, and that use large amounts of water [46, 49]. This includes hybrid poplars, willows, cottonwoods, and aspens because they have the above mentioned qualities and because they are native to many areas across the nation. Some considerations when choosing plants for the project have to do with the general site conditions. For example, the depth to the contamination must be known so as to determine whether the roots of particular plants will be able to reach the targeted area [48].

Plant characteristics - plants that are fairly hardy and tolerant to different stressors are desired because of the stressful nature of contaminated sites [49]. Plants that wilt or die when any fluctuations in living conditions occur are probably not the ideal plants for phytoremediation. Tolerance to pH and salinity in soil and groundwater is necessary [45, 48]. And obviously, tolerance to chemicals in the soil or groundwater is a must given the end goals of the project. Toxicity and transformation rates vary widely from one plant species to the next and even within species so it is critical to review the available data to identify plants that are most suitable for the contaminants that are located on a specific area [13]. Ideal plant characteristics are those that have adequate root depth; rapid growth rate; the potential to evapotranspirate; the ability to bioaccumulate contaminants [41]; and produce degradative enzymes.

The following is a list of maximum root depth for some plant types that may be considered. Maximum root depths are achieved under ideal soil conditions.

- Indian mustard has roots that can extend 6 to 9 inches deep.
- Fibrous roots of grasses can extend between 8 to 10 feet deep.
- Phreatophytic shrubs can have roots that reach up to 20 feet deep.
- Legumes, such as alfalfa, can have root depths up to 30 feet deep.
- Phreatophytic tree roots tend to extend deeper into the ground than other trees, typically on the order of 80 feet deep. Mesquite tap roots can extend 40 to 100 feet deep while river birch tap roots can extend 90 to 100 feet deep [45].

Depth of roots depends upon, among other things, the amount of available water in shallow soils, the type of soil found at depth, and the nutrients available in deeper soils. The lateral extent of root growth is an important factor as well. The production and excretion of enzymes is important when relying on the enzymes to enhance microbial growth in the rhizosphere and to degrade contaminants in the rhizosphere or within the plant tissue [45]. Some plants are known to produce certain enzymes that attack specific contaminants.

Fast growing vegetation is ideal [13]. Growth rate of plants is related to the amount of water that it can consume and the amount of carbon, oxygen, and water that is delivered to the rhizosphere, which can affect the amount of contaminant adsorption or uptake [45, 48, 49]. Transpiration rate and the rate of water use of a plant are critically important for the treatment of groundwater when using phytovolatilization, phytodegradation, and hydraulic control as these rates control the amount of groundwater that can potentially be treated [48]. Factors affecting the amount of water that is transpired and the period of effectiveness of remediation include the season and whether the plant is deciduous or evergreen [48].

Costs - plants that are easy to plant and maintain, based on fertilization and soil amendment requirements, may be chosen in order to keep costs down [48, 49]. Nevertheless, stress from the contaminated environment may change a plant's need for soil amendments and maintenance and could drive up maintenance costs if not properly budgeted [45].

Contaminant characteristics – when dealing with chlorinated solvents (including TCE) it is important to determine soil pH, clay content, water content, and organic matter content at a site because these conditions all influence the uptake of the contamination by the plant and they also help determine which plants are most appropriate to use [48]. When periodic harvest and disposal of the plant is required to maintain phytoremediation effectiveness, the amount of biomass that is produced affects the amount of waste that must be disposed. If contaminants will be accumulating in plant tissue and plant products (leaves or fruit), limiting site access from humans or animals may be a concern as to prevent exposure of those individuals to contaminants in the plants.

Grasses are often planted together with trees when organic contaminants are the concern. The grasses provide a fine root network in surface soils that helps bind and transform hydrophobic contaminants. Grasses may also be planted to provide protection from soil migration due to wind [13]. Along the same lines, plants and trees can be paired together when there is a mixture of contaminants of concern.

When lead is the contaminant of concern, sunflowers or Indian mustard may be effective, but if the contaminant is zinc, cadmium or nickel pennycress has been shown to work [49]. Emergent aquatic vegetation can readily transpire water and are easily harvested if the method of phytoremediation requires harvesting [49]. On the other hand, submerged vegetation does not transpire water but can be used for contaminant uptake and absorption.

Non-native plants - An often controversial decision that must be made when choosing plants is whether to use native or non-native species [45, 48, 49] because of the negative impacts that they can have at the site, and because some are invasive. Onsite impacts include competition with other native plants for natural resources that often results in invasions by the non-native plant; allelopathy [45]; or the plants can spread to neighboring properties. Allelopathy occurs when a plant excretes enzymes that kill another plant. Invasive non-native plants can devastate an ecosystem and their use should be strictly limited, despite the desirable remediation characteristics that some may possess. Luckily, poplars, a common phytoremediation plant is native across the nation. Commercial availability of native species may be a limiting factor to their use [48]. Non-native species can sometimes be allowed under some circumstances:

- The plants had previously been introduced and have become common in the area;
- The plants can not naturally propagate due to sterility or dependence upon human propagation; and,
- Introduction of genetically altered plants.

2.5 Monitoring Plants During Phytoremediation

Plants and trees should be monitored during the duration of the remediation project in an effort to assess the effectiveness at removing contaminants and the plant's health. Methods of monitoring include growth measurements; evapotranspiration and sap flow measurements; tree girth, root depth, tree coring, leaf, stem, and branch sampling; composition analysis in order to identify whether the plant is up-taking the contaminants, if there is a buildup, and whether there are any metabolites present[48].

Monitoring of the contaminated media (water, soil, sediment, or sludge) should occur as well, to determine if a decrease in contaminant levels is occurring. Finally, air monitoring is needed to determine if contaminants are volatilized. This process is discussed further in Chapter 4.

2.6 Regulatory Agencies

Phytoremediation is a relatively new, emerging remediation technology that has yet to be approved by regulators. As such, regulating agencies prefer that they are involved at the beginning stages of a phytoremediation project, since they are interested in gathering data on this new technology as well. However, some states have regulatory laws that discourage or even prohibit long-term remediation projects (which would include most phytoremediation projects) likely because of cost constraints and potential inability to achieve cleanup goals; whereas other state regulatory agencies provide incentives for implementation of innovative remediation technologies (which would include phytoremediation) [59]. Many of the phytoremediation projects that have been implemented thus far have also been the location of EPA studies as well. For example, the EPA's Superfund Innovative Technology Evaluation (SITE) Program has been actively participating in phytoremediation projects. This joint effort benefits all parties involved because the EPA is able to evaluate the applicability and efficiency of phytoremediation as a viable treatment method and scientists involved with the cleanup of the property benefit because they have access to comprehensive data on the phytoremediation project that is gathered by the EPA. This should help phytoremediation to become a more popular choice among regulatory officials and consultants involved in the cleanup of properties. Some regulators may be more inclined to allow phytoremediation if it is used in conjunction with a conventional treatment method such as pump-and-treat [59] so that there is some assurance that contaminant removal will occur if the phytoremediation does not work.

The most important questions that regulators need answered in order approve a remediation method are:

- Does the technology cleanup the site to below regulated levels? On what time scale?

- Does it reduce the risk to human health and the environment?

To date, no federal regulations have been set for phytoremediation practices. Nevertheless, there are existing federal and state regulations that should be consulted prior to beginning phytoremediation as these regulations may provide some structure for remediation. These regulations and cleanup programs include RCRA; Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) also known as the Superfund law; Clean Air Act (CAA); Toxic Substances Control Act (TSCA); FIFRA; Federal Food, Drug, and Cosmetic Act (FFDCA); and rules enforced by the U.S. Department of Agriculture [45]. Each of these programs requires that the remedial actions must prevent exposure and control migration of the contaminant. Steps must be taken in order to prevent exposure of humans and the environment to contaminants above regulatory levels. The EPA's Office of Research and Development as well as the Office of Solid Waste and Emergency Response have programs that pertain to monitoring the efficacy, risk, and cost of phytoremediation projects. Further, the EPA has been involved with research and development of several new remediation technologies including phytoremediation research.

There are other issues that arise during the phytoremediation process that must be addressed that may involve regulatory agencies. These include the following:

- Determining if plant material will become hazardous waste once it has absorbed contaminants into its tissue during phytoextraction. The determination of whether plant material is considered "hazardous waste" is made by state regulating agencies as is based on the contaminant levels in the plant material. If the plant is considered hazardous waste, property disposal must be identified [48].

- Air monitoring and an air permit may be required by local or state regulators in order to quantify the amount of volatile organic compounds are being transpired by the plant into the atmosphere [60]. Adams et al. (2000) speculated that the largest regulatory concern is the release of contaminants or contaminant metabolites into the air.

- Federal, state, or local regulations regarding water quality may need to be reviewed if contaminated groundwater will be pumped to the surface and applied as irrigation water for vegetation [49, 59, 60]. This is because some states regulate the use of contaminated groundwater for irrigation.

- Dredged sediment is regulated by the US Army Corps of Engineers, so if dredged sediments are being remediated, the US Army Corps should be involved in the process [49].

- The use of non-native or invasive species may be regulated by local or state officials [60].

3.0 COMMON REMEDIATION TECHNIQUE – PUMP-AND-TREAT

3.1 Remediation Options for TCE

The remediation of groundwater contaminated with TCE is important because of the widespread nature of this contamination and because of the human effects of TCE exposure can be severe. These conditions have spurred on a multitude of TCE remediation projects. There are a variety of ways to treat groundwater contaminated by TCE. The mechanisms by which TCE is remediated include volatilization, mobilization, dissolution, chemical reaction, dechlorination, electrically induced mobilization, and thermal decomposition [61]. These mechanisms are achieved through remediation methods including activated carbon adsorption, solvent or surfactant injection, steam injection, in-well stripping, in situ oxidation, reactive barriers, biobarriers, physical barriers, electrokinetic systems, air sparging, in situ bioremediation, natural attenuation, and pump-and-treat [41, 61-63].

- Solvent or Surfactant Injection and In-situ Oxidation- Involves injection of chemicals into the soil and groundwater to promote a chemical reaction, dissolution, or mobilization of the contaminant. Sometimes compounds can be injected that will increase the aerobic degradation of a contaminant. It is a conventional technology that can aid in DNAPL source area remediation.

- Steam Injection- Involves injecting steam into soil and groundwater above and/or below the water table to induce volatilization and mobilization of the contaminant. The steam flow and temperature of the steam must be controllable in order for this method to be effective. Conventional technology that can aid in DNAPL source area remediation

- In-well Stripping- This method uses the principles of air sparging and air stripping in order to volatilize the contaminant. The process works by injecting air into a well (air sparging) while simultaneously pumping groundwater out of the well and discharging it back into the top of the well (air stripping). Conventional technology that targets dissolved contaminants and not DNAPL source areas.

- Reactive Barriers and Biobarriers- Installation of a physical barrier across a plume of contaminated water. The barrier contains materials such as chemicals or activated carbon that work to dechlorinate contaminants that are in the aqueous phase. Sometimes iron can be used for the reactive barrier. Biobarriers are a similar idea but they use microbes for the degradation of the contaminant. A newer technology that targets dissolved contaminants and not DNAPL source areas.

- Physical Barrier- Uses an impermeable barrier to contain the plume. A newer technology that targets dissolved contaminants and not DNAPL source areas.

- Electrokinetic System- Electronically mobilize the contaminant. This does not destruct the contaminant so it must be coupled with another technology for removal. A newer technology that targets dissolved contaminants and not DNAPL source areas.

- Air Sparging- Injection of air into the soil and water below the water table and capture of the air above the water table. This method induces volatilization of the contaminant and promotes bioremediation. Must be conducted at the source of the contamination. Conventional technology that can aid in DNAPL source area remediation.

- In-situ Bioremediation- This technique harnesses the natural ability of microbes to degrade contaminants by the addition of oxygen or other nutrients into the subsurface that stimulate the proliferation and activity of the microbes.

- Natural Attenuation- No treatment technology is used, rather nature is allowed to remediate the contaminated groundwater naturally through bioremediation, volatilization, and decomposition.

- Pump and Treat- Pump contaminated groundwater out of the ground and treat ex-situ. This is the most widely used conventional treatment technology, but it targets dissolved contaminants and not DNAPL source areas. One ex-situ treatment method is granular activated carbon adsorption. This method involves the extraction of groundwater that is pumped into beds of activated carbon so that the TCE adsorbs to the carbon granules. Conventional technology that can aid in dissolved contaminant remediation.

Some of these remediation methods are more cutting edge and are not widely used. There are positive and negative aspects to all of these treatment methods and there is not one that works better than all of the rest. Much like phytoremediation, the effectiveness of the treatment depends upon the site conditions. As of 1996, traditional remediation methods were employed at roughly 93% of the current Superfund sites (562 of 603 sites) [64]. Specifically, in 1986, 92% of the National Priority List sites selected pump-and-treat technology for remediation, but this number declined to 30% of sites in 1999 [65]. Up until the 1980’s the more common treatment method for TCE contaminated groundwater was to pump the groundwater out of the ground and treat it using granular activated carbon for filtration and sorption of the TCE to the carbon [66, 67]. This method required large amounts of carbon that had to be routinely replenished in order for the removal efficiency to stay constant. Start-up costs and operation and maintenance costs were high, so alternative remediation methods were sought after [67, 68]. As of 1994, pump-and-treat was the most common groundwater remediation method in the United States with three-quarters of sites with contaminated groundwater using this conventional method for cleanup [63]. In 2004, there were 100 Superfund-financed pump-and-treat projects operating nationwide [69].

A 1992 study of contaminated sites in Santa Clara Valley, California that implemented pump-and-treat remediation was conducted to evaluate the effectiveness of this remediation method to reduce VOC contamination in groundwater. The study evaluated 37 sites that had been using pump-and-treat for at least five years (since 1987) [70]. The study compared the initial groundwater concentrations in 1987 at each site to groundwater concentration results from 1992. The results of the study indicated that in 1992, the number of sites with significant groundwater concentrations (100,000 ppb) of TCA, DCE, or TCE decreased dramatically. For example, the number of sites with TCE concentrations greater than 10,000 ppb decreased from 12 to 6 sites in 1992 and the number of sites with TCE concentrations less than 100 ppb increased from zero to four in 1992. This data indicates a decreasing shift of groundwater concentrations away from initial maximum concentrations. One of the sites reached MCLs for all three contaminants. The conclusion of the study was that the remediation systems were successful in reducing contaminant concentrations, but not to MCL levels.

The treatment technology that was chosen for this thesis to compare to phytoremediation with poplars is the pump-and-treat method utilizing an air stripping tower. Pump-and-treat was chosen over all of the other traditional methods because pump-and-treat is the most closely related to the way that poplars work. Essentially, poplars act as small solar powered pumps that pull the water out of the ground and treat the groundwater inside the tissue or release the contaminant to the atmosphere. Pump-and-treat type technologies involve installing wells and pumping out the contaminated groundwater for ex situ treatment. The water can then be re-injected into the ground or used for other purposes such as irrigation. According to Nicholas Cheremisinoff, author of <u>Groundwater Remediation and Treatment Technologies</u> (1997) pump-and-treat methods should be considered when there is extensive groundwater contamination and may be the only viable option when deep groundwater is impacted. Air stripping, a common pump-and-treat technology [71] had been used in the chemical engineering field since the 1940's but it was not until the 1980's that this method was investigated as a possible remediation technique for volatile organic compounds [72].

3.2 Pump-and-Treat using Air Stripping

Since the 1980's air stripping has gained popularity for treating many of the nation's Superfund sites because of its proven economic value compared to the other mainstream remediation techniques. The most commonly used air stripper is a packed tower air stripper. Other forms of the same process are low profile air strippers, diffused aeration chambers, cooling towers, coke tray aerators, and cross-flow towers [62, 68, 73, 74]. All of these types of machines work from the same principle that air must be injected into the water in order to volatilize the TCE. Nevertheless, the packed tower is the most efficient and the most widely used [73]. These other types of air strippers are configured such that it is more difficult to capture the air emissions for treatment [75].

Air stripping has been proven effective (see Section 3.2.2 for measures of effectiveness) in removing volatile and semi-volatile organic compounds from water, but it can not be used for the removal of metals or inorganic compounds. The main objective for air strippers is to volatilize the TCE (or which ever volatile contaminant is present onsite) from the water into the air [75]. Air stripping is a good method for TCE removal from water because of the chemical's volatile nature and its water solubility because the air can drive the TCE out of solution [12]. TCE is not destroyed or degraded; rather it is just separated from the water and released to the air [73, 76]. In other words air stripping moves TCE from one medium to another.

Figure 3-1 Air Stripping Towers. Photograph depicting two air stripping towers located in Tacoma, Washington.   Source: Longley (2007)

3.2.1   <u>Description of Air Stripping Process</u>

Like with all remediation systems, an air stripping system must be designed based on the specific site conditions that must be well characterized. Site conditions that need to be characterized for the air stripping treatment process include understanding the subsurface conditions such as the geology of the area, hydraulic properties and the behavior of the groundwater, and the types of use of the groundwater in the area [75]. For example, soil types that have a high hydraulic conductivity (sand, gravel, and mixtures there of) are most desirable when utilizing an air stripper because water can easily flow through the soil during groundwater withdrawal. This soil would subsequently allow for easy groundwater infiltration after the air stripping process. Some of the optimal geologic and hydraulic conditions for air stripping would be an aquifer that recharges easily (decreasing the impact on aquifer depletion), one that does not have extensive contamination, one that is not used for drinking water, has homogeneous geology, and limited soil adsorption of contaminant [75]. The nature of the contamination must also be understood including the relative concentrations, regulatory cleanup goals, and the various types of contamination that may be present. Once these are understood an air stripping tower and associated system can be designed to meet the desired specifications. The design process can be quite lengthy and often involves computer modeling and must be conducted by an experienced engineer. Conditions that affect the efficiency and the design of the air stripper are flow rates, water temperature, TCE concentration, and cleanup goals [77].

Air strippers are large towers, typically packed with material, with a stack at the top [77]. The towers are typically cylindrical, but can be rectangular too. Plastic is the most common material that the towers are constructed from, but other materials such as stainless steel, lined carbon steel, or concrete are sometimes used instead [62]. An example of the scale of a tower is five feet in diameter and 30 feet tall. Delta Cooling Towers, Inc. makes air stripping towers with a diameter of up to 15 feet which can handle up to 15,100 liters per minute (4,000 gallons per minute) [78]. Typically the height of a tower is correlated with the contaminant level in the water [76]. The packing material can be a variety of sizes, shapes, and types. The material can be PVC, polypropylene, ceramic, or plastic [71, 73] and can range in size from 1 inch to 3 inches [62]. The shape of the packing material can be Tripacks®, saddles, or slotted rings [73]. Packing material is either randomly placed in the tower or it is packed in specific places [62]. The packing material adds a large amount of void volumes and surface area for the water to come into contact with [68, 76]. The packing material increases the surface area of the water that can be exposed to the air [79]. According to Ball et al. (1984) plastic packing is recommended for water treatment. If the packing pieces were not present in the tower, the water would fall from the top of the tower in a mass and the air would not be able to come into contact with a very large portion of the water, and therefore volatilization would be limited.

Groundwater is extracted from wells and is pumped into a storage tank [80]. The influent water is then pumped up to the top of the air stripping tower where it is discharged, typically via sprayers. Figure 3-2 depicts the air stripping process. Water flow through the tower can be on the order of 1,000 to 7,000 liters per minute (as an example). The water flows down the tower through a maze of packing material, propelled by the force of gravity. In order to keep the water distributed throughout the tower and to prevent channelization, redistributor plates are strategically placed inside of the tower. The plates help force the water in different directions. This redistribution is especially necessary with long columns of packing material. Concurrently, air is injected from the bottom of the tower upward via an air blower and is forced through the falling water. The water forms a thin film on the packing material where it can come into contact with the counter-current of air [73, 80], which maximizes volatilization [76]. The optimum ratio of air to water can range from 10:1 up to 800:1 [73]. The TCE is volatilized from the water as it flows through the packing material and as the air passes through. The TCE vapor is then released to the atmosphere through the top of the tower or it is directed into another treatment system, such as activated carbon [73], designed for removing vapor phase TCE [81]. The treated water (effluent) collects at the bottom of the tower and is either pumped into a storage tank or it is piped back to the first storage tank for another round of air stripping. Sometimes up to five rounds of air stripping is required to achieve the target effluent concentration. Recycling air strippers allow for a portion of the effluent to be circulated back into the influent. This can help augment discharge into the air stripper if the influent pump is discharging below optimum amounts of water and can prevent ice formation inside of the tower [62].

After discharged from the air stripper the effluent can be treated by a secondary method (such as granular activated carbon) as a polishing effect or it may need a more aggressive additional treatment method for the removal of metals or other inorganic compounds that are not treated by air stripping. The treated water can then be sent to a sewage treatment plant, can be used for irrigations, impounded as surface water, or can be discharged back into the ground. The fate of the treated water is determined by site geology and by regulatory restrictions. Preferably, the treated water is infiltrated back into the ground at the project site to re-supply the aquifer with water that had originally been removed, aiding in off-setting potential aquifer depletion. The infiltration can also serve as a flushing mechanism for residual soil contaminants [82]. State or local governmental restrictions may prevent the infiltration of treated water or limit the use of treated water as irrigation. Often times the rate at which the water can infiltrate back into the ground becomes the limiting condition for the amount of water that can be treated by the air stripper at any one time [82].

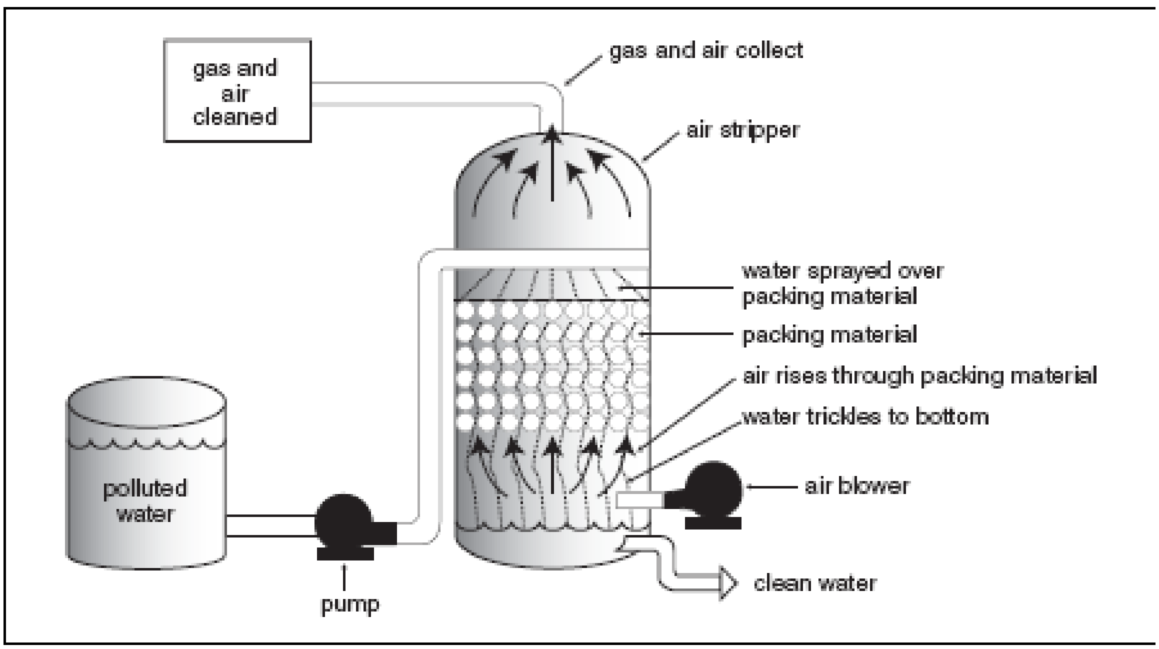

Figure 3-2 Air Stripping Process. This diagram depicts the air stripping process using a packed tower air stripper and an emission collection system. Source: EPA (2001)[71]

Air strippers can operate continuously, seasonally, or intermittently. There are benefits to both continuous operation and intermittent operation. Continuous operation means that more water will be treated and it will decrease the amount of dead space in the tower (dead space is discussed at the end of this chapter). Intermittent operation reportedly allows for consistent stripping performance and energy efficiency [79].

The amount of TCE that is released to the air after the air stripping process is function of a few variables [83]. These variables include the following:

- The quantity of TCE in the influent water;
- The removal efficiency of the air stripper;
- Changes in the quantity of TCE in the influent over time; and
- Period of operation of the air stripper.

The efficiency of the air stripper depends upon a number of variables including how the air stripper was designed including the tower height, the size of the packing material and its arrangement in the tower, the degree of fouling of the packing material, the amount of air in the countercurrent (higher air to water ratio is better), and the duration and energy of the water flow through the tower (continuous or pulsed) [76, 77, 79].

A slight variation of the air stripping practice for remediation purposes is the use of air strippers at a well head for the strict purpose of treating water before it is used for domestic drinking water or irrigation. An example of this is an air stripper on the island of Oahu, Hawaii. The air stripper is not being used to necessarily treat groundwater for re-injection back into the aquifer nor is it used for hydraulic control. It is merely being used to remove enough TCE from the extracted water so that it will meet EPA MCLs (5 ppb) [84].

3.2.2 Effectiveness

The air stripper system is relatively simplistic making it easy to start-up, shutdown, and easy to maintain [80]. The method for measuring the effectiveness of the air stripping technology is by comparing influent contaminant levels and effluent contaminant levels. This aids in determining the amount of contaminant that has been removed. Air strippers are capable of removing between 97-99% of some VOCs that volatilize easily such as TCE [62, 71, 73, 77]. Reportedly, towers that have 15 to 20 feet of packing material can have removal efficiencies of 99% [79]. One must keep this efficiency level in perspective though. For example, the removal of 99% of TCE from groundwater that is highly contaminated with a concentration of 100 ppm, would have a resulting effluent with a residual concentration of 1 ppm. This residual contaminant level is most certainly above drinking water standards and is likely above any cleanup goal, requiring further treatment such as subsequent rounds through the air stripper. For this purpose sometimes multiple stripping towers are erected in a row. There comes a time when the TCE concentration in the water is reduced to a certain level where the amount of air that is required to volatilize the TCE is far greater than what is actually feasible by the system [12].

Air stripper efficiency can be improved by making some modifications to the system. These modifications include adding a second or third air stripping tower or by changing the arrangement of the packing material [79]. Some studies have indicated that by raising the temperature of the influent water the efficiency of contaminant removal can be increased because the mass transfer rate increases, as does the Henry's Law Constant (a measure of volatility), which increases the contaminant's volatilization [73, 79]. This is most effective for volatile organic compounds and semi-volatile compounds that are more difficult to volatilize under ambient temperatures. Even though heating the influent can increase the rate of volatilization, air strippers used for the removal of TCE are more often used without an influent heater [62].

3.2.2.1 Evidence of TCE Removal From Influent

Wurtsmith Air Force Base

At Wurtsmith Air Force Base in Oscoda, Michigan in the late 1970's 6,000 µg/L (ppb) of TCE was detected in the local drinking water and concentrations of up to 10,000 µg/L (ppb) of TCE was found near the center of the contaminant plume [67]. The popular treatment method at the time was filtration through granular activated carbon, but the typical system to treat the amount of water at Wurtsmith would cost $1,500,000 with annual operations and maintenance costs of $400,000 [67]. Air stripping was investigated as a cost effective alternative. A 30 foot tall and 5 foot diameter air stripper was installed at Wurtsmith. Water flow through the tower ranged from 1,100 liters per minute up to 2,200 liters per minute [73]. Initial results indicated that removal efficiency of two air stripping towers ranged from 96 to 99% of the TCE and effluent analysis indicated that TCE levels were below Michigan's discharge limit of 1.5 µg/L (ppb) [67]. The optimum performance was achieved when the air to water ration was 25:1, the water flow was 2,270 liters per minute, resulting in a removal efficiency of 99.9% [67, 73]. Over time performance was hindered occasionally due to a biological growth on the packing material, but this was mitigated by cleaning the packing material. A 1981 report indicated that the system cost for the air stripping system was $200,000 (1981 dollars) and the operations and maintenance was $56,300 [67]. This is considerable cheaper than the activated carbon and just as efficient.

Eau Claire, Wisconsin

An air stripper was used in Eau Claire, Wisconsin to protect public health and welfare due to the presence of four volatile organic compounds (including TCE) found in the municipal wells. A 60 foot tall and 12 foot diameter air stripper with 26 feet of packed material was used. Water flow was approximately 22.7 million liters per day or 15,773 liters per minute (6 million gallons per day). The influent levels for TCE ranged from 2.53-11.18 ppb and the air stripper was able to remove approximately 98% [73].

Manufacturer in Michigan

A refrigerator manufacturer in Michigan had concentrations of TCE in groundwater up to 35,000 ppb. The cleanup level was set at 15 ppb by the Michigan Department of Natural Resources. An air stripper was erected to remove TCE among other VOCs. After the water ran through the air stripper it was sprayed onto the soil at a discharge basin so that it could help flush out any contaminants in the soil and to remove residual contaminants in the influent water. Pilot tests indicated removal performance of one pass through the air stripper ranged from 55-85% but after five times through the air stripper removal had increased to 99-99.9%. Filtration of the water through the soil after discharging from the air stripper gained an additional 93.9% removal of VOCs. After the pilot tests the treatment system became the official treatment method onsite. The average TCE removal was 94.5% from both the air stripper and filtration through soil, which was slightly lower than the pilot study results. It was estimated that approximately 75% of the removal was from the air stripper while 20% was from the filtration through soil [82]. After three months of operation, approximately 352 kg (775 pounds) of TCE had been removed. It was estimated that after a year, 500 kg (1100 pounds) of TCE would be removed. The actual measured concentration of VOCs in the effluent were not given by the authors; however if you calculate 94.5% removal of the average influent concentration of 4,000 µg/L (ppb) the effluent would still contain approximately 220 µg/L (ppb) of VOCs. This is above the remediation goal set by the Michigan Department of Natural Resources, but it is significantly lower than the average pretreatment concentrations.

The EPA conducted a review in 1987 of 46 sites that utilized air stripping technology. Of those, 34 of the sites were remediating groundwater impacted by TCE. The average influent concentration was 7,660 ppb (the range was from 1-200,000 ppb) and the average removal efficiency 98.3% (the range was from 76-100%) [73]. Table 3-1 is a synthesis of the above data as well as some other case studies, all of which had TCE removal efficiencies in the 90% range. As you can see by the above examples, Table 3-1, and the EPA (1991) study, the levels of influent contamination can vary widely from as little as a 2 ppb up to the ppm range with removal efficiency up to 100%. This data appears to indicate that air stripper technology is rather effective at separating the bulk of TCE from the aqueous phase.

Savannah River Site

At the Savannah River Site in Georgia there is considerable VOC contaminated groundwater. The contamination was estimated to be approximately 118,000-204,000 kg (260,000-450,000 pounds) of dissolved VOCs in groundwater, 75% of which was TCE [85]. Contamination ranged as high as 500 ppm in limited areas. An air stripper was installed in 1985 that was 71 feet high and had a capacity of 2,309 liters (610 gallons) per minute, although it was operated at 1,930 liters (510 gallons) per minute. The cleanup goal for TCE in water was 5 ppb and the cleanup timeframe was 30 years. Removal efficiency by the air stripper was greater than 99.9%. Reportedly, portions of the groundwater plume can not be controlled, although the source areas appear to be under control. The zone of contamination with concentrations over 100 ppm of VOCs has disappeared. Data from 1985-1993 indicated that the average TCE influent concentration was 15,006 ppb and the average effluent concentration was less than 1.01 ppb [85].

Table 3-1 Examples of Air Stripper Efficiency Results

Site Name	Influent Concentration (ppb)	Water Flow (L/min.)	Removal Efficiency	Estimated Effluent Concentration (ppb)
Wurturtsmith Air Force Base [67]	TCE: 6,000-10,000	1,100-2,200	99%	60-100
Tacoma, WA [66]	Total VOCs: 100	2,650 each for 5 towers	94-98%	2-6
Eau Claire [73]	TCE: 2.53-11.18	15,773	98%	0.05-0.22
Western Processing [73]	TCE: 8,220	379-757	99.94%	4.9
Refrigerator manufacturer, Michigan [82]	TCE: 35,000	150-190	99.0-99.9%	35-350
Savannah River, Georgia [12]	TCE: 120,000	75-190 each for 2 towers	99.999%	1.2

3.2.2.2 Evidence of Groundwater Contaminant Reduction

Intersil/Siemens Superfund Site

The Intersil/Siemens Site is a Superfund Site with VOC contaminated shallow groundwater and soil. The remediation activities onsite included soil-vapor extraction (began in 1983), groundwater extraction and treatment (began in 1986), and groundwater monitoring [86]. Groundwater contamination is in two aquifers, one between 45 and 60 feet, and the other between 60 and 90 feet below ground surface (bgs). Groundwater extraction wells were used to pump contaminated groundwater to the surface to be treated by one air stripper (Intersil property) before the effluent was discharged into the nearby Calabazas Creek. The Siemens property used two air strippers in series until 2002 when the extracted groundwater was switched to being treated by granular activated carbon. The Final Site Cleanup Report had a clause stating that it is understood that the pump-and-treat remedy that was selected may be technically impracticable for reaching the site cleanup standards that were set (TCE = 5 ppb). Further, the Final Site Cleanup Report stated that if this were to happen, the cleanup standards and the remediation choice may be reevaluated. Groundwater extraction rates are approximately 170 liters per minute (45 gallons per minute) and approximately 87 million liters (23 million gallons) of groundwater are treated each year. Groundwater potentiometric surface maps indicate that onsite and off-site groundwater has been contained and the plume in the lower aquifer is decreasing in its lateral extent thus decreasing in size. Groundwater concentrations in both aquifers have been decreasing over time and those wells that historically contained the highest concentrations of TCE have decreased significantly.

Table 3-2 Groundwater TCE Concentrations at Intersil/Siemens Superfund Site

Well	Concentration ppb (Year)	Concentration ppb (Year)
Intersil - W10A	170 (1999)	79 (2004)
Intersil - W18B	18 (1999)	12 (2004)
Siemens - LF-6A	470 (1990)	50 (1995)
Siemens - H-5B	2,100 (1991)	150 (2004)
Off-site – IQ-1B	10 (1999)	<1 (2004)

The TCE concentrations at the Siemens facility have been decreasing overtime, but recently have begun to decrease to asymptotic concentrations. As a result of this trending decrease in groundwater concentration, the influent to the air stripper and activated carbon has been decreasing overtime as well from a maximum of 153 ppb in 2000 to a minimum of 65 ppb in 2004. Remedial goals have been reached for some VOCs such as PCE, Freon 13, and toluene. Unfortunately, the efficiency of the air stripper has decreased overtime by as much as 61% such that it is removing less mass of VOCs from the influent as it originally was. This decrease has been from 1.59 pounds (0.7 kg) of VOCs per million gallons in December 1999 to 0.61 pounds (0.28 kg) per millions gallons in December 2004[†††]. The report did not speculate as to why the pounds of VOC removed from influent are decreasing or why groundwater concentrations at the Siemens facility are reaching asymptotic concentrations. This remediation has successfully: a) removed VOCs from the soil, b) maintained plume control, c) reduced VOC concentrations in groundwater, and d) recommended the implementation of deed restrictions on the property to prevent the use of shallow groundwater. The EPA and California Regional Water Quality Control Board (CRWQCB) anticipate that even

[†††] These results were reported in pounds per million gallons so it couldn't be changed to the metric form.

though groundwater concentrations have been reduced and the plume migration is under control, the time required for site cleanup "will be significantly in excess of 20 years".

Synertek Superfund Site

The Synertek No. 1 facility was a semiconductor manufacturer. Activity on the property resulted in soil and groundwater contamination by VOCs, including TCE. The shallow aquifer is at 10 feet bgs while the second aquifer is between 30 to 50 feet bgs [87]. Historical maximum TCE concentrations were 490 ppb in the shallow aquifer and approximately 33,000 ppb in the second aquifer [87]. Groundwater pumping and treating began in 1987 by using six extraction wells and an air stripper. Treated water was discharged to an adjacent storm drain. The first five-year review, conducted in 1996 indicated that VOC mass removal rate was declining. From January 1991 through December 1995 approximately 121 million liters (32 million gallons) of groundwater was treated and 29 kg (64 pounds) of VOCs were removed [88]. In contrast, from 1996 to 1999 approximately 151 million liters (40 million gallons) of groundwater was extracted but only 8.8 kg (19.5 pounds) of VOCs were removed. This decline in removal indicates asymptotic levels of contaminants in the groundwater. Concentrations of TCE in groundwater collected from wells in the shallow aquifer in 2000 and 2001 indicated a range of concentrations between 5.7 to 66 ppb [88]. Figure 3-3 depicts the trend of VOC concentration in groundwater at two wells that were located within the plume. The graph begins in June 1996 and ends in December 2001, after the groundwater treatment system had been shutoff. Well 7A generally decreased overtime with the greatest decrease in concentration occurring between 1996 and 1997. Well 12A generally decreased until December 1998 at which time the concentrations began increasing before steeply declining once again. The increase may be attributable to a mass of highly contaminated water moving through the well at that time. Reportedly, at the time of the report (2002) there no longer was a contributing source of VOCs. The agencies determined that VOC concentrations in the groundwater were going to reach asymptotic levels; however, it was determined that the cleanup plan instituted at this site successfully reduced VOC concentrations and prevented further plume migration.

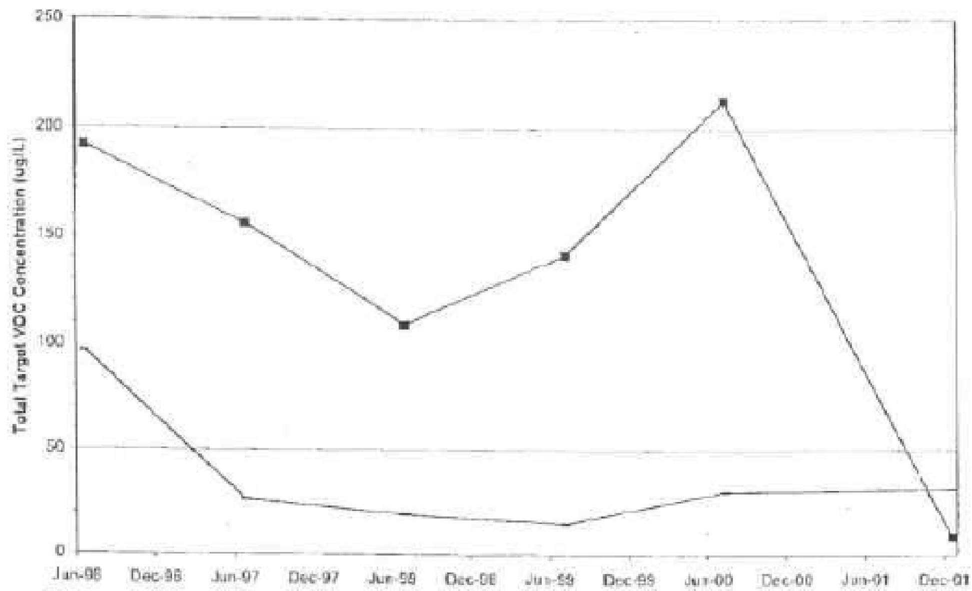

Figure 3-3 Total VOC Concentration Over Time – Wells 7A and 12A Synertek Superfund Site. 7A is depicted as the bottom trend line. 12A is depicted as the top trend line. The Y axis indicates the Total Target VOC Concentration (µg/L) while the X axis is Time. The timeline begins in January 1996 and ends in December 2001. Source: CH2MHILL (2002)

A deed restriction is in place at the site that allowed the treatment system to be shutdown in February 2001 at which time a trial period began for monitored natural attenuation. The agencies involved with this Superfund Site believe that monitored natural attenuation may be a viable long-term option. One drawback to the treatment system being shut off is that well 4B, located in the former source area, has experienced a rebound in concentrations. In 2001 VOC concentrations at this well were 181 ppb and after the shutdown concentrations increased to 883 ppb. Nevertheless, these concentrations are still below the historic highs in this location of 33,000 ppb for TCE [87]. The increase may be due to a residual mass of VOCs in this area. In general though, the CRWQCB concurs that the VOC plume is stable and not increasing in size in the shallow aquifer. In the lower aquifer the plume is not increasing in size but at least one well is experiencing an increase in VOC concentrations. One possible remedy would be to continue monitored natural attenuation in the shallow aquifer and re-institute the groundwater extraction system in the lower aquifer. It is expected that this site will require at least 10 additional years or more to achieve cleanup goals.

Lakewood/Ponders Corner Superfund Site

The Lakewood/Ponders Corner Superfund Site is located in Tacoma, Washington. The site includes a dry cleaners as well as a 2,000 foot radius around the dry cleaners which is the boundary for the contamination in the regional aquifer [89]. The site was discovered in 1981 when two of the Lakewood Water District drinking water wells were identified as having TCE, PCE, and cis-1,2 DCE contamination. The remediation strategy was to continue extraction at the drinking water wells, excavation of one of the source areas (this included bottomless septic tanks where dry cleaning solvent was dumped), installation of a soil vapor extraction system (which only operated for 1 year due to its inefficiency), and institute administrative restrictions at the site that restrict future excavation activities and well installation activities. Two air strippers have been treating the main groundwater plume at the site since 1984. Emissions from the air strippers meet air quality standards. Groundwater in the aquifer continues to be a drinking water source. The source area for groundwater contamination was considered to be eliminated after excavating soil and sludge and the short term use of the soil vapor extraction [90].

Historic PCE concentrations in the drinking water wells ranged from 100 to 500 ppb, while historic PCE levels in other wells were 57 ppb and 3 ppb [90]. After beginning the air stripping, groundwater concentrations began decreasing rapidly and have continued to do so since. Table 3-3 shows the groundwater concentrations that have been measured onsite overtime. Well 20B has had the highest concentrations of all the wells sampled in May 1993, January 1997, and February 2002, but concentrations have been decreasing. The analytical data supports the agency’s conclusion that groundwater VOC concentrations are steadily decreasing. Effluent from the air strippers is meeting drinking water standards before it is discharged into the Lakewood water supply distribution system.

Table 3-3 VOC Concentrations at Lakewood/Ponders Corner

Well	Contaminant	Concentration µg/L May 1993	Concentration µg/L January 1997	Concentration µg/L February 2002
20B	TCE	12[c]	100[a]	200[a]*
20B	PCE	700	373	248
16A	TCE	---	1.1	0.8[b]
16A	PCE	---	54	47
H-1/H-2	TCE	---	0.4[b]	0.2[b]
H-1/H-2	PCE	---	18	12

[a]=The analyte was not detected at or above the reported result.
[b]=Analyte was positively identified. The associated numerical results is an estimate.
[c]=Analysis performed at second dilution.
*=High detection limit due to interference.
Source: EPA (1997) and Ecology (2002)

Summary of Evidence of Groundwater Contaminant Reduction

Some significant conclusions can be drawn from the data presented in the Superfund sites described above and others that were reviewed. First, it appears as through the VOC removal efficiency of the air stripper decreases overtime. This trend represents the concentration of VOCs in the groundwater reaching asymptotic levels. Once asymptotic levels are reached, significant removal of VOCs via air stripping is not likely, and the ability to reach cleanup goals is not likely either. Second, VOC masses can successfully be removed from groundwater plumes. This can be illustrated by groundwater sample results collected from monitoring wells and also from sampling air stripper influent. And finally, plume migration can be arrested and in one case decline in size. Table 3-4 below is a summary of the information gathered from the Superfund site case studies.

EPA and local agencies agreed in the above cases that the cleanup plans were successful because large masses of VOCs were successfully removed from groundwater. California agencies have concluded that remediation experience in California indicates that groundwater extraction may not be able to achieve low maximum contaminant levels. The gravity of this statement depends upon whether it is more important to remove a significant contaminant mass from groundwater or it is more important to be able to use that portion of the aquifer for drinking water. I think more state agencies are looking more toward reducing the mass than to return the aquifer to drinking water use, as was the case at the Synertek Superfund site, especially when the removal efficiency is reaching asymptotic levels and further significant decline using air stripping is unlikely.

Table 3-4 Summary of Air Stripping Case Study Information

The following is a summary of the information presented in section 3.2.2.2. The Lakewood/Ponders Corner reports did not provide some of the data that the other two reports provided.

	Intersil/Siemens	**Synertek**	**Lakewood/Ponders Corner**
# of Stripping Towers	1	1	2
Initial Groundwater TCE Conc. (year)	2,100 ppb (1991)*	<200 ppb (1996)[a]	103 ppb (1985)[b]
Secondary Groundwater TCE Conc. (year)	150 ppb (2004)	7 ppb (2001)	2.6 ppb (1991)
Groundwater Conc. Reach Asymptote?	Yes	Yes	Yes
TCE Mass Removed Over Time	0.7 kg per 1 million gallons	5.8 kg/year**	---
	0.28 kg per 1 million gallons	2.2 kg/year***	---
Liters Treated per Year	87 million	151 million[c]	---
Expected Cleanup Time	++ 20 years	+10 years	+10 years

Siemens well H-5B.
**Average 1991-1995.
***Average 1996-1999.
[a]MW-12A
[b]MW-20B
[c]1991-1995

3.2.3 General Pump-and-Treat Limitations

A 1994 study conducted by the National Resource Council reviewed 77 contaminated sites across the nation that employed some form of a pump-and-treat technology. A portion of the review was to determine if the groundwater treatment system in place is effective and whether achievement of cleanup goals was anticipated. This study found that of the 77 sites, cleanup goals had only been achieved in 8 of them, and 34 of the sites likely would never reach cleanup goals with the pump-and-treat treatment method that was in place [63]. This study exemplifies the fact that contaminated groundwater is extremely difficult to treat and there are no quick fixes no matter which method you choose. The type of contamination further complicates the ability for treatment.

3.2.4 Geology and Aquifer Limitations

Much like all other remediation methods, each site is different and the effectiveness of air stripping at one place can not be ensured to be the same elsewhere. There are some fundamental limitations to this technology that pertain to site characteristics because the performance of the air stripping method is directly related to the site conditions that are present. For example, if the geology of the site is limited to a heterogeneous aquifer that includes zones of low permeable soil, the amount and rate of groundwater that can be extracted and treated (and subsequently injected back into the ground) is curtailed [61, 75]. These heterogeneous conditions sometimes create a situation where the water has a hard time flowing to the pumping wells. As water is pumped from the aquifer, the characteristics of the groundwater change such that contaminants sorbed or precipitated in the soil can dissolve back into the groundwater thereby increasing the contaminant concentrations in the water that is being removed [75]. Other groundwater characteristics that changes while the water is pumped include temperature.

Using air stripping for remediation of TCE contaminated groundwater can be difficult given the DNAPL nature of TCE. This method can remove dissolved TCE, but is ineffective at treating any deposits of concentrated TCE at the bottom of an aquifer [44]. Furthermore, as groundwater is pumped past the DNAPL, there is slow dissolution of the DNAPL pool into the groundwater, serving as a constant source of contamination [75].

While pump-and-treat methods are employed, the DNAPL deposit provides a source for continued dissolved TCE that will exist until the deposit is removed thereby making the pump-and-treat method inefficient.[75]. Some studies have found that pump-and-treat may not be able to remove enough TCE to restore an aquifer to drinking level standards [63]. This often is because of the presence of TCE in the DNAPL form deep in the aquifer; because the TCE has adhered to solid materials in the subsurface; or because drinking water standards can not be practically obtained using the pump-and-treat method.

3.2.5 Time

Another limitation to pump-and-treat utilizing air stripping is the time that is required to extract and treat all of the contaminated groundwater. Utilizing pump-and-treat for groundwater cleanup is a slow process that can take tens or hundreds of years [63]. Obviously, if a treatment system is pumping small amounts of groundwater at a time, it will take far longer than if large quantities are removed. However, high extraction rates are just not feasible at some sites because of groundwater and subsurface geologic conditions and aquifer properties. Utilizing variable pumping rates may help with contaminant dissolution, but it also increases the amount cleanup time [63].

Occidental Chemical Company Superfund Site

The Occidental Chemical Company Superfund site is located on the Hylebos Waterway at the Port of Tacoma, Washington. Groundwater is contaminated with VOCs including TCE. The groundwater treatment system, which included a network of extraction wells and an air stripper were installed in 1994. The air stripper treats approximately 416 liters per minute (110 gpm) of water with concentrations of VOCs ranging from 15,000 to 40,000 ppb [91]. This leads to a mass removal rate of 8 to 10 kg (18 to 24 pounds) of VOCs per day. An evaluation study conducted in 2003 indicated that only the western portion of the plume is being controlled, preventing discharge into the Hylebos Waterway. Some of the monitoring wells have experienced a decline in contaminant concentration of VOC contaminants of concern (for example from 120,000 ppb down to 50,000 ppb since the implementation of the air stripper). The efficiency of the air stripper is approximately 97.65% (for chloroform) but effluent concentrations are still not meeting cleanup goals because of the high original concentrations. The 2003 evaluation determined that the pump-and-treat technology at this site is going to take several decades (rather than the projected 30 years), possibly even centuries, to reach clean-up goals; however, this form of treatment was deemed as the only one that can be successful at capturing the contaminant plume and treating the extremely high contaminant concentrations.

3.2.6 Fouling

The most common problem with air strippers is that the packing material can become fouled by organic and inorganic impurities in the water [77, 79, 92]. Impurities can include bacteria, fungi, metals, salts, or fine particles [76]. For example, iron in the water can be oxidized, due to the injection of air into the water, to form ferric iron, which precipitates onto the packing material [75, 92]. This can occur when iron in the water is at concentrations greater than 5 ppm [79]. Manganese can be oxidized and precipitate onto packing material [75]. Calcium carbonate scaling can occur when carbon dioxide is actively stripped from the water [62]. A biological sludge can form on packing material when there is excessive microbial action. The aeration of the water can enhance microbial growth as does exposure to ultra violet light [92] and heating of the influent water [62]. The precipitation of metals or the microbial growth on packing material helps provide a base for the accumulation of one another [92]. Impurities in the influent groundwater such as iron precipitates can form a sludge in the tower that must be removed [73]. Water that is rich in fouling minerals can decrease efficiency of contaminant removal due to headloss, air flow constriction, decreased capacity, and channeling of the water caused by the packing material becoming fouled [73, 75, 79, 92]. Contrary to the claims of some packing material manufacturers, the shape of the packing material can not prevent fouling from occurring [92]. Having the packing material routinely removed and wash or replace the packing material is costly because of the maintenance and resource requirements. The buildup of fouling materials on the packing material can greatly increase the weight of the internal structure [92]. Figure 3-4 (below) shows a clean piece of packing material (center top) and two fouled pieces of packing material (left and right).

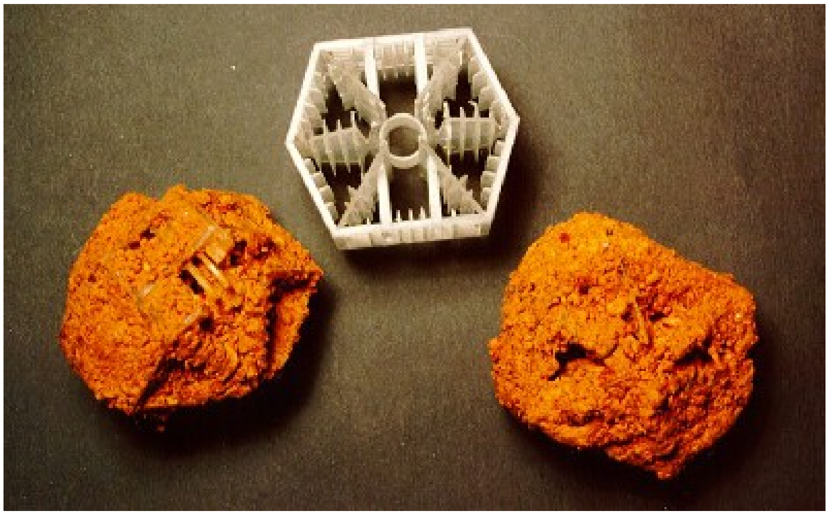

Figure 3-4 Fouled Packing Material. This photograph depicts two fouled pieces of packing material and one clean piece of packing material as a reference. Source: Jaeger Products Inc. (1996)

Fouling of inside of an air stripper is inevitable, even when pre-discharge filtering occurs. Variables that affect the fouling of the interior of an air stripping tower include the contents of the water, the rate of water discharge into the tower, and the water temperature [92]. These variables can be reduced or eliminated by modifying the operation of the air stripper system. For example, fouling sometimes occurs in areas that only receive water on a sporadic basis or when air is allowed to blow up through the tower when influent water is not being discharged thereby causing the packing material to dry [62]. The "dead spots" allows an environment for precipitation, scaling, and bacterial growth to occur. By increasing the amount of water that is being discharged through the tower, the dead spots should be eliminated or at least minimized [92]. The contents of the water can be altered if it is treated prior to discharging into the air stripper. Changes in the pH, microbial, and metal content of the water can occur during water pretreatment with sequestering agents, acids, and biocides [92]. Adjustments in the pH by adding agents to the influent may be necessary to bring the influent close to a neutral pH because it has been found that water with a pH greater than 11 or less than 5 can corrode the air stripping system [73]. Pretreatment of the influent can also reduce the amount of algae that could lead to fouling, and can keep metals from precipitating in the tower [92]. Ozone and chlorine addition to influent water can help mitigate microbial growth. The tower can also be periodically flushed with chemicals (including mild acids such as phosphoric or nitric acid; detergent solutions; potassium permanganate; hydrogen peroxide; and phosphates) to help remove any build-up on the packing material. The air stripper would be temporarily taken off-line while the chemicals are injected and collected for recycling. This is so that the chemicals will not get into the effluent groundwater, which could lead to secondary contamination.

Fouling of the packing material can lead to the water forming channels that run down along the sides of the tower preventing the water from trickling through the various orifices of the packing material and thereby limiting the aeration [72]. This can be mitigated with the use of redistributor plates that redirect the water back onto the packing material.

3.2.7 Air Emissions

The air stripper system is designed to emit TCE to the air and this is considered a limitation of this technology [93] because from that perspective it becomes a source of air pollution [80]. It is a source of pollution because an air stripper can emit more TCE into the atmosphere than what natural processes can handle. TCE is considered a hazardous substance and the emissions from the air stripper are regulated by the Clean Air Act [75]. Emission of TCE to the air requires a permit from the local environmental regulating agency. One of the examples of successful treatment described earlier was the Wurtsmith Air Force Base. The Wurtsmith Air Force Base was used as an example of the successful treatment. Assuming this system was pumping 6.6 million liters per day, approximately 3.3 kg per day (7.3 pounds) of TCE would be emitted to the air [67]. At the Savannah River Site in 1993 approximately 8,845 kg (19,500 pounds) of VOCs were emitted to the air, which correlates to approximately 1 kg (2.2 pounds) per hour [85]. TCE was estimated to compose approximately 75% of the contamination that was treated by the air stripper, which equates to air emissions in 1993 of approximately 6,634 kg (14,625 pounds) of TCE. The Savannah River Site has a permit with the South Carolina Bureau of Air Quality Control allowing the emission of approximately 31 metric tons (34 tons) of VOCs to the air per year [85]. Similarly, in the Puget Sound region, the Puget

Sound Clean Air Agency requires permits for emissions from air strippers. Because of the air pollution concern, the volatilized TCE is often treated once it is produced.

An EPA report from 1987 discussing air emissions from air stripping towers contained data from 52 sites in the US using air stripping to remove contaminants from water. The amount of volatile organic compounds that were emitted to the air on an annual basis ranged from as little as 1 kg per year to as much as 24,000 kg (24 tons) per year [94].

The treatment of the off-gas is yet another costly treatment, but is often required. Typical off-gas treatment is through granular activated carbon filtration [75, 93] or thermal oxidation [62]. Off-gas treatment can typically treat 90-99% of the emissions [95]. The granular activated carbon used for treatment of stripper off-gas is very similar to that which was used for aqueous adsorption of TCE. The difference is that the carbon used for off-gas adsorption is coarser and has a greater fraction of small micro-pores [62]. Treating vapor phase TCE by granular activated carbon is more efficient than treating aqueous phase TCE [62].

3.2.8 Aquifer Depletion

Aquifer depletion is a serious problem that the U.S. and even the world are facing, but part of this problem is also depletion of potable aquifer sources. This includes the contamination of potable sources. Air stripping and other pump-and-treat remediation techniques are trying to control and mitigate the contaminated aquifer problem, but part of the trade-off is removing (often temporarily) the water from the ground for treatment. With air stripping, most often the water is returned to the ground via infiltration or through irrigation. The return of the treated water helps offset the aquifer depletion and potentially returns the water to the aquifer meeting standards that suit the typical water use of the surrounding area (i.e. drinking water standards if adjacent to drinking water sources or to industrial standards if water is only used for industrial purposes).

There is always the risk of aquifer depletion when large quantities of groundwater are being pumped to the surface. This is more of a risk when conducting pumping for treatment by an air stripper given the quantities of water that are removed at a time. For example, at Schofield Barracks on Oahu, Hawaii using air stripping towers to control a TCE plume and address aquifer restoration was estimated by one model to require the pumping and re-injection of approximately 64 to 212 million liters (17 to 56 million gallons) per day and the water was to be used for domestic use instead of directly infiltrating the effluent back into the aquifer [96]. A second model estimated an extraction/reinjection rate of 818 million liters (216 million gallons) per day to restore the groundwater based on the plume boundaries. This alternative for remediation was not chosen because of the shear volume of water that was required to be extracted at one time. An interesting side note is that in order to be able to pump this amount of water, it required more energy than what is available on Oahu's power grid.

3.2.9 Energy Requirements

The amount of energy that it takes to support an air stripper is high [79]. The pumps that bring the groundwater from the wells to the storage tank and then from the storage tank into the stripping tower require energy to operate. The air blower requires energy as well. The amount of time that the air stripper is operated obviously controls the amount of energy that will be used. If a granular activated carbon treatment is utilized for stripper off-gas treatment, the off-gas is typically heated and therefore the heater requires energy as well. At the Savannah River Site in Georgia, the 1993 cost of electrical energy to support the air stripping tower was estimated to be $26,000 ($0.052/kwh) [85] and was likely derived from coal fired or nuclear power plants.

3.2.10 Other Limitations

Other limitations to this technology include:

- Aesthetics and noise [68, 76]. These two issues might be of greater importance if the remediation site is located near a residential or recreation area where the general public may be exposed. It is more likely for the air stripper to be seen as a nuisance (or its installation be protested) if it is located in an area that is not already industrially developed. The public may also stand in protest of the emissions from an air stripper if it is located in a residentially populated area.

- The pumping rate could fail to cease the migration of the plume.
- There is always the chance of mechanical failure when using machines for treatment [75].

4.0 PHYTOREMEDIATION OF TRICHLOROETHYLENE

Research and field studies using phytoremediation for cleaning solvent contamination has constituted a sufficient body of positive evidence that the methodology is nearing the point of becoming an accepted technology by regulators [51]. TCE is a good candidate for phytoremediation because of its chemical properties that make it readily available for uptake by plant roots. Furthermore, TCE is a contaminant that has significantly affected aquifers throughout the country (and perhaps even the world). Many of the sites that are contaminated with TCE span hundreds of acres, making it expensive to treat the entire land area using conventional remediation methods. This section discusses one of the main means for the phytoremediation of TCE contaminated groundwater.

4.1 Types of Plants

Alfalfa, legumes, loblolly pine, soybeans, and black locust species are among those plants that have been used to treat TCE contaminated groundwater and eucalyptus has been suggested as a viable option as well [45]. Nevertheless, trees of the *Populus* species have proven to be extremely effective at phytoremediation because of some of the plant characteristics and the ease at which these plants can be installed and maintained.

4.2 *Populus* Species

The genus *Populus* includes varieties of poplars, cottonwoods, and aspens [41]. *Populus* species, referred to as poplars or even popple, are a member of the *Salicaceae* family, which includes other phreatophytic trees such as willows. There are 30 species of *Populus* in the Northern Hemisphere that grow in a variety climatic conditions, eight of which are indigenous to North America and can be grown as north as Alaska and as far south as Central America [97]. One or more types of *Populus* species are native to every state in the nation, except for Hawaii.

The following are the poplar species that are found in North America. The list also includes the type of climate that the poplars typically thrive in.

- Aspens and white poplar are found circumpolar in the sub-arctic regions in cool temperate environs and some mountains further south. These include quaking aspen (*Populus tremuloides)* in North America and bigtooth aspen *(P. grandidentata)* in eastern North America [98].

- Black poplars and cottonwoods are typically found in North America, Europe, and western Asia in temperate climates. These include black poplar (*P. nigra),* eastern cottonwood (*P. deltoides)* in eastern North America and Fremont cottonwood (*P. fremontii)* in western North America [98]. The black poplar is not native to the United States but is found in many of the states.

- Balsam poplars are found in North America and Asia in cool temperate environments. These include willow-leaved poplar or the narrowleaf cottonwood (*P. angustifolia)* in central North America, Ontario balsam poplar (*P. balsamifera*) in northern North America and western balsam poplar or black cottonwood (*P. trichocarpa)* in western North America. Ontario balsam poplar, also known as black cottonwood is a native to the coastal areas of the Pacific Northwest [99].

- Necklace poplars or bigleaf poplars are typically located in eastern North America and eastern Asia in warm temperate environments. These include swamp cottonwood (*P. heterophylla)* in southeastern North America [98].

Natural and laboratory cross breeding is successful, creating many different potential hybrid combinations [97]. Selective cross-breeding has been used by foresters for many years in order to select for ideal characteristics such as fast growth rates [41]. Another goal of poplar cross-breeding is heterosis, which means the result when the genetic traits of the hybrid exceed that of the parents [41]. Heterosis is a common practice in the agricultural field as scientists have strived for decades to create the most hearty, high yielding, disease, drought, and pest resistant crop possible to maximize the amount grown with the least amount of inputs. This is similar for the phytoremediation field such that scientists want to create hybrid species that are fast growing, large leaved, disease, drought, and pest resistant, hyperaccumulating, and tolerant to high levels of contaminants because these traits effectively maximize the plants ability to perform phytoremediation functions. The following are the most commonly used poplar hybrids in TCE phytoremediation projects:

- Black cottonwood and eastern cottonwood (*Populus trichocarpa x deltoides*. This hybrid is commonly used for phytoremediation because it has leaves that are approximately four times larger than the leaves of the parent trees. The increased leaf size increases the potential evapotranspiration rates because of the increased leaf surface area [41]. In laboratory and greenhouse studies, this hybrid has shown the ability to take up and degrade TCE [100]. Black cottonwood species and hybrids are often used at phytoremediation projects in the Pacific Northwest because they are native to this region.

- Eastern cottonwood and black poplar (*Populus deltoides x nigra*) is another popular cross that has been named Imperial Carolina [13]. These hybrids are often used in laboratory experiments.

- *Populus charkowiiensis x incrassata*. This hybrid was used at a highly contaminated site in New Jersey [41].

On average, poplars can grow 3 to five meters per year [41, 48]. Poplars are long lived and can live between 25-30 years [41]. Hybrid poplars, such as Imperial Carolina (*Populus deltoids x nigra)* can survive approximately 30 years [100]. This is a sufficient timeframe for a remediation project [13].

The root systems of poplars are strong and are often referred to as invasive as they tend to extend vertically and horizontally in search for a water source, reaching up to 15 feet deep [101]. This trait can be harnessed to the benefit of the phytoremediation project by planting the trees in such a way that the roots are directed down towards the impacted aquifer and away from shallow, perched, or surface water. This is an important concept because poplars will take advantage of water that is relatively close to them, such as soil water or surface water. Poplars also vary where they get their water based on climate and changing transpiration needs [50]. So, in order to maximize the amount of contaminated water that is used by the poplar and to maximize the efficiency of the phytoremediation project, precipitation and any other uncontaminated water sources should be limited by planting the roots of the trees several feet bgs such that only a few inches of the tree is above the ground. Downward root growth can also be achieved by planting the roots inside of plastic tubes that prevent the lateral root migration. A final method for downward root growth is to install an impermeable barrier in the soil (impermeable soil or a manufactured barrier) that prevents rainwater from percolating through the soil, which makes the roots of the trees search for water in other locations when the shallow source is eliminated.

Figure 4-1 Young Cottonwood Tree. This photograph depicts a young cottonwood tree at a phytoremediation site in Pasco, Washington. Source: Golder (2003)

Hybrid poplar trees are typically planted at 1,000-2,000 per acre. Depth is 12-18 inches or they are installed in trenches from 1-6 feet deep. The trees are typically planted two feet apart and rows of trees are typically ten feet apart. Poplars can also be planted as whips or cuttings that will root and grow rapidly within the first season [13]. The dense initial planting is to ensure a large amount of evapotranspiration (and therefore contaminant attenuation) in the first year. Planting a large number of trees in the beginning can also act as a safeguard against loss from disease or from hungry animals. Over the first six years the trees will naturally thin themselves to approximately 600-800 per acre. Hybrid poplars can be harvested on a six-year rotation. Harvested trees could then be sold for fuel or pulp and paper, assuming that levels of TCE in the tissue will not pose a human health risk or risk to the environment. The poplar trees should naturally grow back from the harvested stumps, allowing for the root system to stay in place, which provides stability to the surrounding soil, much to the benefit of the remediation project since no time is wasted waiting for the new plants to take root and waiting for transpiration to begin again.

Figure 4-2 3-Year Old Cottonwood Tree. This photograph depicts a stand of young cottonwood trees after their third growing season at the Carswell Air Force Base phytoremediation site.
Source: EPA & DOD (2003)

Advantages for using poplars in phytoremediation include:

- Fast growth rate;
- High transpiration rates;
- Not a food source for many animals;
- Harvested phytoremediation trees can subsequently be used for pulp and paper production or as biomass fuel;

- Trees do not have to be harvested in order for effectiveness to be maintained;
- Long lived;
- Roots provide an addition of organic material to the subsurface; and
- Grow easily from cuttings and can re-grow from stumps utilizing established roots.

4.3 Processes of Remediation

Poplars are known to degrade contaminants such as TNT, atrazine, and nutrients from groundwater through phytodegradation [45]. Poplars also effectively removed 95% of carbon tetrachloride from water originally contaminated by 50 ppm [45]. It stands to reason that based on the biological characteristics of poplars, their varying habitats, and their ability to treat other contaminants that they would be a good tree to use for phytoremediation of TCE contaminated groundwater.

Laboratory, greenhouse, and large-scale field studies have proven the fact that poplars can remove TCE from contaminated groundwater [102]. As mentioned earlier, some research has shown that results from laboratory studies on TCE (and other contaminants for that matter) do not necessarily directly correlate with the same outcomes in full-scale field applications due to the varying conditions (and the ability to control variables) inside a laboratory as compared to field conditions. This can occur because of artifacts that are introduced during laboratory studies [103]. The artifacts include the type of sampling equipment that is used or even the level of stress that the plants undergo [103]. Studies have shown that stress has caused plant roots to become more permeable. It is not to say that laboratory results produce false results. This cautionary note is to merely point out that the results from laboratory studies on TCE and poplars (and in particular studies on phytovolatilization) must be followed up by field based research. Because of this finding, one can not rely solely on laboratory data to support hypothesis and one certainly can not design field scale remediation plans based on findings that were never tested in the field. If the laboratory findings did not hold true in the field, a great amount of money and energy would have been wasted on a remediation design that was doomed to fail because of a lack in prevailing practical data. Accordingly, the true test of the laboratory data would be field studies. Some field studies on the interaction between TCE and poplars (although the overwhelming majority of research has been in laboratories or greenhouses) have supported the laboratory data showing that poplars have the ability to degrade TCE initially, but long-term data (discussed later in this chapter) from field applications is still limited.

Studies using poplars planted in soil imitate field conditions far better than hydroponic grown trees and therefore may be better indicators of the effect of TCE on poplars [102]. One of the problems with studies utilizing soil grown plants is that the contaminant can be adsorbed to the soil particles and therefore not be readily available for plant uptake, limiting the ability to observe the maximum uptake ability of the plants. Nevertheless, absorption of TCE to organics in the soil is a process that happens in natural settings and must be contended with during field applications of the remediation method.

Poplars ability to efficiently remove TCE from groundwater and soil water varies from plant to plant, attributable to plant age, plant size, season, growth conditions, stress, root proliferation, and soil conditions [102]. We can say with somewhat certainty that poplars can remove TCE from groundwater, but the actual rate at which it can be removed is limited and variable by the above factors. The most critical component of a poplar's ability to treat TCE contamination is the ability for the tree roots to extend through the soil. Reportedly, a typical poplar plantation can grow 75,000 miles (accumulative root length) of fine roots per acre [45]. This allows the trees to cover a substantial extent of the hazardous waste site.

The process of remediation of TCE contaminated groundwater by poplar trees uses some of the phytoremediation mechanisms that were outlined in Chapter 2. These include hydraulic control, rhizosphere biodegradation and microbial degradation, phytodegradation, and phytovolatilization. When poplar roots reach into an aquifer contaminated with TCE, the roots are able to uptake the TCE as they draw in water for their growth. The act of drawing the contaminated water in can sometimes stop the movement of plumes. TCE is also drawn to the plant through adsorption to the roots and absorption through the roots. Sometimes microbes in the rhizosphere that are stimulated by the poplars can degrade the TCE. As the water and TCE is drawn up inside the plant, the TCE can be degraded by plant enzymes or metabolized by bacteria within the plant vascular tissue [57]. As TCE moves up through the plant it is oxidized from its roots up through the aboveground portions of the plant [97]. TCE can also be volatilized from the plant leaves. These methods, as pertaining to TCE removal by poplars, are discussed in further detail in the following subsections. Figure 4-3 shows the process of contaminant uptake by trees.

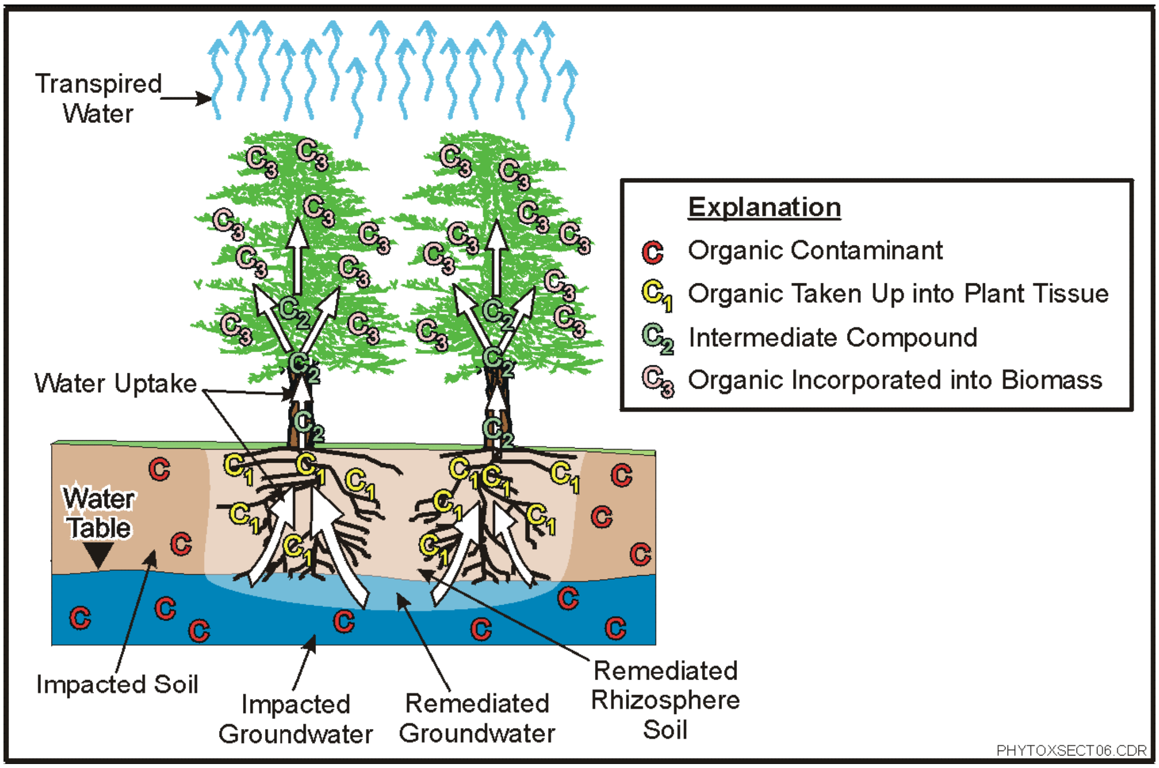

Figure 4-3 Contaminant Uptake by Poplars. Source: ITRC (2001)

4.3.1 Hydraulic Control

Poplars are known for being phreatophytic vegetation that take up large amounts of water. Uptake rates of the plants vary by species, age, size, location, and climate, but on average a five year old tree can take-in between approximately 100 to 200 liters (26-52 gallons) per day [41, 45]. Evapotranspiration and water uptake is greater in the summer months due to increasing solar energy and more fully developed leaves with greater surface area [41]. Evapotranspiration in summer months may decrease mid-day during the hottest parts of the day if there is a shortage in water supply. A study by Newman et al (1999) measured the amount of water added to cells constructed as artificial aquifers planted with poplar trees and the amount of water that was removed from the cells. This experiment showed that large amounts of water, on the order of 43,000 liters, were removed by the trees from the cells during the growing season. It was reasoned that because of this ability to remove large quantities of water from the ground, poplars have the potential to reduce the rate of groundwater flow, which could lead to a reduction in the spread of contaminants in the groundwater [100]. This is a very significant finding (as will be discussed in following sections) because this characteristic is an important phytoremediation process that poplars are known to successfully perform.

Table 4-1 Typical Poplar Transpiration Rates

Poplar	**Age**	**Transpiration Rate (lpd per tree)**
Cottonwood	2 years old	8 - 14
Hybrid Poplar	5 years old	76 – 151
Cottonwood	Mature	189 – 1,325
Weeping Willow (*Salix sp.)*	Mature	757 – 2,028

lpd = liters per day
Source: ITRC (2001)

Tree roots can reach down into the groundwater aquifer [48]. The deepest aquifer on record that has been affected by phytoremediation, specifically by tree roots is 40 feet bgs [48]. A stand of poplar trees with roots in the contaminated aquifer can have an impact on the groundwater resulting in a depression in the water table ranging from a few inches to a few feet [41]. This depression in the water table leads to a general flow of the localized groundwater plume toward the poplars, which can in fact prevent the plume from migrating any further down gradient. This in essence is how poplars hydraulically control groundwater plumes.

4.3.2 Rhizosphere Biodegradation

Rhizosphere biodegradation is also a mechanism of TCE degradation [41]. This degradation can occur both aerobically and anaerobically by different microbes in the rhizosphere. TCE in the soil can also be degraded by exudates excreted by the plant through the roots. There are two methods through which degradation occurs, aerobic and anaerobic. Aerobic degradation of TCE occurs co-metabolically [26]. Co-metabolites include methane, toluene, and phenol. The plant produces exudates in the rhizosphere that stimulate anaerobic methanogens to produce the methane. The methane then stimulates aerobic methanogens to metabolize TCE. This process produces similar metabolic products as are produced in the plant tissue, which are depicted in Figure 4-4 [41]. This process was suspected to be occurring in the root zone of naturally occurring vegetation growing over TCE contaminated soils and groundwater at the Savannah River Site in South Carolina. Aerobic degradation was suspected to be occurring here because of a study that was conducted on microbial activity in rhizosphere soils spiked with TCE and because TCE degrading bacteria have been observed as being methane oxidizers that have an affinity to soils that periodically flood and drain [54]. The soil experiment was conducted on soil collected from the rhizosphere of *Paspalum notatum* (a grass), *Lespedeza cuneata* (a legume), *Salidago* sp. (an herb), and *Pinus taeda (*Loblolly pine). The study showed that there was more organic carbon in vegetated soils than in unvegetated soils and there was a significantly greater amount of CO_2 efflux from the vegetated, contaminated soil. Furthermore, a greater amount of TCE was lost from the headspace of soil slurries (using rhizosphere soil from the above plants). The loss of TCE in the headspace represented the biological transformation of TCE. Unfortunately, poplars were not used in this experiment however; this study represents the ability for TCE degrading microbes to be stimulated by plants in the rhizosphere.

Table 4-2 Microbial Activity in Rhizosphere Soil

Soil Source	% Organic Carbon	Net CO_2 efflux	TCE Loss from Headspace
Non-vegetated non-contaminated	0.20 (± 0.04)	0.62 (± 0.04)	40%
L. cuneata	1.35 (± 0.01)	4.93 (± 0.17)	55%
Solidago sp.	1.20 (± 0.05)	5.90	---
P. notatum	1.43 (± 0.05)	4.17 (± 0.68)	---
P. taeda	1.26 (± 0.03)	3.52 (± 0.49)	---

There is missing data for some of the soil sources because not all of the headspace loss values were provided in the data.
Source: Walton and Anderson (1990)

Anaerobic degradation of TCE in the rhizosphere is also stimulated by plant exudates and organic matter that help increase the density of the methanogenic microbial population, which in turn dehalogenate TCE [26, 41]. Eastern cottonwoods have been shown to have the potential to add organic carbon matter to the rhizosphere to support anaerobic degradation of TCE in the form of reductive dechlorination [104]. Anaerobic dehalogenation of TCE produces 1,2-dichloroethylene, vinyl chloride, ethene, and ethane [41]. It is determined that these are products of TCE degradation when there is no known source of these constituents. Figure 4-4 depicts the anaerobic degradation of TCE (and PCE) that can occur in soil.

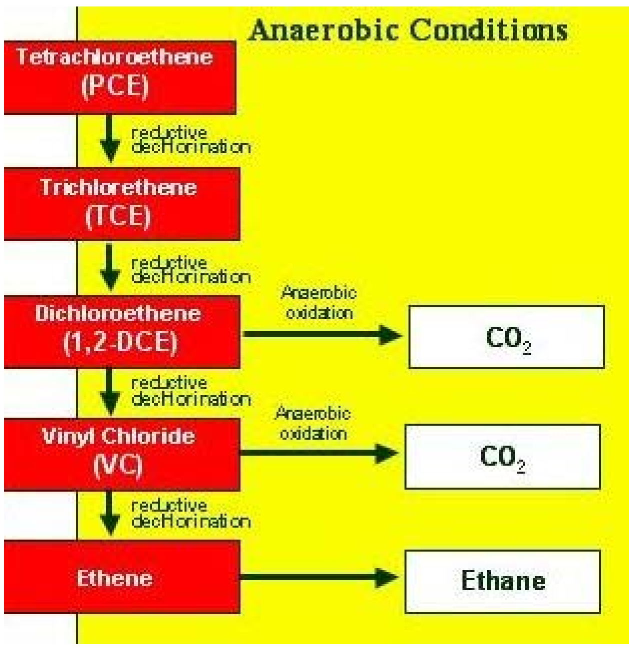

Figure 4-4 Anaerobic Degradation Pathways. This figure depicts the way that TCE is degraded under anaerobic conditions. Source: Hazardous Substance Research Center (2005) www.hsrc.org/prague/major

Newman et al. (1999) detected reductive dechlorination products cis-1,2-dichloroethylene (cis-DCE), trans-1,2,-dichloroethylene (trans-DCE), vinyl chloride, 1,1-dichloroethane, and 1,1,2-trichloroethane in effluent from poplar planted artificial aquifers. These compounds were assumed to be the products of microbial and anaerobic reduction of TCE in the anaerobic zone of the soil, but it is not likely that microbial community was enhanced by poplar exudates, except for organic matter provided by the roots. They found no evidence to support enhanced microbial degradation of TCE in aerobic soil conditions. This is not to say that rhizosphere biodegradation of TCE does not occur, rather the results of this study (showing marked TCE degradation within the plant tissue) indicated that rhizosphere biodegradation was not a major mechanism of TCE loss from the groundwater and that poplars did not enhance the microbial community like other plants can do.

Because poplars do not always enhance the microbial communities for TCE metabolism (as the Newman et al. (1999) study indicated), it is assumed that rhizosphere biodegradation is not a major mechanism for TCE removal from groundwater, though it has been observed taking place in a limited manner at some project sites. However, results from the Carswell Air Force Base phytoremediation plantation (discussed later in this chapter) indicate that microbial degradation below a mature cottonwood (at least 20 years old) is occurring. This may indicate that it takes time for a poplar to be able to change the soil and groundwater conditions to those that support microbial degradation of contaminants. All of the studies, except for Carswell Air Force Base, were drawing conclusions on microbial degradation by poplars from studying young poplars. Enough of the data indicated that poplars take at least a decade to begin efficiently degrading and volatilizing TCE, so it stands to reason that a tree's ability to aid microbial degradation will take that long as well [61, 104-106]. Most likely it is not a major mechanism for TCE removal from groundwater (though there is only very limited data on mature poplar microbial degradation), but likely it is a measurable one.

4.3.3 Phytodegradation

The uptake of contaminants by plants through their roots is dependent upon the hydrophobicity, solubility, and polarity of the contaminant as discussed in previous chapters [45]. Those organic contaminants with moderate hydrophobicity (log k_{ow} between 0.5 and 3.0) are most readily taken up by plant tissue. TCE is a moderately hydrophobic chemical with a log k_{ow} of 2.33 and is a polar substance. Molecularly polar contaminants can be taken in by plant tissue whereas non-polar (those with molecular weights less than 500) will only sorb to root surfaces [45]. Because of TCE's hydrophobicity, it can easily pass through the cell membrane of plant roots. Burken and Schnoor found that organic contaminants, such as TCE, with log k_{ow} values less than 3.0

had a greater potential for sorbtion to hybrid poplar roots [107]. This means that TCE can be readily taken up by plant roots and into the plant tissue [108]. Once the TCE is taken into the plant, a number of things can happen to the contaminant. TCE can be metabolized, mineralized, or accumulated in the tissue.

TCE can be metabolized within poplar plant tissue. This is a more desirable method of TCE sequestration than phytovolatilization because the TCE is being broken-down aerobically to less toxic metabolites rather than being reintroduced back into the environmental (atmosphere) as the toxic parent product [35]. Anaerobic degradation of TCE typically does not occur in plant tissue at very significant concentrations if at all, so there is not a risk of producing vinyl chloride [57]. Through the process of phytodegradation, TCE has been metabolized by enzymes produced by the tree. As the enzymes aerobically breakdown TCE they produce trichloroethanol, TCAA, and DCAA within the tissue and leaves of hybrid poplar trees [35, 41, 45, 109]. This process is depicted in Figure 4-5.

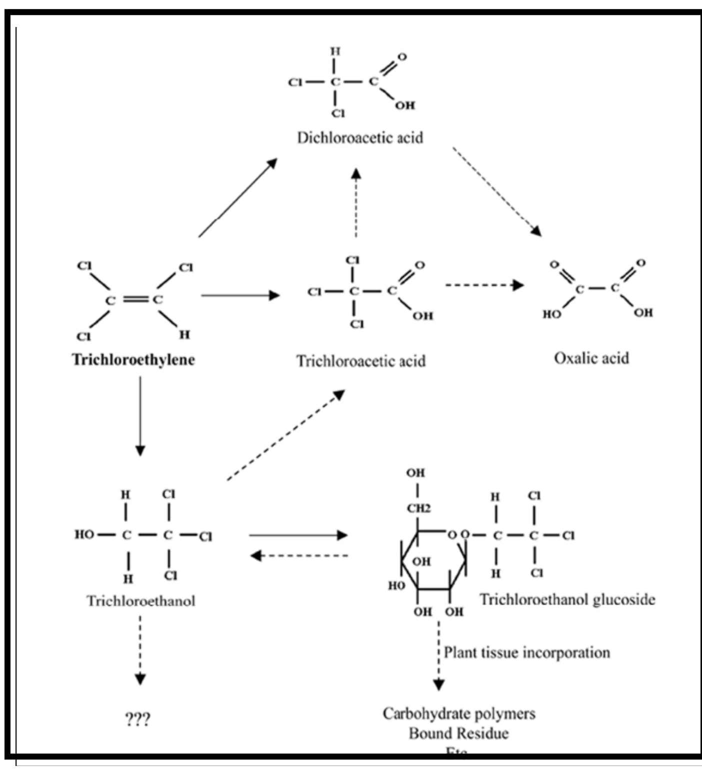

Figure 4-5 TCE Metabolism in Poplars. This figure depicts the various compounds that result from the metabolism of TCE in poplar trees. Source: Strand (2003)

These degradation products have also been identified in the livers of humans that have been exposed to TCE [13, 97]. In the liver, TCE has been degraded by the enzymes of the cytochrome P450 (oxygenases), which have also been identified in some plants as well [41]. This is how the term "green liver" was coined for plants that use the enzyme cytochrome P450 as the metabolic process using this enzyme is similar in both plants and mammals [56]. Unfortunately the literature did not identify specifically which enzyme within the family of cytochrome P450 is responsible for degradation of TCE.

Poplars may also degrade TCE and use the carbon for plant tissue growth and emit chloride ions out through the roots of the poplar and into the soil [45]. This has been identified by analyzing the amount of chloride ions in the root zone of soil planted with poplars and a control area that was not dosed with TCE. The chloride ions were excreted from the plant roots into the soil possibly because of an excess of free chloride that is being produced by the plant due to the act of TCE dechlorination [100]. The chloride ions adsorbed to particles and precipitated in the soil. Excess chloride in soil identified by Newman et al. (1999) lead them to believe that dechlorination within the poplar was a major degradation method.

Insoluble C^{14} from TCE was also found to bind with woody tissue cells within the plant [9, 14, 35]. There is also some speculation that the enzyme dehalogenase may also metabolize TCE to CO_2 but more research is needed on this subject [41]. Poplars can also cause, to some extent, the mineralization of the carbon in TCE as CO_2. Newman et al. (1997) also identified the mineralization of TCE as CO_2. Another mechanism is the degradation of TCE in the rhizosphere by exudates excreted by the poplar through its roots. Exudates commonly excreted by poplars include enzymes dehalogenases and laccase [110]. This degradation mechanism does not involve microbes in the rhizosphere and does not require the uptake of water into the plant for degradation to occur.

Newman et al. (1999) analyzed roots, leaves, and trunk and branch tissues of poplars planted in artificial aquifers to identify if TCE was being taken up by plant roots and if metabolism of TCE was occurring. These trees were dosed with water containing approximately 15 ppm of TCE [111]. This was a follow-up study to their 1997 laboratory and greenhouse work. They found that in the first two years after planting, DCAA and TCAA were the highest metabolites found in leaves while past greenhouse studies found DCAA and TCAA were the highest metabolites in tree tissue. During the third summer, the concentrations of DCAA and TCAA decreased as the levels of TCE increased in branches from 0.10 millimols (mM) in 1995 to 41 mM in 1997, indicating that less degradation was occurring and more of the TCE was being taken in and stored. TCE was the main chlorinated compound found in branch and trunk samples, most likely because these parts of the plant are less metabolically active than leaves and roots so the TCE is not degraded. Branch samples collected in the third summer had high concentrations of cis-1,2-dichloroethylene (0.29 mM in 1996 increasing to 7.2 mM in 1997), indicating that some form of anaerobic degradation of TCE was occurring within the plant tissue.

This study also measured the amount of the chloride ion that remained in the effluent as compared to the levels in the soil. Their results indicated that the chloride ion levels in the soil planted with poplars was ten times higher than the control soil that was not exposed to TCE. These results indicate that TCE was taken up by plant roots, dechlorinated in the plant tissue by degrading and metabolic processes, and the resulting excess chloride was excreted through the roots into the soil. The dechlorination of TCE and subsequent excretion of chloride into the soil is still a hypothesis posed by Newman et al. and must be further tested. The major TCE reducing mechanism at work during this field study was phytodegradation, although other mechanisms of reduction were identified as well [57]. Approximately 99% of the TCE was degraded within the plant tissue. These results support the findings of the Newman et al. 1997 laboratory and greenhouse studies on poplar cell and poplar tree metabolism of TCE.

Hydroponically grown plants were investigated for their ability to remove TCE in a laboratory study mimicking a natural environment [103]. Results showed that TCE was recovered in plant roots, leaves, and stems but that little phytovolatilization occurred, only volatilization straight from the soil. Roots had the greater concentrations. Aerobic metabolites of TCE were found in roots and shoots, although the root concentrations were greater. This lead the authors to believe that the primary location of the dechlorination was near the roots. The Doucette et al. (2003) findings from poplars growing in Utah and Florida above TCE plumes also found levels of TCE and its metabolites in tree tissues. These results further exemplify the ability of poplars to degrade TCE within plant tissue.

If the trees are going to be harvested for disposal or to be used as a cash crop, there is the issue of TCE remaining in the tissue of the tree. If the trees are to be disposed of or used for wood right away, there is the potential for the concentrations of TCE in the wood to be considered hazardous waste. However, often in the lumber industry logs are left outside for a season to "weather." In this case, the TCE has sufficient enough time to either volatilize from the wood or to be dechlorinated [57].

4.3.4 Phytovolatilization and Diffusion to the Atmosphere

Because of the high transpiration rate of poplars and the hydrophobicity of TCE, it can rapidly be taken-up by poplars and enters the transpiration stream of the tree [108]. This is one of the reasons why poplars are frequently used for TCE remediation. Once in the transpiration stream, TCE can be released as vapor during evapotranspiration, primarily from the leaves of the tree. Because the leaves are an integral part of this process, it is easy to understand why this process occurs during the day and during the spring, summer, and fall when the deciduous trees have leaves and there is plenty of sun to provide energy. Phytovolatilization of TCE is a known occurrence, but the amount of the contaminant that is actually volatilized, whether phytovolatilization is an effective method for removing TCE from groundwater by poplars, and whether the volatilized TCE is detrimental to human health or the environment are often questioned and are part of the focus of this thesis.

The volatilization of the contaminants or its byproducts to the air is not as desirable as treating the problem in situ, but it is sometimes seen as a viable alternative to allowing the prolonged exposure to the contaminant in the soil or groundwater and risking further contaminant migration [13]. Since anaerobic degradation of TCE typically does not occur in plant tissue at significant concentrations if at all, there is no risk of vinyl chloride being transmitted to the atmosphere via phytovolatilization [57]. At this point in time typical volatilization studies have focused on that of TCE from trees.

Much of the literature on TCE volatilization from poplars is conflicting. Some results indicated that some amounts of volatilization had occurred while other studies did not detect any volatilization. This can be due in part to volatilization measurement techniques (some are better than others) or due to varying site conditions such as TCE concentration, weather during volatilization measurement, the types of poplars used, the location on the tree where volatilization was measured, and most importantly, whether the research was conducted in a laboratory or in the field. As mentioned earlier, a few discrepancies have been identified between laboratory and field results. One of these discrepancies is the amount of volatilization that occurs in laboratory experiments and the amount incurred in practical field experiments.

Volatilization Laboratory Studies

During laboratory studies, it is important to be able to discern volatilization from foliage from volatilization from soil. Not all of the studies on TCE volatilization from poplars made a concerted effort to distinguish between the two volatilization routes. Volatilization from poplar leaves can only be determined when the roots and foliage are separated so that volatilization from the soil is not mistaken as volatilization from leaves. Even when taking into account only those laboratory studies that segregated roots and leaves, there is still great variability in the study results.

Burken and Schnoor (1998) found that 20% of the total TCE added to hydroponic plants was volatilized by plant leaves. In comparison, Orchard et al. (2000) designed a laboratory study to attempt to eliminate laboratory artifacts that are typically introduced in most laboratory research with TCE volatilization by poplars. This series of studies was designed to investigate the uptake of TCE by hydroponically grown poplars in a laboratory atmosphere that represented a natural plant environment. Artifacts commonly introduced in the laboratory include the use of low-flow, semi-static or simplistic plant growth chambers; static root zones that may cause stress to the plant; including root zone volatilization in foliar volatilization results; and plant stress [103]. The Orchard study designed a growth chamber and sampling system that attempted to remove all of these artifacts in an effort to get a more accurate evaluation of the fate of TCE. This study was able to identify that less than 1% of the TCE was volatilized by plant leaves and the data was not statistically different from the control plants that were not dosed with TCE. This is in stark contrast to Burken and Schnoor's (1998) laboratory study described above.

Hybrid poplars grown over eight months in a laboratory setting that were dosed with a total of 8 g of TCE (added over time) in water had varying volatilization results. The results ranged from zero detectable volatilization up to 2.6 µg TCE per leaf per hour with an average around 1.0 µg TCE per leaf per hour [97]. These results indicated that less than 1% of the added TCE was volatilized.

The 1997 greenhouse study by Newman et al. also found that TCE was phytovolatilized by poplar trees that had been dosed with water containing 50 ppm TCE; however, the proportion of volatilized TCE was not calculated because the conditions in the greenhouse were not conducive for a mass balance or transpiration study.

The amount of TCE in the transpiration stream was analyzed in a laboratory experiment and found that the TCE decreased in the transpiration stream with increasing height indicating a loss of TCE due to diffusion from the tree stems and trunks to the air as measured from diffusion traps, leaf analysis or tree cores in these locations [9, 108]. The 2003 Ma and Burken study found that less than 0.05% of the added TCE was in tree tissue. The decrease in diffusion with increasing height was supported by data collected at a field site and the results were also shown in a mathematical model that was used [9, 52]. This diffusion from stems and trunks before the TCE can reach the leaves may play a part in why experiments measuring the volatilization from leaves have had varying results. The studies by Ma and Burken (2002, 2003) also indicated that the amount of TCE in the transpiration stream corresponds linearly with the amount of TCE in the solution fed to the poplars.

This laboratory data confirms that volatilization/diffusion does occur from poplars, but the rate and concentration at which TCE is volatilized is unpredictable. In the case of diffusion, TCE is still being emitted into the atmosphere, but this term was used to differentiate between TCE being transported through the transpiration stream to the leaves where it is volatilized versus the TCE that is lost from the transpiration stream through the trunks [57].

Volatilization Field Studies

Newman et al. (1999) measured phytovolatilization of TCE from poplar leaves using a Teflon bag in an artificial aquifer study. During the second growing season, an average rate of $2x10^{-8}$ mol per hour per leaf of TCE was volatilized (equates to approximately 1.6μg per leaf per hour). The amount of TCE that is volatilized from all of the 15 trees planted in the artificial aquifer was estimated (based on leaf area) to be approximately $1.2x10^{-4}$ mol of TCE per hour. Assuming a 210 day growing season and that evapotranspiration takes place approximately 12 hours per day during the growing season, this artificial aquifer volatilized approximately 0.30 mol TCE in a year. For this study, the authors estimated 0.30 mol of TCE was lost via volatilization, which represented approximately 9% of the total TCE that was lost in 1996 by other means (degradation, microbial degradation, etc). No volatilized TCE was detected in the third growing season. Further, this study did not detect any TCE in the atmosphere surrounding the canopy of the poplars (which would essentially be able to measure both volatilization from leaves and diffusion from stems, branches and trunks). Given these results, it does not seem that phytovolatilization constitutes a substantial portion of TCE loss. But it is important to remember that phytovolatilization still had an impact on the loss of TCE, at least in the first two years of TCE uptake. It is unknown why volatilization was not observed in the third year. Doucette et al. (2003) was also successful at detecting TCE volatilization from poplars growing in sampling chambers at a site in Utah with a TCE groundwater plume. The highest transpiration stream concentration, 2.2 mg/L of water, was used to calculate the maximum amount of TCE that each tree is capable of transpiring (assuming 200 liters per day of water uptake by each tree). Each tree would volatilize 0.44 g of TCE per day. A more conservative estimate was calculated using the minimum transpiration stream concentration of 0.44 mg per liter and water uptake of 40 liters per day, which estimated a volatilization of 2 mg per year per tree.

Some scientists argue that VOCs naturally volatilize from groundwater and soil into the atmosphere. Further, natural succession of vegetation in contaminated sites will also naturally volatilize VOCs, even when phytoremediation has not been established. Both of these situations are examples of natural volatilization of contaminants into the atmosphere. The addition of plants in a phytoremediation project would thus speed up the volatilization process that would otherwise occur naturally on a smaller scale [41].

Further research into the TCE volatilization led scientists at the Savannah River site in South Carolina to find a correlation between the amount of TCE in groundwater and the amount in the transpiration streams of poplars [14, 108]. These results mean that as TCE travels through the transpiration stream toward volatilization it is slowly diffused through the wood of the tree to the atmosphere. The diffusion therefore limits the amount of TCE that is available for volatilization from the leaves of the tree. The results also seem to indicate that the higher the concentration of TCE in the groundwater, the higher the concentration of TCE in the transpiration stream. This may also indicate that volatilization rates would also be linearly correlated with TCE groundwater concentration, but no literature has been viewed that supports this claim.

Ma and Burken (2003) found that diffusion of TCE to the atmosphere from stems and trunks is a major end result for TCE in groundwater that is removed by poplars. This is supported by the fact that water vapor is known to be lost through the lenticels of bark [108]. Newman et al. (1999) also noted the importance of diffusion of TCE through stems. The diffusion finding can probably be attributed to other studies that saw large amounts of TCE removed from groundwater that were not able to identify the various removal mechanisms. For example, only 70% of the TCE loss was accounted for (as shown by estimated values for recovered TCE chlorine found in plant tissue, in soil, and through transpiration measurements) and the remaining 27% is thought to have been lost through diffusion [57]. These diffusion and volatilization results are also fairly important since they have been seen in several laboratory experiments by Ma and Burken (2003) as well as in field applications by Burken and Ma (2002) and Vroblesky, Neitch, and Morris (1999). This is noteworthy because field studies were able to reproduce similar results found in the laboratory, which is not always replicable because of the differing conditions that are present in the laboratory versus the field. To further define mass balance studies, and to identify the proportion of total loss that can be attributed to phytovolatilization, Burken and Newman have begun collaborative research [51].

Air toxics calculations can be done in order to estimate the atmospheric concentrations being emitted by the plants, so as to determine if the emissions are acceptable [13]. Davis et al. (1996) calculated an estimate of the maximum transfer rate of TCE to the atmosphere (given some specific assumptions) as 10 g/m^2/day for water that is saturated with TCE at 1.5 g/L (a concentration that poplars would most certainly not be able to survive in). Davis et al. then modified the transfer rate by using more realistic groundwater concentrations (1-15 mg/L) and mixing height estimates (100-300 meters) to come up with a transfer rate that was 4-6 orders of magnitude smaller than the original transfer rate estimate. The latter estimate would constitute a very low concentration of TCE in the air [41]. Other calculations have also shown that the release of contaminants through phytovolatilization is typically at low concentrations [49] and are typically not unacceptable in the regulatory sense [48].

4.3.5 <u>Efficiency of TCE Removal from Groundwater</u>

Very few, if any, mass balance studies have been completed that have shown the direct proportion of TCE that was removed via phytodegradation, rhizosphere biodegradation, and phytovolatilization. Some studies, however, have examined the amount of TCE in groundwater leaving an area planted with poplars as compared to the amount of TCE in water entering the planted area. In general, the amount of TCE that is removed from a contaminated aquifer increases with water uptake by trees [53].

Newman et al. (1999) compared the amount of TCE in effluent in artificial aquifers planted with poplars versus the amount of TCE in effluent in artificial aquifers without trees. After one year, approximately 94-98% of the TCE had been removed from effluent in the planted artificial aquifers. After three years between 98-99% of the added TCE had been removed from the planted artificial aquifers, while in contrast only 33% of the TCE was removed from effluent of the non-planted artificial aquifers [97]. These results indicate that in the unplanted cells, some of the TCE is possibly binding with the soil, organic particles within the soil, or microorganisms in the soil. In planted cells almost all of the TCE is being removed, possibly by the soil, organic particles within the soil, or microorganisms in the soil but most likely through mechanisms spurred by the poplars. The poplar trees used by Newman et al. (1999) continued to remove consistent amounts of TCE from the groundwater during all three growing seasons that the trees were being studied. The data from this study also suggested a link between the recovery of TCE in effluent and the amount of water being transpired by the trees. For example, during low transpiration periods (winter) the amount of TCE recovered in the effluent was higher than when transpiration was high. This linkage further suggests that the poplars were the greatest contributing factor for TCE removal and that water uptake was the largest mechanism [100]. The results also showed a correlation between transpiration rates and the amount of TCE that was removed from water. During months of low transpiration (winter) the proportion of TCE removed from the water was much lower than months of high transpiration (spring, summer, and fall). This means that the major mechanism of TCE removal from groundwater is through plant uptake.

This study, among others, has shown that the amount of TCE that is detected in water downstream of poplar plants is greatly reduced in comparison to the TCE in water upstream of the poplar plants. This indicates that the poplar trees are reducing the amount of TCE in groundwater, but it does not show how the TCE is being removed by the trees.

4.4 Case Studies

There have been numerous field applications conducted using poplars to treat TCE contaminated groundwater. It is important to distinguish these field applications from those described as Volatilization Field Studies above. The primary difference is that these studies were implemented at sites that were actually contaminated with TCE (among other constituents) whereas the large majority of the field studies discussed earlier were purely research based in a field type setting using artificially contaminated water. Some of the following field studies were only implemented for a limited period of time to see if the phytoremediation objectives could be obtained and were mostly for research purposes. This is why long-term data (greater than 3 years) on phytoremediation processes at field sites is so limited- other than the fact that this is such a new science. Some of the field sites that short term data is available for include:

- Fort Lewis Army Base in Tacoma, Washington [112]
- Hill Air Force Base Operable Unit 4 in Salt Lake City, Utah [113]
- Metal Plating Facility in Findlay, Ohio [113]
- Northern Iowa Chlorinated Solvent Plume [113]
- Portsmouth Gaseous Diffusion Plant in Piketon, Ohio [113]
- Unspecified chemical manufacturing facility in Aurora, Illinois [113]
- Savannah River Site in Savannah, South Carolina [114]
- Edward Sears Property – New Gretna, New Jersey [41]

The Edward Sears Property is an interesting project because the site is less than one acre in size and is actually the backyard of a residential home. Typically phytoremediation sites are much larger than one acre.   I mention this project because it is an example of a site where positive phytoremediation results were observed in a very small area with a limited number of trees.

All of these field site examples, which were implemented across the nation, showed some sort of successful phytoremediation after a couple of years being planted with poplars. The success ranged from hydraulic control to reduced concentrations of TCE in groundwater. Some of the results from these studies were limited because of limited data gathering and the short term nature of the project, but showed positive phytoremediation progress potential. These sites are not discussed further in this text because they only represent short term data and the goal of presenting case studies was to present the long term affect that poplars have on TCE contaminated groundwater.

The next portion of this chapter discusses case studies that have more "long-term" data. These projects are considered more long long-term because they are ongoing phytoremediation projects that are being used as a basis for research, but are also intended as the mechanism for reducing TCE concentrations in groundwater. These projects give a true indication of what can be expected when applying phytoremediation at a site because it is real time, real life data. The effectiveness seen in these studies varies, but that is to be expected given the different site conditions and the variable nature of this treatment method. In all, the following projects prove that phytoremediation is a viable option for site clean-up.

4.4.1.1 Aberdeen Proving Grounds - Edgewood, Maryland [105]

<u>The Site:</u>

The Aberdeen Proving Grounds was used for military weapons testing and disposal. These activities have caused groundwater contamination with volatile organic compound, including TCE. The prime source for the contamination is the Toxic Burning Pits. The maximum detected amount of TCE was 240,000 ppb. Down gradient of the source plume is a freshwater marsh where 200 ppb of TCE has been detected. The distance between the source area and the freshwater marsh is 100 meters. Natural biodegradation through biotic and abiotic processes are reducing TCE concentrations in the plume as evidenced by the sharp decline in contaminant levels and the presence of TCE anaerobic byproducts such as vinyl chloride and ethane. The presence of biotic and abiotic conditions is also indicated by the redox conditions of the groundwater such that a predominant portion of the groundwater is anaerobic. This natural biodegradation is being monitored.

<u>Alternative Technologies Investigated:</u>

Other remediation technologies that were proposed (some of which were tested) for this site included soil washing, soil-vapor extraction, pump-and-treat, and groundwater circulation wells. These traditional remediation technologies were not implemented because complex site subsurface characteristics precluded their efficiency. The complex site characteristics included low permeability aquifer, the presence of TCE in the DNAPL form, unexploded military ordnances, and low productivity of wells. Test well pumping yielded only one gallon per minute which would not be a sufficient yield for pump-and-treat applications. It was not identified until 2001 that DNAPL TCE is present in the aquifer, which is feeding the contaminant plume.

Modeling of the future performance of the aquifer in regards to transpiration and hydraulic control was conducted. Using the maximum transpiration rates (2,000 gallons per day) the model predicted that the poplars will have a "well developed zone of capture" and will cause groundwater flow velocities to slow. The depth that poplars will have the greatest influence is in the upper 16 feet of the aquifer.

The effects of using alternative treatment methods such as groundwater circulation wells was also predicted using models. The model showed that groundwater circulation wells would not be effective at removing sufficient mass of VOCs from the groundwater because of the poor yield from wells of 2 liters per minute (0.5 gpm). At 2 liters per minute, the extraction wells would only be pumping approximately 2,880 liters per day (720 gallons per day). This extraction rate is lower than that of the poplars and would likely affect the wells ability to properly contain the plume. The model predicted that this remediation method would only be able to remove less than 23 kg (50 pounds) per year of VOCs. For scale, air strippers have the capability of removing 6,800 kg (15,000 pounds) of TCE per year. 23 kg per year would not significantly improve the groundwater quality, especially if the contaminant plume has a TCE concentration in the ppm range.

Phytoremediation Project:

In 1996 as part of a pilot-scale investigation, 183 hybrid poplars were planted in a 1-acre area down gradient from the Toxic Burning Pits. The plants were first planted so that their roots were surrounded by a plastic sleeve to promote downward growth of the roots. But in 1998 it was discovered that the roots had only extended approximate seven feet because the plastic sleeves and the highly clayey soil were preventing the roots from prolific extension to the aquifer. The second round of tree planting excluded the plastic sleeves and planted the roots in deep holes that were well aerated.

A model for transpiration rates was run in order to show the potential amount of transpiration that occurs onsite.

<u>5-Year Results:</u>

The results of the 5 year study show that the poplars are helping to contain and remove VOCs, including TCE, from the groundwater plume. Three years after planting the trees the plantation was transpiring 4,126 liters (1,090 gallons) per day, but are expected to increase their transpiration to 7,570 liters (2,000 gallons) per day once the trees have sufficiently matured, in 30 years. On average, each tree was transpiring approximately 49 liters (13 gallons) per day. The actual transpiration rates include the pumping of a sufficient amount of water to change groundwater flow direction, velocity, and the ability to contain the plume preventing it from moving further down gradient toward the freshwater marsh. A discernable cone of depression was evident below the poplar plantation.

Using the same model as was used to predict the removal of VOCs by groundwater circulation wells, and the actual transpiration rates of the poplar trees in the spring and summer, the model predicted that the trees would remove up to 163 kg (360 pounds) of dissolved VOCs after 30 years. Per year, this amount is less VOC removal than what the extraction wells were predicted; however the trees were able to extract a larger volume of water which contributes to better hydraulic control over the plume.

Natural attenuation is the primary way that TCE is being degraded in the groundwater at this site. Despite the natural attenuation through biodegradation that is occurring, the poplars are not significantly contributing to rhizosphere biodegradation. This is because the trees are adding carbon dioxide to the rhizosphere causing this zone to be less reducing than other areas. Further, the trees are not adding significant amounts of organic carbon to the groundwater as well as evidenced by root exudates. The amount of reductive dechlorination occurring in the rhizosphere was measured using a dialysis sampler inserted into the rhizosphere of one of the poplars in the plantation and into a control tree outside of the plantation [115]. The study concluded that reductive dechlorination was occurring in the control tree indicating natural attenuation. The results from the poplar were inconclusive because of highly variable concentrations of VOCs indicating that biodegradation and uptake was highly spatially variable. Further, the rhizosphere environment at the poplar was less favorable for reductive dechlorination activities as compared to the control location. The study was conducted on only one tree from the plantation, so the sample size is extremely small and may not be representative of general conditions found on the plantation.

TCE is being taken up by the poplars from the groundwater and is being broken down within the trees and the byproducts are being stored in the tree tissue. Tree core and tissue analysis provided the best way to measure the degradation products in the tree. TCE was found throughout the trees at concentrations ranging from 0.1 to 75 μg/g of plant by dry weight. The highest tissue concentrations were correlated with the highest groundwater concentrations. The leaves had measurable concentrations of TCE byproducts. And some had 14 to 210 ppb by volume TCE off gassing from leaves [9]. Compton et al (1998) also determined that 1,1,2,2 tetrachloroethylene was also volatilizing from the leaves of the trees. TCE concentration within a tree decreased with increasing height. This indicated that the TCE was being volatilized through the trunk, while very little was being volatilized through the leaves. Transpiration of TCE from the leaves was monitored and the results supported the tissue results in that only three trees had TCE volatilizing from the leaves. Those trees that did have measurable amounts of TCE volatilizing from the leaves were located in the area with the highest groundwater concentrations. Ambient air monitoring for volatilized TCE in the area of the plantation could not detect TCE above the instruments detection limits. A second sampling event using a Flux-chamber instrument detected TCE volatilizing from the shallow groundwater through the soil at concentrations ranging from 9.4 to 38 ppb by volume (identified in 3 of 8 samples).

Phytoremediation, after five years, appears to be successful. It is working in concert with natural attenuation. The modeling that was conducted and the results collected thus far indicate that the effectiveness will increase over time as the trees mature. This phytoremediation project is predicted to successfully remove contaminants and contain the plume.

4.4.1.2 Argonne National Laboratory –East - Lemont, Illinois[61]

The Site:

The site has soil and groundwater contaminated by some VOCs and low levels of tritium that cover approximately five acres. The groundwater contamination is estimated to be as deep as 30 feet bgs and is moving off-site [59]. The contamination stemmed from the disposal of laboratory solid and liquid waste. VOCs included TCE, PCE, benzene, carbon tetrachloride, chloroform, methylene chloride, 1,2-dichloroethane, cis-DCE, vinyl chloride, and 4-methyl-2-penanone. All of these contaminants were identified above the remediation objectives for the property. The goal of the remediation projects onside were to prevent future releases of contaminant from the soil into groundwater; minimize groundwater plume transport; and reduce contaminant releases to storm water.

TCE was identified in soil at concentrations of 47,000 ppb and up to 8,600 ppb in groundwater. The remediation objectives for soil were 80 ppb, 127 ppb in groundwater in one of the plumes onsite, and 5 µg/L at the second plume and on the property boundary.

A small, seven well pump-and-treat system was installed prior to the phytoremediation project as an interim fix. The wells were extracting 26,500 liters per day and were sending the groundwater to the laboratory's storm water treatment plant for treatment. Soil remediation was conducted using hot air and vapor extraction as well as zero-valent iron injection in order to remediate soils and increase permeability. The phytoremediation system was installed to augment and eventually replace the pump-and-treat system.

Alternative Technologies Investigated:

The alternative remediation method proposed by the Department of Energy was a baseline technology of 36 extraction wells (instead of the seven well system) and the planned asphalt cap. Phytoremediation was chosen because it was seen as a less costly and more efficient means for achieving remediation goals.

Prior to plant installation the site managers had to prove to regulators that emissions of VOCs and tritium from the trees would not be released at hazardous concentrations. An EPA assessment package was used to estimate worst case scenarios for VOC emissions using the highest detected concentration found onsite. The emission rates were estimated for a mature plantation of trees that were transpiring between 7.6 to 189 liters (2 to 50 gallons) per day per tree. The range in transpiration rates is dependent upon the season. The calculations indicated that the amount of VOCs that potentially would be released was several orders of magnitude lower than the National Emissions Standards for Hazardous Air Pollutants. Calculations for the NESHAP standards can be found in the Clean Air Act 40 CFR Part 63 Appendix A to Subpart DDDDD.

Phytoremediation Project:

809 hybrid poplars and hybrid willows were installed in 1999 within and down gradient from the contaminant plumes. A total of 609 of the trees were hybrid poplars (*P. charkowiiensis x P. incrassate).* The trees were two years old at the time of planting. Trees were also planted to remediate contaminated soil and herbaceous plants were planted as a vegetative cap. The hybrid poplars were installed with their root mass at depths between 10-15 feet bgs within a 20 foot plastic casing liner.

Up until this investigation, phytoremediation systems typically could only affect media that was 20 feet or less bgs, but the trees at the Argonne National Laboratory were installed by Applied Natural Sciences, Inc., who designed the system to reach up to 30 feet bgs. This was attempted by planting the trees inside a casing lining that prevented the shallow aquifer from reaching the roots, causing the roots to grow in a downward direction to the contaminated portion of the aquifer. A piece of aeration tubing was also installed inside the casing lining. The trees had trouble growing in their first two years likely due to transplant shock and approximately 5% of the tress perished. But after the second year the trees began growing at faster rates, which also indicated that transpiration rates were increasing as was root depth.

Monitoring for the first three years was rather intensive due to the research nature of this project, although the ultimate intent of this project was to remediate the soil and groundwater. 60 wells were installed up-gradient, down gradient, and within the phytoremediation project. Wells were sampled and analyzed for the presence of TCE, among other constituents. Sap flow instruments, groundwater instruments, and a weather station were also installed.

Modeling was performed to predict future outcomes of the phytoremediation system. The models showed that one of the contaminant plumes would be fully contained while the second plume would be mostly contained.

<u>3-year Results:</u>

Transpiration rates calculated during the months of July through October in 2001 indicated that on average, the poplars being monitored were transpiring 2.0 (October) to 3.9 (July) liters per day per tree. This is quite a bit less than the original predictions that each poplar tree could potentially transpire 150 liters per day per tree when fully mature. The results clearly show that the trees onsite had not reached maturity and still have the potential to transpire far greater amounts of water from the contaminated aquifer. Groundwater elevations were monitored continuously throughout the site. The water level results indicated that there was diurnal cycling of the water levels corresponding with the fluctuations of night and day, as well as high sunlight and low sunlight. These changes in water elevations were an indication of the effect that the trees were having on the aquifer.

Analysis of groundwater samples, and transpiration/sap-flow rates indicated that the deep roots of the trees had extended into the saturated zone and had begun taking up contaminated groundwater. VOC degradation has begun occurring and the amount of contaminated groundwater reaching the pump-and-treat system has been reduced. However, the data from some of the wells showed that there was a slight increase in TCE concentration (and most other VOCs) in comparison to baseline data. But some declines in concentration were observed as well. Table 4-3 is an abbreviated version of the data collected and only includes TCE concentrations detected at monitoring points within the plantation.

Table 4-3 TCE Concentrations in Groundwater within Plantation

Location	Baseline Data 1999 (ppb)	Mid-term Data (ppb)	Final Data 2002 (ppb)
317322 FDP	4.3	5.3	2.1
317332 FDP	0.38	0.40	0.76
317342 FDP	0.090	0.058	0.069
317151 HCP	2.9	2.1	1.6
317181 HCP	0.27	0.43	0.72
317221 HCP	0.012	0.0054	0.13
317452 HCP	<0.001	<0.001	<0.001
319171 HCP	<0.001	<0.001	<0.001
319261 HCP	<0.001	<0.001	<0.001

Source: EPA (2003)
FDP= French Drain Plantation; HCP=Hydraulic Control Plantation

The authors attributed the increase in concentration in some of the wells to contaminant transport. The mechanism of contaminant reduction in one of the plumes was estimated to be from dechlorination due to anaerobic conditions. In the other plume, contaminant reduction was estimated to be from weak aerobic and anaerobic conditions. Mean soil sample results indicated an increase in TCE and PCE concentrations. Three of the wells in the hydraulic control plantation (317452, 319171, and 319261) did not have detectable levels of TCE during any of the sampling events indicating that the plume had been contained enough by the poplars such that the plume did not migrate past these wells. A non-parametric test was conducted on the soil data and the results for TCE still indicated there was not a positive removal. Table 4-4 provides a summary of the TCE soil sample results.

Table 4-4 Non-Parametric Test of TCE Soil Concentrations

Sample Count	TCE
# sample pairs with no change	37
# sample pairs with increase	23
# sample pairs with decrease	24
Total # pairs	84

Source: EPA (2003)

Tissue samples collected from willows indicated levels of TCE in branch tissue and TCAA in leaf tissue. These constituents were detected in branch and leaf tissue during all three growing seasons. These results indicate that TCE is being taken in by the trees, deposited in some tissue, and degraded in the leaves.

Authors of the EPA report concluded that the major mechanism at work at the phytoremediation site is phytostabilization/hydraulic control of the contaminant plume through groundwater capture. However, it was determined that the trees had not attained their maximum transpiration rates at the time of this report. Willow tissue analysis detected the presence of TCE and its degradation compound TCAA in the leaves of the trees. VOCs and their degradation products were also found in groundwater, indicating metabolism by microbes. Conditions in the rhizosphere are progressing toward anaerobic dechlorination. Anaerobic microbe communities have been found in one of the plume areas. These results indicate that the phytoremediation project is actively containing the plume and dechlorination of TCE is beginning to occur. As the trees mature they are predicted to become better at hydraulically controlling the plume and taking in TCE from the groundwater for degradation.

4.4.1.3 Carswell Air Force Base – Fort Worth, Texas[104, 106]

<u>The Site:</u>

Shallow groundwater on the air force base (AFB) and down gradient from the site are contaminated with TCE due to decades of use of TCE in aircraft manufacturing activities. Contamination was due in part to spills and leaks from tanks. The site that was part of this investigation was 9.5 acres at the northwest corner of the AFB golf course, and encompasses just a miniscule portion of the actual TCE plume. Groundwater ranged from 8 to 13 feet bgs and the shallow aquifer was approximately 6 to 15 feet thick [106].

The maximum TCE concentration identified onsite was 970 µg/L and for DCE, an anaerobic break-down product of TCE was 141 µg/L [50, 104].

Alternative Technologies Investigated:

Natural attenuation was reportedly occurring prior to the installation of the phytoremediation system. The natural attenuation included sorption of the contaminants, dispersion, dilution, and volatilization. Phytoremediation was chosen in order to investigate the effectiveness of eastern cottonwoods at reducing the mass of dissolved TCE.

Phytoremediation Project:

420 1-year old whips and 210 6.5-foot tall seedling eastern cottonwood trees installed in 1996 [106]. Trees and whips were installed at two separate plantations in seven rows perpendicular to the flow of groundwater so that the groundwater is intercepted by the trees as it flows [104, 113]. The trees were planted three feet bgs. Irrigation was added for the first two growing seasons. Eastern cottonwoods were chosen because of their biological properties as well as the fact that they are native to this region of Texas [104].

Groundwater, surface water, and precipitation were all measured during routine monitoring. A mature, native cottonwood tree located south (down gradient) of the plantations was also monitored. Sapflow measurements were taken to estimate transpiration. Groundwater samples were collected from up-gradient, down gradient, and within the plume as well as from beneath the mature cottonwood for analysis of TCE and break-down products. The microbial populations were investigated. Roots, stems, and leaves were analyzed for TCE and its break-down products. Phytovolatilization was not assessed because “data from a previous study (Newman and others, 1997) indicate that phytovolatilization likely is not a major process associated with phytoremediation of TCE-contaminated ground water” [106].

Results:

Roots of the whips and trees reached the water table at some point during the second growing season [104]. Over time, TCE and cis-DCE (a reductive dechlorination byproduct) were found in the tissue of an increasing number of trees on the plantation. Tables 4-5 and 4-6 show the TCE concentrations found in tree organs at the whip and tree plantations onsite, respectively. The concentrations were greater in stem samples than leaf samples. Root samples were not analyzed. Concentrations of TCE and cis-DCE were identified in the plantation trees leaves and stems at greater levels than in the mature cottonwood. Cis-DCE concentrations were identified in the mature cottonwood in October 1996 at 1.2 µg/kg, but was not identified in plantation trees until October 1997. See Table 4-7 for cis-DCE concentrations. TCE appeared more readily in the stems of the mature cottonwood than in the leaves. Over time, the TCE and cis-DCE generally increased in concentration and the number of trees containing the contaminant also increased. The amount of TCE in the trees tended to decrease in areas of the plantation with decreasing groundwater contaminant levels [104]. Leaf samples of the plantation trees and whips indicated that reductive dechlorination of the TCE was occurring and this was supported by leaf samples collected from other mature trees on the property. TCE oxidative byproducts (TCAA and DCAA) were also identified in leaf samples from the plantation trees. TCAA concentrations ranged from 1,300 to 2,540 µg/kg wet weight in harvested leaves. DCAA was detected in leaves from the mature cottonwood at a concentration of 1,210 µg/kg wet weight. The occurrence of both reductive and oxidative byproducts indicates that there are multiple dechlorination mechanisms occurring onsite. The levels of these byproducts were higher than the levels of TCE in the leaves. This data indicates that the predominant TCE removal mechanism is not volatilization (though it was likely occurring) and that degradation was a major removal mechanisms along with hydraulic control [104].

Table 4-5 Average TCE Concentrations in Tree Organs (Whip Plantation)

Sampling Event	Leaf (µg/kg)	Stem (µg/kg)	Root (µg/kg)
October 1996	ND	26 (1)	ND
July 1997	ND	ND	--
October 1997	1.6 (2)	10.1 (3)	--
June 1998	ND	44 (1)	140 (1)
October 1998	ND	32.8 (5)	--

ND = Not Detected
Numbers in () are the number of trees in which analyte was detected.
Source: Eberts et al. (2003)

Table 4-6 Average TCE Concentrations in Tree Organs (Tree Plantation)

Sampling Event	Leaf (µg/kg)	Stem (µg/kg)	Root (µg/kg)
October 1996	ND	ND	ND
July 1997	ND	ND	--
October 1997	10.4 (3)	9.6 (3)	--
June 1998	4.5 (2)	71 (1)	13 (1)
October 1998	ND	24.6 (5)	--

ND = Not Detected
Numbers in () are the number of trees in which analyte was detected.
Source: Eberts et al. (2003)

Table 4-7 Average cis-DCE Concentrations in Tree Stems

Sampling Event	Whips	Trees	Mature Cottonwood
October 1996	ND	ND	1.2
July 1997	--	--	--
October 1997	1.9 (3)	1.6 (3)	10
June 1998	14 (1)	15.7 (3)	ND
October 1998	13.5 (5)	8.9 (4)	2.8

ND = Not Detected
Numbers in () are the number of trees in which analyte was detected.
Source: Eberts et al. (2003)

After five years of generating groundwater data suggested that in general the aquifer was aerobic, except for underneath the mature cottonwood, which was anaerobic. Total organic carbon in the aquifer below the plantation was limited (below the detection limit of 1.5 ppm), but under the mature cottonwood it was 2.0 to 3.1 ppm [104]. It appears that the mature cottonwood was changing the groundwater and soil conditions on a micro-scale, right below the tree. Increasing the amount of organic carbon leads to the increase in dissolved organic carbon in the groundwater. The dissolved organic carbon feeds aerobic microbes that in turn use up the dissolved oxygen in the water creating anaerobic conditions that lead to the reductive (anaerobic) microbial dechlorination of TCE. At the end of the fifth year (during the dormant period) groundwater results from below the plantation lead to the fact that the poplar (and willow) trees were finally beginning to have an effect on the aquifer geochemistry based on changing dissolved oxygen, dissolved organic carbon, and TCE/cis-DCE ratio levels. These changes support the theory that the plantation can have an effect on changing the groundwater characteristics to support anaerobic microbial degradation.

After seven years as an operating phytoremediation project, scientists involved with the project felt that the data support their hypothesis that eastern cottonwood trees can reduce the mass of dissolved TCE in an aquifer. Further, the data supports that poplars can degrade the TCE within the trees and stimulate microbial degradation of TCE. Groundwater data indicated that anaerobic microbial degradation of TCE began occurring during the end of the first seven years of the study [106]. Essentially, the groundwater chemistry had been changing over time and especially between five and seven years after planting, the groundwater began shifting towards anaerobic conditions. By 2001 no significant decreases in the concentration of TCE was observed in the groundwater. However, the mass of TCE in the groundwater decreased by 11% down gradient of the phytoremediation site [113]. The amount of groundwater moving down gradient past the plantation was reduced by 12% [116]. This is an indication of hydraulic control of the plume and perhaps of TCE uptake by the trees. It was estimated that the entire plantation was up taking and transpiring approximately 3,600 liters per day during the second growing season [117]. During the 3rd growing season, a maximum drawdown of the water table that is attributable to the trees was 10 centimeters [104]. A two order of magnitude increase in biodegradation rates was observed after 6 years and the plume decreased in size by one order of magnitude [116]. TCE was not present in leaf tissue [9].

Hydraulic control was considered the primary route for TCE mass removal and attenuation after seven years [104]. Since the inception of the plantation, the trees have increased in their effectiveness to control the TCE in groundwater [59]. Degradation within the tissue and in the rhizosphere was occurring as indicated by the TCE and byproduct concentration in the plant tissue and in the soil. Volatilization was likely occurring as well.

Long Term Results:

In order to predict what long-term effects might be, a groundwater-flow model was used. The model indicated that the down gradient end of the plantation will have a reduction in the volumetric flux of groundwater [104]. If a larger area was planted with trees, the hydraulic control may be greater.

Hansen (1993) found that over time the amount of organic carbon that is given to the soil increases with increasing age after 6 to 12 years of age. This is supported by the Carswell Air Force Base (Caswell AFB) data showing that the mature cottonwood provided more organic carbon to the soil and groundwater than the plantation, although the plantation began contributing organic carbon after five years [118]. The plantation's effect on groundwater is expected to increase within the next five years after planting. The findings also suggest that anaerobic microbial degradation of the TCE plume may become an increasing removal mechanism in the future.

Both whips and calipers were installed here in order to study whether one type of planting worked better than the other. During the first few years of the project the whips and the trees appeared to be performing at the same rate. But nearing the end of the study it appeared as the calipers were outperforming whips and seemed to be better in the long-term for phytoremediation because of growth rates and transpiration rates [104].

The presence of a mature cottonwood in the vicinity of the phytoremediation plantation makes this project unique in that the performance of a mature tree can be monitored and perhaps used as an example of how the plantation trees may perform in the future. The data suggests that the mature cottonwood was capable of changing the groundwater and soil below the mature tree to more anaerobic conditions. This is valuable information that has not been gathered to date.

4.4.1.4 Keyport, Washington[119]

The Site:

The project is located on a 9-acre landfill for the Kitsap Naval Base in Keyport, Washington. The landfill operated from the 1930s until 1973 and typically accepted domestic and industrial waste. VOC plumes are located in the shallow and intermediate aquifers underneath the landfill. VOCs have also been identified in surface water in the marsh down gradient from the landfill, which is where groundwater from the landfill discharges. Reportedly the onsite soil conditions were poor. Groundwater data was collected in 1995 and 1996 to supplement the remedial investigation report.

Alternative Technologies Investigated:

Monitored natural attenuation is considered an alternative, in case the phytoremediation does not efficiently work [120].

Phytoremediation Project:

Two hybrid poplar plantations were installed in spring 1999 on the landfill in 'hot spot' locations. The objective was to control the migration and remove and treat TCE, among other VOCs, in the shallow groundwater [119, 120]. The remediation goal for TCE was 56 ppb. TCE concentrations in groundwater range from non-detection (detection limits ranged from 0.12 to 130) to 90,000 ppb at piezometer[‡‡‡] P1-9. The highest concentrations appear to be in the southern plantation.

6-Year Results:

The trees were growing at a moderate rate, despite poor soil conditions. Groundwater analytical data for 1995 to 2005 indicate that in general TCE concentrations are slowly declining in most wells within or down gradient of the plantation. However, remedial goals for TCE have not been achieved for some of the wells. Furthermore, it is unknown as to how much phytoremediation is contributing to the declining contaminant

[‡‡‡] An instrument that measures the pressure of fluid. Similar to a well.

concentrations. TCE reductive byproducts, ethane and ethene were identified in the groundwater in the northern plantation. DCE, vinyl chloride, ethane, and ethene were identified in the groundwater in the southern plantation. These byproducts are characteristic of and support the idea that anaerobic dechlorination of TCE (among other VOCs) is occurring. This is also supported by the fact that strongly anaerobic conditions were identified in five of the 16 areas of the upper aquifer in 2005, while the remaining areas had mildly anaerobic conditions. These conditions provide the ideal climate for anaerobic microbial dechlorination of TCE; however it is unknown if the plantation is adding to the intrinsic biodegradation that is known to occur beneath the landfill.

Transpiration rates were calculated using sap flow measurements in 2005. These results showed the trees were transpiring approximately 7.5 to 15 liters (2-4 gallons) of water per day per tree. This is convoluted by the fact that 10 to 20 percent of the water that is transpired is from irrigation water. The addition of approximately 177,915 liters (47,000 gallons) of irrigation water to the plantation is most likely affecting the uptake of contaminated water from the aquifer by poplars.

The ground water data collected by URS Group Inc. (the consulting firm managing this project) did not indicate a change in ground water elevation, gradient, or flow direction associated with phytoremediation uptake; however, Dr. Lee Newman analyzed groundwater elevations, sap flow measurements, and precipitation data and determined that fluctuations in November and December may be related to plant interception of rainfall and transpiration during the summer months.

The largest effect that the poplar plantations appear to be having onsite is on the amount of precipitation that is infiltrating. As the poplars grow and reach full canopy cover, it appears that their leaves are capturing the precipitation, preventing it from infiltrating the ground. This is seen as a positive attribute because the poplars are preventing precipitation from leaching contaminants from the soil into groundwater. Hopefully with more time for maturity, the trees will be able to begin to hydraulically contain the plume and to markedly increase the dechlorination of TCE such that more noticeable changes in TCE concentrations in groundwater are observed.

4.5 Variables Affecting the Technology

There are a variety of factors that impacts the effectiveness of phytoremediation. The most critical of these are discussed in the following sections. The benefits and limitations of phytoremediation are discussed in Chapter 5.

4.5.1 Geology

Soils with high organic matter are difficult to phytoremediate because the polar nature of TCE causes the molecules to tightly bond with organics in the soil [41]. Nevertheless, this characteristic also helps to slow down the migration of TCE in the groundwater. The migration rate of TCE plumes can be calculated using, among other variables, the amount of organic carbon contained in the soil of the impacted aquifer. Poor quality soil can prevent an adequate community of microbes to colonize the rhizosphere. This obviously can critically limit the amount of microbial degradation that potentially could be possible under less limiting conditions.

The type of soil can also impact the ability of a phytoremediation project to work. Predominantly sandy substrates that have good hydraulic conductivity will allow trees to be better able to take-in water because the water can move more freely through the soil column. Subsurface conditions that have a higher percentage of fine grained material such as silt and clay have lower hydraulic conductivity and therefore trees will have a harder time taking in water. This can be somewhat mitigated by changing the planting practices to include digging deeper holes and aerating the surrounding soil. Eberts et al. (2003) have evidence to support this from poplar trees grown in sand and gravel versus trees planted in clay-rich material. The sand and gravel planted trees were able to transpire more water than the other poplars planted in clay-rich soil. The proliferation of tree roots also helps breakup the soil particles.

4.5.2 Climate

Climate plays a part in the removal of TCE from groundwater by poplars. The reasons for this are the influences that climate plays on transpiration rates of the trees. Climate affects transpiration rates through precipitation rates, air and soil temperature, solar radiation, humidity, and wind [45, 48]. Regions with a longer duration of solar radiation, or less weather variability during the four seasons will have a greater proportion of days when water uptake and evapotranspiration are possible. This will affect the ability to take in contaminants through water uptake as well as the potential for phytovolatilization. Therefore, the duration of weather conducive for evapotranspiration can have a sizeable impact on the potential that poplars can have to phytoremediate TCE contamination groundwater. As mentioned earlier, precipitation and the creation of surface water can impact the maximum root depth of poplars, as the poplars will not extend deep roots down to shallow aquifers if there is sufficient available shallow water, and therefore will not take-in very much contaminated groundwater. Likewise, if the availability of precipitation and surface water is seasonally available, contaminant uptake will vary based on the seasons. Doucette et al. (2003) studied the affect that precipitation had on poplars treating TCE contamination in Utah and Florida. The authors found that TCE concentrations in the Florida poplars were considerably lower than in Utah and phytovolatilization was not occurring. This was attributed to the frequent precipitation in Florida during the summers causing the poplars to use less of the contaminated groundwater for transpiration. This study helped to support the theory that poplars that grow in semi-arid regions will uptake a greater portion of their water from the contaminated aquifer because demands are not met by precipitation or surface water [109].

Reportedly, phytostabilization of contaminated groundwater plumes is most readily achievable in regions where annual evaporation exceeds yearly rainfall values [61]. This is essentially because annual inputs are less than annual outputs. In areas where the ratio of evaporation to yearly rainfall is greater than one, phytostabilization and hydraulic control should be able to be done through the lowering of the water table by the trees. In areas where the ratio is less than one (for example in the Pacific Northwest, west of the Cascade Mountains) other techniques must be utilized in order to decrease the amount of precipitation that infiltrates into the ground in an effort to control where the trees are obtaining their water.

4.5.3 Contaminant Concentration & Phytotoxicity

Some studies have suggested that plant growth is impacted by contaminant concentration. Still other studies have shown that a much larger dose is required for phytotoxicity. Poplars have shown to be tolerant of high levels of chlorinated solvents. Tree growth was not limited by and phytotoxicity did not occur in water containing up to 0.76mM (approximately 100 ppm) of TCE, which were considered by the authors as levels typical of heavily polluted waters [100]. In this study, the average concentration of TCE added to the trees was 0.38 mM (approximately 50 ppm), which is similar to the concentrations found in polluted aquifers. However, trees in a greenhouse study dosed with 50 ppm TCE for eight months only grew to 85% of the height of control trees and the fine roots did not extend as far into the saturated zone as control trees [35]. Newman et al. (1997) reasoned that those portions of the plant that were in direct contact with the dosed TCE had their growth impacted the most. Signs of phytotoxicity such as yellowing leaves and a decrease in transpiration were observed in poplar whips dosed with 820 ppm of TCE [9]. Plants dosed with 131 ppm of TCE had their growth stunted to zero [52]. Ma and Burken, as well as others, have shown that poplars have tolerated up to 550 ppm of TCE [48, 52]. For chloride (which can be excreted into the soil during dechlorination within the tree tissue) it was estimated that phytotoxicity would occur at concentrations around 1,000 ppm [119]. These studies show that the concentrations at which phytotoxicity occurs can vary, but in general it occurs in poplars exposed to concentrations in the ppm range.

An example of phytotoxicity occurred at a poplar plantation at the Pasco Bulk Fuel Terminals Site in Pasco, Washington. Approximately 35 trees were installed between April and October 2003 in 2 rows at the site [121]. Nineteen of the trees were installed in a row (named the southern line) over a VOC and petroleum hydrocarbon plume while sixteen trees were installed in a row (named the northern line) over a plume containing only petroleum hydrocarbons. By June 2003, all of the trees in the southern line began showing signs of phytotoxicity including mottled brown leaves and stunted growth as compared to only three trees in the northern line that showed phytotoxicity signs. Six of the trees in the southern line died while only two died in the northern line. The growth of the trees in the southern line was also stunted as compared to the growth of the trees in the northern line. It is suspected that the VOCs in the groundwater were what caused the phytotoxicity. The phytotoxicity was unexpected though because the concentration of TCE in the groundwater ranged from 0.3 to 33 ppb, whereas typical phytotoxicity occurs with concentrations in the range of 131 to 820 ppm [121]. One potential cause of the phytotoxicity at low levels of VOCs was the presence of a second type of contamination (petroleum products) that may have caused a synergistic affect on the trees. However, other potential causes (such as lack or water or nutrients) were ruled out because the southern line of trees received the same treatment as the northern line of trees, and the only difference between the two was the presence of VOCs in the groundwater below the southern line. The analysis of the tree growth data did not show statistically significant differences in growth or survival rate between planting variables at both lines of trees.

4.5.4 Toxicity of degradation products

The toxicity of TCE and its degradation products was discussed in Chapter 1. There is no risk of vinyl chloride being emitted via phytovolatilization or levels of vinyl chloride being stored by poplars because the metabolism that occurs within the plant tissue is primarily through aerobic processes and therefore does not produce vinyl chloride [35, 57]. As mentioned in Chapter 1, some of the degradation byproducts are toxic themselves. Exposure of humans or wildlife to the tissue of the poplar may allow exposure to the toxic byproducts as well.

4.5.5 Recontamination

As mentioned earlier, recontamination of soil and groundwater may occur when leaf litter and plant products fall back to the earth and decay, thereby releasing stored contamination back into the soil or groundwater. Newman et al. (1999) detected elevated levels of TCE reductive dechlorination products (TCE/R) from effluent in study cells after leaves were dropped in the fall. For example in the fall of 1995 the TCE/R levels in the effluent were around zero. Near the beginning of December the mass of TCE in the effluent increased to more than 10 millimoles.

4.5.6 Depth to Groundwater

Obviously, poplars will be better able to remediate groundwater that is within the reach of their roots. Phytoremediation is only successful when the aquifer that is contaminated is within reach of the roots of the poplars (typically within 15-20 feet of the ground surface). This is also complicated by climatic influences, precipitation, such that the roots of the trees will not actively seek out the aquifer if its water needs are met by surface water or other shallow water sources.

Phytoremediation is typically an in situ form of remediation, most of the time, but ex situ remediation can occur as well when the roots of plants are not deep enough to reach the contaminated groundwater [49]. It can be used as an ex situ remediation form in conjunction with groundwater extraction and irrigation for the poplars. Using contaminated water to irrigate plants is still considered a phytoremediation technique and not pump-and-treat because it still relies upon action by the plant for remediation. The drawback to pumping contaminated groundwater out of the ground and using it for irrigation is that it may be a regulated activity and because there are costs associated with extraction the groundwater from the ground. This is why ex situ remediation methods (including air stripping) are not as preferred as in situ methods.

4.5.7 Tree Age

Tree age (maturity) has shown to play a role in the extent and the manifestation of TCE uptake and degradation. Nzengung and Jeffers (2001) noted measurable differences in the aerobic degradation products or TCE accumulation found in young (less than 10 years old) and mature trees growing at the Carswell AFB remediation site. Furthermore, differences in accumulation were observed as the young trees developed. For example 1.34 (±0.45) mg/kg DCAA was found in the leaves of two cottonwood trees near the young plantation whereas the 4-6 month and 2-3 year old trees did not have any detections of DCAA in their leaves [53]. As mentioned in the case study section of this chapter, the microbial community found in the rhizosphere of the mature cottonwood growing within the plume at the Carswell AFB was well established and appeared to be degrading TCE whereas rhizosphere biodegradation is typically limited if not absent from the rhizosphere of young trees. The water uptake and transpiration ability also increases with increasing age.

4.6 Discussion of Findings

This section is provided for a summary of the data that has been presented thus far on the effectiveness of poplars to treat and contain TCE in groundwater.

The way that TCE is broken down or removed by a poplar tree is dependent upon a variety of conditions. These conditions include tree age, growth stage, species, and duration of exposure to TCE [53]. This was exemplified by the differences between studies and the differences identified within studies through the course of their evaluation period and across the poplar plantations. These conditions are some of the reason why the outcome of phytoremediation projects can not be predicted ahead of time.

All of the studies presented thus far provide conclusive evidence of poplars uptake, sorption, and transformation of TCE. Newman et al. (1999) identified dechlorination of TCE within plant tissue as the most significant mechanism for TCE removal from groundwater by poplars in a field simulated study. Other removal mechanisms were identified, such as microbial degradation and phytovolatilization but did not contribute to TCE removal at significant levels. The major TCE reducing mechanism at work during this field study was phytodegradation, although other mechanisms of reduction were identified as well. In personal communications with the lead author, Lee Newman, it was pointed out that although the 1999 study found that degradation through dechlorination was the most effective phytoremediation method, this did not hold true for studies they had conducted in the laboratory that found that phytovolatilization accounted for the greatest amount of TCE removal from the groundwater [57]. For example, this is consistent with other laboratory studies that found phytovolatilization from leaves and diffusion from stems and trunks is the major removal mechanism for TCE [9, 52]. These same studies found that degradation and storage of metabolites in plant tissues is a minor component of the overall uptake of TCE. The results of the Ma and Burken studies (2003, 2004) and those conducted by Newman (1997, 1999, 2004) show how conflicting the results of studies can be, especially when comparing results gathered in a laboratory versus data from field studies.

Rhizosphere degradation was seen in a few of the research studies, including at Argonne National Laboratory, but it appeared not to be a primary mechanism for TCE removal. However, the Carswell AFB project has shown that as the trees mature, the effectiveness of rhizosphere degradation increases and may become a primary removal mechanism. This is contrary to occasional studies that claimed microbial degradation is not enhanced by poplars. If the Carswell AFB study is a glimpse into what to expect from most *mature* poplars, perhaps the microbial results observed at most phytoremediation field sites were gathered too early, before the rhizosphere had enough time to adequately develop a hospitable environment for TCE degrading microbes.

An interesting bit of information that was identified during the case studies was that volatilization may be linked with concentration in the groundwater. This is evidenced by the data from the Aberdeen Proving Grounds in that the only trees that volatilized TCE from their leaves were the trees in the hottest zone of groundwater. All of the other trees only had TCE diffusing from the trunks. This may be because the TCE continuously diffuses from the trunks as it is brought up through the transpiration stream of the tree and those trees using water with lower amounts of TCE lose all of the TCE before the water reaches the leaves. Along the same lines, the field studies showed that the concentration of TCE in the tree tissue tends to be greater in trees that are located in areas of the TCE plume with higher concentrations. This was identified in a couple of the case studies discussed above too.

Given this information, it can be said that laboratory studies have tended to show that phytovolatilization was the main removal mechanism whereas field simulation and greenhouse studies show that hydraulic control and degradation are the leading mechanisms and that phytovolatilization was not a major contributing factor. The case studies that were discussed support these field simulation research results. It should be fair to say that the results gathered in field simulation and greenhouse studies better characterize how poplars accomplish remediation of TCE contaminated groundwater in real field applications. The laboratory studies are an indication of what the poplars are capable of doing, but typically did not characterize realistic growth conditions.

This comprehensive review of available literature has revealed that there is not one single phytoremediation mechanism that has been identified as the most successful at removing TCE from groundwater; except hydraulic control was observed as being successful at all of the case studies that were examined. This may come as a surprise to some people because "surely some mechanisms work better than others." In a sense this statement is true, based on specific site characteristics, but sweeping generalizations about (for example) phytovolatilization being the best TCE remediation method can not be made as they are unsubstantiated by a portion of available reputable scientific literature. This is because conditions at each remediation site are so highly variable. This is exemplified by the fact that studies conducted in the laboratory and in the field by the same scientists can have such disparate results. One sweeping generalization that can be made is that poplars can effectively treat TCE contaminated groundwater and hydraulic control (though it is not degradation) is the most cited effect that poplars can have on TCE plumes.

4.6.1 Phytovolatilization Hazard

One of the research questions that was posed at the beginning of this thesis was if phytovolatilization occurs, does it provide any inherent risk to human health or the environment? The previous paragraphs clearly outlined that indeed volatilization/diffusion of TCE from poplars does occur, regardless of whether it is a major removal mechanisms or not. The task then is to identify whether it is emitted at concentrations that are harmful. Frequently through the literature phytovolatilization has been noted as posing a potential threat to human health and the environment because it is emitting TCE vapor into the air that we breathe. Much like manufacturing degreasing operations or dry cleaning activities emit vapor. This may be true, but it is important to put in to perspective the actual amount that is emitted.

The calculations indicated that the amount of VOCs that potentially would be released at the Argonne National Laboratory phytoremediation site using worst case scenario data were on the order of several magnitudes lower than the National Emissions Standards for

Hazardous Air Pollutants (NESHAP). Calculations for the NESHAP standards can be found in the Clean Air Act 40 CFR Part 63 Appendix A to Subpart DDDDD. It may be beneficial, in order to achieve regulatory approval of phytoremediation systems that may aid volatilization of TCE from trees that the EPA's Clean Air Assessment Package-1988 model be employed in order to calculate potential emissions, as it was used in the case of the Argonne National Laboratory site. Even though it is unlikely that phytovolatilized TCE will pose a threat to human health or the environment, utilizing both the model calculations and short-term monitoring (as compared to NESHAP regulator levels) may be an effective way to prove that there is not a threat. This could be conducted into the future until the practice of phytovolatilization is officially recognized by regulators as not posing a threat to human health and the environment.

Air emissions of TCE were sampled at the Aberdeen Proving Grounds using an open path Fourier and a flux-chamber. The Fourier samples were collected around the phytoremediation plantation to measure TCE emission from the leaves, stems, and trunks of the poplars. The results of this sampling event indicated that volatilization from the trees was below the detection limits of the instruments (<1.6 ppm per meter of path length) and are considered insignificant amounts that do not present a threat to human health or the environment. The second sampling event was using a flux-chamber to monitor volatilization of TCE from the shallow groundwater. Of the eight locations that were sampled, three of them had TCE concentrations between 9.4 and 3.8 ppb by volume in the flux chamber at the sample locations. This is because TCE is a contaminant with a high vapor pressure that can easily be volatilized. This is a significant finding because it shows that TCE in groundwater naturally contributes to emissions to the atmosphere at detectable levels.

Davis et al (1996) stated that "Very few contaminants are sufficiently water soluble, non-toxic to plants, and volatile enough to reach atmospheric concentrations that would be of concern by [evapotranspiration]." Once the TCE is volatilized into the air, it only has a half-life of as little as 1.5 days due to the rapid photodegradation that occurs. This is coupled by the fact that TCE is readily diluted once it is emitted into the atmosphere. That being said, it is likely that TCE is not likely being volatilized to the atmosphere at concentrations that will be harmful, but necessary precautions could be implemented until a conclusive body of evidence is identified on this subject. For example, phytovolatilization should be monitored in an attempt to quantify the amount and concentration of TCE and break-down products that are being transpired by plants that are located in the areas of the highest plume concentrations. These trees are likely to emit the highest concentrations of TCE, if any at all.

4.7 Short and Long-term Effectiveness

The literature reviewed suggested that laboratory, greenhouse, and field experiments report poplars as capable of removing TCE from contaminated groundwater. However, the literature also suggests that the TCE removal pathways are inconsistent and conflicting, such that study results identifying major removal pathways conflict with one another. This does not discredit the fact that poplars are clearly capable of removing detectable quantities of TCE from groundwater; rather it highlights the fact that removal of TCE is highly variable and more research needs to be conducted. Furthermore, research should be focused on the effectiveness of mature poplars to remove TCE from groundwater. This should be the focus because few studies thus far have investigated mature poplars [109].

Part of the goal of this thesis was to identify the long-term effectiveness of poplars to remediate TCE groundwater plumes in order to compare this technology to a traditional remediation method. In order to analyze this effectiveness, a search for long-term projects was conducted. In this case, “long-term” is defined as greater than five years of data on a site, since phytoremediation is such a new technology. Unfortunately, it was extremely difficult, if not impossible, to find any data on field projects more than three years after the initial planting of the poplars. The reason for this was explained by Lee Newman in personal communication. Dr. Newman explained that many of the phytoremediation sites were only funded to collect data for two or three years to see if the treatment method was working (2007). After it was deemed by regulators and scientists to be working, no significant money was devoted to monitoring the system. Any annual monitoring that was conducted was not enough to generate data worthy of being published in a yearly basis. My initial thought in regards to this perceived lack of long-term data was to hypothesize if there is no data proving that phytoremediation works long-term, then how can one know if the plants have a certain saturation point (like, for example, the case of hyperaccumulating plants involved in phytoextraction) and cease remediating the contaminant after a certain period time? No literature was found supporting this hypothesis; however Doucette et al. (2003) identified the need for more information on the effectiveness of mature poplars. The long-term effectiveness of poplars is supported by the data obtained from the mature cottonwood tree located at the Carswell AFB above a TCE plume, as discussed in Section 4.6.1.3. This tree is more than 20 years old and the groundwater contamination could potentially be as old if not older, based on the decades of contaminant generating activities at the AFB. The investigations here indicated that the mature cottonwood continues to help take-in contaminated water and remove TCE.

In order for phytoremediation of TCE contaminated groundwater using poplars to excel as a viable remediation method more research needs to be conducted on the various sites and situations that it works well in. Chappell (1998) recommends some main areas where phytoremediation research needs to be pursued:

- Validation of rhizosphere biodegradation mechanism.
- Contaminant mass balance to determine the fate of TCE in the system of phytoremediation removal.

5.0 COMPARATIVE EVALUATION OF GROUNDWATER TREATMENT METHODS

There are benefits and drawbacks to all remediation techniques that must be weighed when choosing a method for cleanup. As we saw in Chapter 2 and 4, phytoremediation is an effective, economic, aesthetic, ecological, and natural way to remediate contaminants from a property. Phytoremediation not only has positive impacts on the environment, but also on people as well. There are no other remediation methods that can potentially have community involvement with the maintenance and monitoring of the project, like phytoremediation has. Nonetheless, there are conditions that limit both phytoremediation and pump-and-treat methods of remediation. This chapter is a comparative analysis of phytoremediation and the classic remediation method of pump-and-treat using an air stripper, for the treatment of TCE contaminated groundwater. This chapter focuses on comparing and contrasting the two remediation methods in a variety of different categories.

5.1 Site Conditions

5.1.1 Contaminant Concentrations

According to Chappell (1998), the physical nature of TCE makes it difficult to be remediated from groundwater using traditional methods [41] because of, for instance, the DNAPL nature of TCE. This characteristic makes it extremely difficult to remove those pools using the pump-and-treat technology, but it is possible to slowly dissolve the pool. It is possible to treat the aqueous phase TCE (that which has been dissolved in the groundwater) using pump-and-treat methods but not to directly treat the pools of un-dissolved chemical. As the contaminated groundwater is removed, the un-dissolved pool of TCE begins to slowly dissolve in the groundwater. This slowly continues as groundwater is pumped from the ground and can in fact contaminate clean groundwater as it is drawn towards the extraction wells past the pool of TCE. Total dissolution of the DNAPL TCE can take many years, on the order of decades to centuries. Many scientists believe that it is more efficient to use trees as mechanisms for long term treatment of TCE contamination. Nevertheless, there are also those that disagree. Cunningham et al

(1996) stated that "TCE and PCE are a relatively poor choice of targets for phytoremediation because they tend to form dense pools near the bottom of an aquifer, out of the reach of tree roots" (cited in [41]. However, one can argue that poplars may provide the hydraulic control that is necessary to prevent groundwater that has the potential to migrate through the area of the DNAPL pools from spreading the contamination any further down gradient. According to Pankow and Cherry (1996), the pump-and-treat method is typically not an effective method to use at sites that are contaminated with TCE that is in the DNAPL form. There are very few remediation methods (chemical oxidation, surfactant flushing, and thermal technologies) that can effectively target and eliminate DNAPL pools.

The contaminant concentrations that each approach can effectively remediate differ for phytoremediation and air stripping such that air stripping is more flexible in the range of concentrations and contaminant depths it can remediation. The ideal site for phytoremediation has low to medium TCE concentrations in shallow soil and groundwater. Low to medium TCE concentrations are ideal because above a certain threshold (in the hundreds of ppm range) the contamination can become phytotoxic to plants. Plants may die because of phytotoxicity if the contamination is too high or their growth and subsequent ability to handle the contamination may be critically limited [13, 41]. This problem is sometimes dealt with by using a multi-method approach to remediation in that hot spots are treated using a conventional remediation method and low to medium spots are treated using phytoremediation. Air stripping is able to remove a broad range of TCE concentrations from water; however, often there comes a point where the TCE can not efficiently be removed from the water because the energy required to blow an adequate amount of air into the water can not reasonably be done.

5.1.2 Geology

The geology of an area can be limiting to both technologies when there is low hydraulic conductivity due to the type of soil. Typically some silts and clays can have very low hydraulic conductivity which limits the rate at which water can move through the substrate and the rate at which the water can be withdrawn from the ground. As mentioned earlier, when the yield from a well is low (due to low hydraulic conductivity) a pump-and-treat remediation system is not going to be able to remove enough water to have an impact on the groundwater contamination in a realistic amount of time (within a decade or two). In order to be efficient, the air stripping tower must be able to discharge a specific amount of water at a time. If the groundwater pumping is not able to produce an adequate amount of water, the water must be stored onsite until a sufficient amount has been collected, during which time the air stripper stands idle. On the same token, if groundwater recharge is part of the air stripping system, soil that has low hydraulic conductivity will have a difficult time allowing discharged treated water to infiltrate the soil to recharge the aquifer. The soil type can also impact the efficiency of trees by limiting the depth to which the trees can send their roots as well as their ability to remove water from the ground (much in the same manner as air stripping is limited). This effectively limits the ability for the roots to extend into the contaminated aquifer. This can be improved by the way that trees are planted in the ground. By making deeper planting holes and by aerating the surrounding soil, the water uptake efficiency of a tree and root depth can be increased, as Eberts et al. (2003) has shown.

Organic matter that is added to the soil by plants can interfere with contaminant degradation by microorganisms (a concern during rhizosphere biodegradation). This is not a concern with air stripping; however, naturally occurring organic matter in soil can cause some of the TCE to adsorb to the organics, preventing it from being extracted with the groundwater.

5.1.3 Depth to Groundwater

As mentioned above, the ideal phytoremediation site will have shallow contaminated groundwater. Shallow groundwater is typically considered within 10-15 feet bgs. Shallow groundwater and soil is ideal for phytoremediation because the tree roots must be able to reach the contamination. One drawback to phytoremediation is the time that it takes for roots to grow to sufficient depths is also a limitation. This is a major limitation because oftentimes contamination resides at depths well below the depth to which roots can reach. Root depth growth may also be limited by soil conditions. One solution is to pump the contaminated groundwater and use it as irrigation for the phytoremediation plantation. In cases where the contaminated aquifer is deep, it may be more advantageous to use an alternative remediation method such as air stripping.

In contrast, when dealing with pump-and-treat technologies such as air stripping, the depth to contaminated groundwater does not matter as long as the groundwater can adequately be extracted from the ground via extraction wells.

5.1.4 Climate

The climate at a site will have a great impact on the design and successfulness of a poplar phytoremediation system. This is because a site's climate drives many factors, most importantly the amount of water available, sunlight, and length of seasons. Furthermore, climate even determines whether poplars can even grow in an area. For example, a TCE contaminated site in Hawaii will have to utilize alternative vegetation because poplars will not thrive in this region.

Some sites require irrigation for the first few years after planting to allow the growing trees adequate water if the type of weather in that area precludes adequate precipitation. Overtime the irrigation inputs can be steadily decreased. The amount of irrigation required can also depend upon the hydrogeology of the site. Irrigation and other surface water sources can however, interfere with the uptake of contaminated water by the plants. Climate really is not a concern with pump-and-treat technologies or air stripping.

5.2 Efficiency

Potentially, phytoremediation can be just as effective, if not more so than traditional conventional remediation methods [49]. The following is a discussion of the efficiency of the two remediation methods. In this sense, efficiency is used to mean a culmination of variables including how much time it takes to clean the groundwater; how clean the groundwater becomes; and the inputs that the methods require for success.

5.2.1 Uncertainties of Biological Systems

Many of the benefits and limitations of phytoremediation have to do with the fact that this is a biological treatment system [41]. By using phytoremediation as a treatment method over more traditional methods another element of complexity is added because plants are their own unique systems that do not conform to standard engineering practices [45]. This means that some element of uncertainty remains when using plants because there are so many other variables that are involved with plants than just using an engineered remediation method where most outcomes can be predicted. Some natural events may inhibit the success of a phytoremediation project such as frosts, wind storms, disease, infestation [13], nutrient deficiencies, phytotoxicity, and species competition among others. Tree uprooting during high winds may even expose waste [45]. Wind storms may also affect air stripping towers due to the potential for damage by the wind and also due to power outages. Pipes can also become frozen during low temperatures. Biological events are not a concern with air stripping, but natural and biological fouling of packing material in air stripping towers can greatly impact TCE removal efficiency.

5.2.2 Energy Consumption

Another contrasting point between the use of phytoremediation and the use of air strippers is their respective energy consumption. As mentioned earlier, poplars are often called solar pumps because the trees can act as a natural pump, using solar radiation as energy to draw water from the ground for transpiration and thus does not require large energy inputs [41]. Electrical pumps and air blowers consume copious amounts of energy and require a tremendous amount of money to pay for the energy consumption. Using the energy costs incurred at the Savannah River Site, as discussed in Chapter 3, and assuming an air striping remediation system would be online for 30 years, the energy costs could reach $780,000.

Another cost that should be kept in mind is the environmental cost of generating the electrical energy that supports the air strippers. In general, the electrical energy will be derived from a coal fired power plant, hydroelectric dam, or nuclear power. There are significant environmental costs associated with these conventional methods. These are intrinsic, lifecycle considerations of cost when using anthropogenic energy that are not directly reflected in the monthly bill from the electric company. There is also the energy cost to fabricate and transport all of the components of the air stripping tower, as well as its blowers and pumps. Despite the fact that poplars are often referred to as solar powered pumps, poplars can not draw a constant rate of water all year long because of seasonal variations in solar radiation and subsequently the limitation of their transpiration rates. Furthermore, in winter months the trees lose their leaves and subsequently cease evapotranspiration thus limiting hydraulic control of a contaminant plume and uptake of contaminated groundwater.

5.2.3 Contaminant Removal

Poplars can remove up to 99% of the TCE concentration in groundwater effluent as shown in an artificial aquifer field study [100]. The case studies discussed in Chapter 4 indicated that poplars were able to reduce, in some cases significantly, the TCE concentrations in the groundwater, though none of the case studies discussed (nor the other long term projects that were reviewed) had TCE concentrations diminished to below regulatory levels. Nevertheless, the mechanisms involved in the removal of TCE by poplars include the destruction of the contaminant either within the plant tissue or in the rhizosphere soil. The effectiveness of phytoremediation is greatly influenced by season and climate and can also increase overtime [49]. Phytoremediation works better in the growing season than in the winter season. In winter, deciduous trees lose their leaves, contaminant transformation and uptake stops, and transpiration ceases [13]. In general, evergreen trees (with the exception of loblolly pine [*Pinus taeda])* have not been investigated as phytoremediating trees. Attenuation of contaminants in the first year may be rapid, followed by a marked decrease as the plants naturally begin to thin themselves out from the initial planting density [13]. Nevertheless, as the trees mature, the amount of water that they remove increases and thus the contaminant withdrawal increases as well. Furthermore, as trees mature over time it has been shown that rhizosphere degradation increases.

Studies conducted in laboratories on the effectiveness of phytoremediation often times are not transferable into field applications [45]. Laboratory studies are a good indication of what plants are capable of doing; however they do not necessarily reflect what the major reduction mechanisms are. For example, laboratory studies have indicated that phytovolatilization is a major TCE removal mechanism with poplars; however, studies conducted in the field indicate that phytovolatilization occurs on a limited basis and is not considered a major removal mechanism.

The actual efficiency of an air stripper may be less than the designed efficiency. Data on air strippers also indicates that they too can reduce TCE concentrations in influent by up to 99%, but if concentrations were high enough in the first place, removal of 99% could still mean that measurable (and sometimes significant) levels exist in the water. Furthermore, air strippers are capable of removing large quantities of TCE and other VOC mass from groundwater thereby drastically reducing aquifer contaminant levels. For example, the Synertek Superfund site was able to decrease TCE concentrations in one well from over 200 ppb to less than 20 ppb in 5 years. The problem that pump-and-treat systems, including air stripping towers, run in to is that after a number of years of operation, the removal efficiency diminishes such that groundwater concentrations reach asymptotic levels. Pump-and-treat effectiveness can also be affected by seasons such that season changes can impact concentrations in the groundwater. The extraction and recharge of groundwater to and from the air stripper can also be affected by seasonal variations in the groundwater level and groundwater properties. Air stripping removal efficiency is great in the first few years of operation but slowly begins to decline until asymptotic groundwater concentrations are reached and mass removal is negligible.

There have been very few cases of air strippers being able to remediate an aquifer such that TCE concentrations were below regulatory levels, as illustrated in the cases discussed in Chapter 3. Quite often the cleanup goal for a groundwater remediation project is set to drinking water standards by regulators, but some people contend that this is an unreasonable goal because reaching this in a reasonable time frame may be near impossible, no matter which remediation method is chosen [63]. As indicated by the

CRWQCB, groundwater extraction (pump-and-treat) may not be able to achieve low maximum contaminant levels. Other regulatory goals that more realistically might be strived for include technology based standards, restricted use standards (deed restrictions), and hydraulic containment [63]. Technology based standards are standards that are set based on the ability of the specific remediation method that is chosen. This eliminates the possibility for setting unrealistic goals that are not achievable by some remediation methods. Restricted use standards are limitations that are recorded on the property's deed that prevents some land use from ever being conducted on the property. These are typically called deed restrictions or restrictive covenants. For example, if TCE in groundwater is known to be present, a restriction that may be put on the property would be that future use of the groundwater as drinking water is prohibited but use for irrigation is permitted. And lastly, hydraulic containment may be chosen as the remediation goal if removal of the contaminant from the groundwater is deemed unlikely or too costly. Hydraulic containment is chosen to prevent the contamination from spreading any further, and more importantly prevented from contaminating adjacent properties. The above regulatory goals are easier to obtain in reasonable timeframes and make more sense for groundwater that is not a potable water supply and perhaps projects that are located in an industrial zoned area where there is no likelihood that the property will be converted to a use that may potentially present a threat to people that live, work, or play there unless specific measures are taken to prevent that from happening.

Phytoremediation could satisfy all three of these alternative regulatory goals without creating a large amount of waste as a byproduct. In order for air stripping to be able to hydraulically contain a contaminant plume, a number of extraction wells must be strategically installed across the site (and adjacent sites as well when the plume impacts multiple properties) in order to create a groundwater zone of influence strong enough to contain the plume. Depending upon the type of geology, trees (especially poplars) can be more effective at creating a zone of influence than extraction wells in an effort to hydraulically control a contaminant plume [61]. Poplars can often times more effectively create a zone of groundwater influence because of the ability of thousands of miles of fine roots (an accumulative length of all of the roots of a tree) to extend across much of a site. This is in contrast to the difficulty that can be encountered when choosing a network of appropriate well locations for a groundwater extraction system that can adequately penetrate the varying layers of the subsurface such that the network can work in concert to create a zone of groundwater influence.

Phytoremediation works well as a ‘polishing’ treatment (used after a different remediation method to remove residual contamination) or in combination with other methods [13]. For example, the soil contamination on a site may be addressed using soil vapor extraction and the remaining groundwater contamination may be treated with phytoremediation. Air stripping can be used in this manner as well (see the case studies in Chapter 3).

5.2.4 Fate of TCE

Volatilization

Air stripping involves large scale emissions of TCE to the air on the order of kilograms per day (thousands of kilograms per year) whereas a single tree may only emit less than one-half of a gram per day. One must also keep in mind that the removal of TCE by air strippers from water is merely discharging TCE into the atmosphere. Air stripping towers can saturate the air immediately surrounding it with TCE if the air emissions are not captured and treated by another source. This saturation can occur because of the shear volume of TCE that is released at one time, which may not be able to be diluted and photodegraded fast enough. One medium is cleaned-up while another is being impacted.

It is true that poplars can also emit TCE to the air during phytovolatilization but the volume of TCE is quite small as compared to the volume emitted during air stripping, as illustrated in Table 5-1. There are fewer air and water emissions with phytoremediation [41] and therefore fewer (and less significant) secondary impacts to other mediums. The amount that is volatilized by a poplar, or a plantation of poplars is distributed across a large land base (typically at least an acre) and can be quickly diluted in the air, photodegraded by the sun, and therefore does not saturate the surrounding air. As mentioned earlier, TCE has a half-life in the air of 5 days because of photodegradation. The rate of photodegradation of TCE was discussed in Chapter 2. Also an important point to address is that if poplars in a plantation are in fact actively phytovolatilizing TCE it has been shown through numerous studies that the amount of TCE volatilization varies from tree to tree. Some trees in the plantation may not volatilize TCE at all! That being said, the flux of TCE to the atmosphere will not be consistent across a plantation, thus further decreasing the potential for TCE saturation. Furthermore, volatilization from trees varies seasonally as well, such that no volatilization occurs when the trees do not have leaves. So, the total amount of TCE that is volatilized by trees per year is far less than by air strippers.

Using the half-life of 5 days in the air, the residence time of TCE in the air was calculated (not taking into account any other degrading or mixing factors) using the emission rates in Table 5-1. After the emission of 24 kg of TCE into the air from an air stripper, it would take approximately 60 days for the TCE to be photodegraded down to less than 1 g. In contrast, using the maximum emission rate for poplars from Davis et al. it would take less than 20 days to reach a concentration below 1 g (though this maximum emission rate first proposed by Davis et al. was orders of magnitude larger than the emission that is actually observed in the field as it was based on grams of TCE per liter of water). This is significantly different than the amount of time it would take after emissions from an air stripper. A more in depth description of emissions from air stripping towers, see Chapter 3.

Table 5-1 Emission Rate Estimations

Source	Emission Rate	Reference
Air Stripping Towers	3.3 kg/day	Gross and TerMaath (1985)
	24 kg/day	FRTR (1995)
Poplar	0.44 g/tree/day	Doucette et al. (2003)
Poplar Plantation	352 g*/day	---

*This estimate is assuming 0.44g emission per tree for a plantation with 800 trees.

As mentioned in Chapter 3, granular activated carbon can be used to adsorb volatilized TCE from the air in an effort to prevent atmospheric emissions. Once the carbon is spent it is just another source of contaminated waste that must be dealt with. The disposal or recycling of the carbon is yet another cost that must be included in the operations and maintenance cost of the treatment system. Carbon scrubbers are used quite often to treat the volatilized TCE, but there are still some sites where the volatilized TCE is allowed to be emitted into the air. For example, at the "MEW" Superfund Site located in an industrial park adjacent to residential neighborhoods in California, there are three 45-foot tall air stripping towers that were constructed before 1989 that do not have off-gas treatment for the volatilized TCE (though towers built after 1989 do have off-gas treatment) [122]. One of the towers is even located in the middle of the office courtyard of a prominent internet company. Phytoremediation generates less waste, than air strippers and other alternative remediation methods [41].

Degradation

As discussed in Chapter 4, TCE can accumulate in the tissue of poplars. The accumulation is minimal compared to the hyperaccumulation of metals by some plants, but enough can accumulate to raise the question about the fate of the tissue stored TCE. If poplars are to be harvested for pulp and paper or fire wood, it has been shown that allowing the wood to season for one year allows enough time for TCE in the tissue to be degraded [57].

The other risk of TCE residue in tree tissue is the exposure of animals to TCE that consume aboveground parts of the trees (leaves, stems, bark, fruit, nuts) and the potential for impacts to the food chain [13, 45, 49]. This is one of the issues that factor into the public acceptance of phytoremediation [123]. "Even though residues can persist in plant tissues for extreme periods of time, bound metabolites may or may not have toxicological impacts of a chronic nature" [124]. One study indicated that some animals avoided eating plants that had elevated metals levels [125]. Animals can also be affected by TCE contaminated groundwater when the groundwater is brought to the surface via natural or manmade processes. Animals may drink the contaminated water, eat contaminated soil, or eat species that had been impacted by the contaminated water. This is another food chain exposure mechanism. Wildlife can be impacted by TCE contamination through the ingestion of contaminated water. As discussed earlier, the likelihood of biomagnification of TCE through the food chain is not likely because of its low octanol-water partition coefficient. Furthermore, as shown earlier, TCE is metabolized in the bodies of humans and animals (rats and mice were discussed in Chapter 1). Nevertheless, some residual TCE (or its metabolic byproducts) may be consumed during the predator/prey process.

A fact that is often overlooked is that natural vegetation that was on the site prior to the introduction of phytoremediation, potentially could already have been contributing to food chain exposure. Nevertheless, a way to minimize exposure is by limiting human and wildlife access. Some scientists suspect that the ecological exposure is outweighed by the habitat benefits that phytoremediation sites provide, in areas that often had seen heavy industry and little habitat. Measures to control caterpillars, rodents, deer, squirrels, etc. from eating plant products include site perimeter fencing, overhead netting, pre-flowering harvest, and plastic shields along the trunks of trees [45].

Another fate of TCE that occurs with phytoremediation and not pump-and-treat is re-contamination of the soil or groundwater from plant droppings (bark, cones, leaves, and limbs) or through the use of the plants as firewood or mulch [13, 49]. Exposure of TCE from firewood, mulch, or pulp can be avoided if the wood is left to season for a year [57].

Hydraulic Control

Sometimes the main goal of a remediation project is just to control the migration of a contaminant plume. Hydraulic control of the contaminant plume can be achieved by phytoremediation and by pump-and-treat technologies. Phytoremediation may be seen as more desirable when hydraulic control is the objective because this can be efficiently achieved by trees, as Chapter 4 has shown.

5.2.5 Time Requirements

Cleanup time is highly variable based upon site specific conditions and their interaction with contaminants. This is true for any remediation technique. The cleanup of groundwater is especially challenging because of its fluid nature and transport processes. Something that is sometimes difficult for site owners to understand is that groundwater is difficult to cleanup and it can take a very long time. For phytoremediation, it may take a few years after planting the trees to see results since it takes time for the trees to grow, establish themselves, and mature. As mentioned in the previous chapter, tree maturity (age) appears to play a large part in how successful a tree is at extending its roots to an aquifer, uptake and transpire water, and provide enough carbon and nutrients to the rhizosphere to benefit soil microbes. Estimates for the cleanup time for phytoremediation projects have been on the order of 10 to 30 years due to the rate at which plants up-take or metabolize contaminants, and because of the seasonal changes in contaminant uptake. Except for some soil amendments and the practice of planting older trees, there is very little that can be done to speed up the phytoremediation process. You must let nature run its course! For example, the Argonne National Laboratory project anticipates 20 years of remediation at their plantation. It is difficult to say if this is an accurate estimation because there are no phytoremediation projects that have been in operation for more than 10 years.

The amount of time that it takes to remediate using plants can be longer in comparison to some methods such as excavation or incineration, which can take weeks to months to remove contaminants from media to achieve regulatory levels [13, 45, 49]. Nevertheless, many project sites where phytoremediation may be used are places where excavation is impractical due to the sheer quantity of soil that has been impacted. In these situations conventional remediation methods that could be reasonably employed would most likely take many years to effectively clean-up the contamination, just like phytoremediation. Several of the Superfund cases reviewed that are utilizing air stripping indicated that the cleanup time was going to take many decades longer than originally anticipated. In essence, neither treatment method is a quick fix. Given this, if human health is acutely impacted by the concentrations of TCE in groundwater at a site, it may be more advantageous to implement a remediation technique that can have greater benefit in a shorter amount of time.

Potentially long lead time may occur as you are waiting for tree roots to reach groundwater [48, 49]. As demonstrated in Chapter 3, air stripping can take many decades to reach cleanup goals because of the shear volume of water that has to be treated and because of the amount of water that must be pumped in order to contain a plume. Cleanup estimations provided in cost estimates were typically for 10 to 30 years; however, little information was found on successfully completed air stripping remediation programs for TCE contamination. Even so, the results of the conventional remediation would be seen immediately whereas patience must be practiced when looking for phytoremediation results.

5.2.6 Efficiency Example

As shown by the Argonne National Laboratory project [61], the phytoremediation system was preferred over the pump-and-treat system because it was thought to be more effective at reducing the size of the plume of contaminants (as evidenced by the smaller amount of contaminants that are reaching down gradient monitoring wells) because of the ability of the tree roots to penetrate through the glacial till soil into the aquifer to control the flow of the groundwater. The phytoremediation system was also seen as a better way to remove the (DNAPL) sources of the contaminants whereas the extraction wells were not involved with the actual destruction of the contaminant pools, thereby allowing them to continue to provide a source of dissipation into the groundwater as water was pumped past the pools. And finally, the alternative system would create a large amount of secondary waste (the withdrawn contaminated groundwater) that would still need to be treated once it was drawn out of the ground. The phytoremediation system eliminated the need for secondary treatment of waste and the trees allowed for the volatilization of the extracted water as vapor into the atmosphere. The volatilization was modeled (to appease regulatory concerns) and was demonstrated to be below the regulatory threshold for air levels. Therefore, the volatilized TCE was not of concern as a secondary contaminant.

5.3 Cost

5.3.1 Cost of Phytoremediation

Because phytoremediation is an emerging remediation technology, the availability of cost information is limited. Furthermore, many of the projects thus far that have used phytoremediation as a cleanup technique have been pilot scale studies implemented not only for the cleanup of a contaminated site but also for research purposes. This means that much more sampling and analysis was involved and thus the cost of the project would reflect the extra investigations and would not accurately reflect the cost of a typical remediation project. The capital cost for phytoremediation includes the plants, the plant installation equipment, soil amendments, impermeable barriers (if required), and labor [126]. Operations and maintenance costs are typically related to replanting, irrigation equipment, water, soil amendments, power for irrigation equipment, labor, and harvesting [126]. Occasionally some of the cost of a system can be offset if the plants or trees can be harvested and sold.

Presumably, the cost of obtaining, planting, and maintaining the trees is far less than designing, fabricating, and constructing an air stripping system. As an example, hybrid poplar plantations (in the 1990s) ranged in capital cost per hectare from $12,350 to $247,000, depending upon the level of infrastructure required [126]. Some have estimated plants as costing between $8-80 per tree or $0.20 for whips [45]. Maintenance requirements and maintenance costs are low for phytoremediation [45, 48] but can be labor intensive because of mowing, replanting, pruning, harvesting, monitoring vegetation for contaminants, fertilizer additions, irrigation, and performance monitoring requirements [13].

5.3.2 Cost of Air Stripping

The cost for the blower and the water pumps is often the control on the capital costs for the system [72]. The way that the air stripper is designed also affects the cost of the system. There are varying prices for packing material, tower structure, tower internals, blowers, and pump equipment depending upon the material and product grade that is selected as well as which vendor is used [72]. Air stripper vendors include Jaeger Products, Inc. and Delta Cooling Towers, Inc. However, cheaper is not necessarily better. The efficiency of the system is also connected to the materials that are used to construct the tower, so this must be kept in mind when making a selection of the various pieces of the system. The addition of an air emissions treatment system can increase, double and sometimes even triple the capital cost of the air stripping system [62, 73]. Operations and maintenance costs are typically resulting from labor, repair, parts, and energy for the mechanical components [73]. Delta Cooling Towers, Inc. (2007) reported that air stripping has become the most popular treatment technology for VOCs because of its cost effectiveness when it comes to initial operations and maintenance cost. This statement is ignoring the large capital cost of an air stripper system.

The reported costs for an air stripper (per 1,000 gpm) vary widely based on the source reporting it. The EPA (1991) reported the cost ranging from \$0.04 to \$0.45 per 1,000 gpm. The \$0.45 per 1,000 gallons estimate was based on a 10 year remediation schedule, while a \$0.14 per 1,000 gallons per minute estimate was assuming a 5-year remediation schedule with average treatment of 7 million gallons per day[§§§] [73]. An example of the cost of air stripper system is from the refrigerator manufacturing facility in Michigan, which spent \$3,000,000 for capital costs, constructing an air stripping tower treatment system for the remediation of groundwater impacted by TCE and other VOCs [82]. Annual operations and maintenance for this facility were estimated at \$145,000. If this system was to operate for 10 years (not including interest or inflation) the total cost would be about \$4,450,000. The cost for operating the system for 15 years would be \$1.70 per 1,000 gallons of water per minute. Table 5-2 provides other system costs that were gathered by the EPA. The sites shown in Table 5-2 were for ongoing projects that used air strippers as their sole remediation system for TCE (and other VOC) contaminated groundwater. These projects had been in operation for four to nine years [127].

Table 5-2 Cost of Air Stripping Systems

Site	Total Capital Cost	Average Annual Operation Costs
TCAAP, Minnesota	\$12,000,000	\$810,000
Des Moines, Iowa	\$2,200,000	\$140,000
Savannah River, South Carolina	\$5,200,000	\$170,000
Solid State, Missouri	\$1,000,000	\$300,000

Adopted from EPA, *Remediation Technology Cost Compendium – Year 2000*, 2001.

With air stripping, maintenance can be costly and time consuming because there are so many mechanical components involved (pumps, blowers, etc.). Further, the tower and packing material must be regularly maintained in order to prevent fouling.

[§§§] The cost was calculated in gallons per minute, so it was not converted to metric.

The environmental costs sustained generating electrical energy are rarely discussed when considering air stripping or other conventional methods of groundwater treatment that require large inputs of energy. But when lower-impact, “natural” or ecologically sensitive alternatives to conventional methods are being considered, these are the types of costs that must be weighed.

5.3.3 Comparison

By nature, phytoremediation is less expensive than pump-and-treat methods of remediation. Typically, phytoremediation costs less than other traditional remediation methods [45, 48, 49] such as air stripping. Often, phytoremediation is most practical at sites where traditional remediation methods are not cost effective [13].

Often cost is a limiting factor in remediation projects but phytoremediation provides a low cost alternative to a variety of different cleanup needs, including the use of poplars for TCE contaminated groundwater and provides a low cost alternative without sacrificing the efficiency of remediation. For example, in order for air stripping to effectively control a contaminant plume, many wells must be installed throughout a waste site. In contrast, a poplar plantation can grow tens of thousands of miles of fine roots that can cover a great extent of a waste site at the cost of just the trees. This large root coverage can allow the trees better control on the plume.

The following table is an estimate for hydraulic control using trees as compared to using an unspecified form of pump-and-treat. As with other phytoremediation methods, hydraulic control is clearly less expensive than conventional methods. The table below supports David Glass’ (1998) estimation that total system costs for phytoremediation projects are 50-80% lower than conventional remediation methods.

Table 5-3   Cost Estimate for Hydraulic Control of 1 Acre Site with 20’ Aquifer

Type of Treatment	**Cost**
Pump-and-treat	\$600,000
Hydraulic Control with trees	\$250,000

Source: Adams (2000); Schnoor

The capital cost for typical phytoremediation projects is as low as approximately a few hundred thousand dollars, depending upon the size of the plantation (typically one or two acres in size); the number of trees required to adequately control plume advancement; the amount of monitoring that is built into the remediation program. In contrast, the capital cost for typical pump-and-treat systems using one air stripping tower can range from $600,000 up to a few million dollars. The average annual operations cost for Superfund sites using pump-and-treat was $570,000, as determined by EPA contractors [65] (though this estimate included those pump-and-treat sites that were not employing air stripping technology). According to Hyman and Dupont (2001) basic air stripping equipment cost ranges from $200/gallon/minute down to $130/gallon/minute (for systems that accommodate 30 to 500 gallons/minute). This cost is dependent upon how easy the contaminant is to remove from the water. When air emission controls are introduced, the capital cost can be doubled or even tripled [62]. Air injection pumps can range from $5,000 to $25,000. For better estimates of air stripping costs, there are computer programs that can be used to generate cost estimates: COMPOSER GOLD and RACER/ENVEST™ [62].

The following are some real cost examples for both pump-and-treat and phytoremediation and some comparisons of the two alternatives as well:

- It was estimated that $3,000,000 was spent for capital costs of the air stripper system at the refrigerator manufacturing facility in Michigan [82] and annual operations and maintenance was estimated at $145,000.

- The estimated cost for the installation 800 trees on 2.67 acres and long-term monitoring (20 years) of the phytoremediation system at the Argonne National Laboratory is $4,592,632, which equals approximately $38 per square foot. This cost is so high, as compared to the cost estimates referenced above likely because of the long-term monitoring program that was factored into the price. The phytoremediation mechanisms that are being used at this site are phytovolatilization, phytodegradation, hydraulic control (largest mechanism) and limited rhizosphere biodegradation. 32% of the 20 year cost ($1,480,000) was incurred designing and installing the plantation. The largest portion of the overall cost, approximately 55%, is operations and maintenance [61]. The estimated cost for the alternative pump-and-treat technology proposed at this site was $6,994,520.

- Quinton (1997) provided a cost analysis for PCE contaminated groundwater remediation (TCE is a daughter product of PCE so their chemical make-up and behavior in the environment is very similar). For a site with a PCE plume at 1 ppm concentration and a remediation timeframe of 30 years, a pump-and-treat system using air stripping and carbon absorption would cost approximately $9,800,000. Phytoremediation was not included in Quinton's analysis, but Chappell (1998) estimated that under the same site conditions, it would cost between $1,000,000 and $3,000,000.

- The Solvent Recovery Systems of New England site had 2.5 acres of solvents in groundwater turned to degradation and hydraulic control as remediation methods. The installation cost and initial maintenance for this site was $200,000 as compared to the expected cost of the traditional pump-and-treat method for this site that is $700,000 per annum [45]. In this case, phytoremediation was 1/3 of the cost of pump-and-treat methods.

At the time of the introduction of air stripping into the field of groundwater remediation in the 1980's, it was considered a cost-effective way to remove volatile organic compounds, as compared to the most widely used treatment method at the time- granular activated carbon filtration. After seeing the remarkable cost difference between phytoremediation and air stripping it is interesting to think that air stripping was once considered a cost-effective alternative, whereas these days the cost for air stripping can be prohibitive, and phytoremediation is an even more cost effective method. Table 5-4 is a rough estimate of the various costs associated with each method. The costing data was derived from the sources used above. Of course there are other costs associated with each system, but many are not published, or are rolled into general costs such as operations and maintenance. This table just illustrates the drastic difference between the two remediation methods.

Table 5-4 Comparison of Approximate Cost for Methods

	Phytoremediation	Pump-and-treat Air Stripping
Capital Costs	$10,000-1,500,000	$600,000-5,000,000
Operations & Maintenance (yr.)	$0-150,000	$60,000-500,000
Replacement Parts	Trees: $8-80 Whips: $0.20	Pumps: $3,000 Blower: $1,700-6,000 Extraction Well: $20-40/ft.
Labor	Planting: $180,000 Pruning: $500 Harvest: $2,500	N/A
Energy	---	$20,000+ ($0.052/kwh)

N/A= not available

Woody plants, such as poplars, that are being used to treat non-accumulating contaminants may be put on a crop rotation such that once harvested, the trees are used for pulp, fuel, or timber [45]. This provides an economic return for those that are paying for the remediation costs. In essence, the plants provide a dual purpose: remediation and a cash crop. At this time there is no known profitable return that can be generated by an air stripper.

5.4 The Public & Phytoremediation

There is high public acceptance of phytoremediation [41]. The public acceptance may be due to many of the points discussed thus far in this chapter including the use of solar energy, ecological restoration, cost, and aesthetics. The following is a further discussion of the impact that phytoremediation can have on the public.

Many of the phytoremediation projects that have been conducted in the field thus far have been at brownfields, which are often located in lower economic, minority neighborhoods that have been the scene of social and environmental injustices. Cleaning up the brownfields and improving the aesthetics of the neighborhood by implementing phytoremediation projects can have great social and mental health benefits beyond just cleaning up contamination.   Research on the effect of green spaces or their absence has shown that green landscape can reduce stress and violence, improve overall health, and strengthen community bonds [47]. For example, hospital patients with a view of a green landscape have shown to require lighter doses of pain killers and fewer post-operative health complications [47]. Public housing neighborhoods with green space have reduced domestic violence and improve people's ability to cope with severe poverty. Employees with a view of a green landscape have a tendency to be more efficient on the job. Commercial areas that have green landscaping are seen as more desirable areas of commerce. In essence, having a view of a green landscape at some point during your day whether it is a park or just some landscaped areas of trees and plants, can improve a person's wellbeing.

In contrast, if a conventional treatment method had been chosen, the view would be obstructed by machinery, for example stripping towers, storage tanks, or fields of wells. Not to mention there would be an audible impact from conventional treatment methods including air strippers because of the constant drone of pumps, blowers, or other electrical equipment. A report by Environment Canada (Canada's equivalent of the EPA) indicates that public acceptance for air stripping is low [128].

There are several drawbacks to phytoremediation in the context of public perception and the public's wellbeing. First, periodic tree removal can be part of a phytoremediation program, but this can cause some people to be upset because of their attachment to the trees [47]. This may be compounded by the fact that people may perceive the loss of trees as an indication that the positive green space may be removed all together. A remedy for this is public education and public involvement. Getting the public involved in phytoremediation projects is one way to gain public support and understanding of a project. Public participation could be in the form of a community group adopting a site and providing monitoring data such as bird use, plant growth and survival, or wildlife counts [49]. Second, there is some risk of public exposure to the site [47]. Green landscapes are inviting to people, which may encourage the public to access the site. Direct access should be strictly limited to the public when the contaminants onsite present a threat to human health. And finally, the public may not see phytoremediation as favorable as other methods that provide faster remediation [129].

5.5 Other Comparisons

5.5.1 Aquifer Depletion

On average a five year old poplar can take in 100 to 200 liters (26-52 gallons) of water per day [41, 45]. For a plantation with 200 poplars this would equate to approximately 20,000 to 40,000 liters (5,200-10,000 gallons) per day for the plantation. Air strippers on the other hand can consume any where from 150 to 3,000 liters per minute, which translates into 216,000 to 4,320,000 liters per day. Phytoremediation does not necessarily present the threat of aquifer depletion because of the scale of groundwater removal by trees versus that of pump-and-treat systems and because some of the degradation of contaminants can be conducted without the removal of water (through adsorption to the root surfaces, rhizosphere biodegradation, and through degradation in rhizosphere from root exudates). Furthermore, trees undergo evapotranspiration which emits much of the water taken up into the atmosphere as water vapor, thereby returning water back to the hydrologic cycle. In theory when an air stripper is to be used at a site, the amount of groundwater that can safely be withdrawn per hour or per day would be calculated to get an idea of what the maximum water withdrawal rate can be without jeopardizing the aquifer. Nevertheless, groundwater that is treated by an air stripper is not always returned back to where it was withdrawn as it is sometimes sent to wastewater treatment plants.

As the Schofield Barracks air stripping example showed in Chapter 3, sometimes astronomical amounts of water are required to be extracted and re-injected each day in order to effectively capture the contaminant plume and provide enough water back into the aquifer to prevent aquifer depletion. This example shows that air stripping (and pump-and-treat remediation methods) are not an ideal choice for remediation at all sites.

It should be recognized that groundwater treatment methods that are removing contaminated water from an aquifer and thereby preventing the migration of contaminant plumes are often helping to protect down gradient drinking water sources. This objective is effectively met with phytoremediation’s ability for hydraulic control of a plume. In this sense it may be in the public's best interest to remove enough water to contain the plume.

5.5.2 Land Requirements

The land requirements for an air stripping system depend upon how many air stripping towers will be used. Typically, the requirements are for enough land to accommodate a contaminated water holding tank, a pump, a blower, the air stripping tower, and an infiltration area (if the treated water is being infiltrated back into the ground). This equipment requires much less than an acre of land; however this is not including the area that will be used for monitoring wells.

In contrast, plantations of poplars for phytoremediation typically need at least an acre, often several acres to be effective. Nevertheless, the amount of land that is required for a project depends upon the extent of the contamination and the aquifer properties. Oftentimes the size of the plantation depends upon how many trees are required to adequately capture the plume and for degradation of the contaminants [130]. The size of land required can be determined using models such as MODPATH and MODFLOW [130]. For example, the Argonne National Laboratory phytoremediation site was 5-acres in size. Further, each tree must be planted a certain distance from its neighbor in order to limit competition for resources. In some instances, the poplars are planted as whips in a high density in order to start the hydraulic control and degradation process immediately and the site operators rely on the poplars to naturally thin themselves out over time. The one example of a poplar plantation in an area smaller than an acre is the Edward Sears property. This plantation was in a residential backyard. Positive phytoremediation results were observed in a very small area with a limited number of trees. If limited open space is a factor at a waste site, then phytoremediation may not be an effective remediation method. The size requirement limits the number of sites that could potentially be remediated using plants to those sites that have the acreage requirements so that enough plants can be planted in order to have an effective phytoremediation system [49]. Many urban areas may not be ideal for phytoremediation. Likewise, there are some areas that are not suitable for air stripping towers including residential neighborhoods, or other areas where people might complain at the site, noise, or emissions from the stripping tower.

5.5.3 Aesthetics

Air stripping towers are not aesthetically pleasing. They are very industrial looking and are a constant reminder of the impact that industrialization has had on our earth. An alternative to the typical 40-foot stripping tower is a low-profile stripping unit that is more compact, but is less efficient. The noise associated with an air stripper may also be considered a nuisance.

Poplar plantations improve the aesthetics of the neighborhood and provide great benefits beyond just cleaning up contamination. Green landscapes have been shown to have positive influences on people's stress levels, violence, and health. It is rare that a phytoremediation plantation is considered unsightly. Furthermore, it is sometimes thought by the public that areas with flourishing vegetation are not in as hazardous condition as a barren lot [111].

The poplar plantings can be incorporated into the site's long-term landscaping goals. Trees can be used for shading or for visual screens. Many sites are even being turned into parks [45]. The aesthetic nature of plants provides a visually pleasing view in a location that perhaps used to be devoid of vegetation or an industrial development [13, 49]. Vegetation can also be used as a landfill cover or as a final layer at a hazardous waste site.

5.5.4 Ecological Restoration

Phytoremediation provides a remediation technology that is less disruptive to the ecosystem [41]. Ecological restoration, aside from the remediation of contaminated groundwater, is something that is addressed by poplar plantations and not by air stripping systems. Typical phytoremediation projects involve changing an industrial or other disturbed site (such as Brownfields or Superfund sites) in poor ecological condition and re-introducing vegetation. Natural re-vegetation of a contaminated industrial or other disturbed site can take decades to hundreds of years to occur because it must rely on seeding by animals and wind [45]. Therefore, human induced planting of vegetation speeds up that process and can reach maturity in a matter of years.

Phytoremediation is harnessing natural systems to reverse harms to the environment that humans have created through the process of industrialization and mechanization, instead of using more engineered and invasive procedures. An example of this is injecting chemicals into the soil and groundwater that will aid in the degradation of contaminants. It seems counterintuitive and counterproductive to expose the environment to even more chemicals!

Ecosystem benefits include providing habitat (shelter and food) for a variety of species including insects, amphibians, birds, and small mammals, and restore natural species populations as well as increase species diversity and density. The fact that most phytoremediation sites have low levels of human activity helps support ecological benefits by allowing animals to re-colonize low-traffic areas where vegetation can readily grow, except in the cases of contaminant concentrations in the plants, where access to the area must be limited. Planting a diverse group of vegetation (trees, shrubs, and grasses) can provide shelter and food for species [45]. Access by animals may need to be limited though if they are damaging the plantation, which could potentially lead to death of some of the plantings. The trees also provide soil stabilization and erosion protection through the growth of their roots. The trees also act as a windbreak that helps prevent soil erosion and wind damage to other trees or to personal property. There is a great social value in ecological restoration. Phytoremediation is far less an invasive procedure than conventional treatment methods. Further, phytoremediation may also be more appropriately located in areas of dense population because of its added “green” benefits, its low volatilization of TCE into the atmosphere, and because of aesthetics. The goal of phytoremediation projects is not to return an area to pristine pre-human conditions; rather phytoremediation projects provide opportunities to improve ecosystem conditions.

Air stripping on the other hand does not aid in ecological restoration or soil preservation, rather it perpetuates the industrial condition of a property and continues to limit the use of the property. Air strippers provide a constant reminder of the consequences of industrialization and act as a monument for the presence of groundwater contamination.

5.5.5 Regulatory Acceptance

Regulatory acceptance of phytoremediation as a viable alternative is still underway and many regulators may still be unfamiliar with the technology [13, 41]. Regulatory acceptance of pump-and-treat systems, including air stripping, may be diminishing because of the mounting evidence that air stripping efficiency decreases over time, the length of time for cleanup, and the typical inability to reach cleanup goals.

5.6 Final Comparison of Methods

The following table is a summary of all of the important data that has been presented in this thesis that lends to an adequate comparison of the methods.

Table 5-5 Comparison of Methods

	Phytoremediation Poplars	Pump-and-treat Air Stripping
Depth to Groundwater	Shallow - < 30 ft.	Shallow - Deep
Volume of water withdrawn	100-200 L/d/tree 20,000-40,000 L/d/plant.	150-3,000 L/min. 216,000-4,320,000 L/d
Fate of withdrawn water	Tree uptake followed by evapotranspiration	Extraction followed by discharge to ground or treatment system.
Time to clean-up contamination	Unknown	20+ years
Fate of TCE	Degradation, Volatilization, Hydraulic Control.	Volatilization (and capture if emission controls are used).
Removal Efficiency	99%	99%
Contaminant volatilization rate	0.44 g/tree 10 g/m^2/day plant.*	~24 kg/day
Waste needing treatment	No**	Yes***
Ecological Restoration	Yes	No
Energy Consumption	Solar	Electrical

*=Assuming 800 trees in a plantation.
**=Typically treatment of the trees is not needed, but occasionally harvesting does occur.
***= Treatment is needed when air emission controls are used such as granular activated carbon.

6.0 CONCLUSION

This goal of this thesis was to determine if TCE contaminated groundwater could effectively be remediated using poplars for phytoremediation in comparison to the pump-and-treat method of air stripping. If phytoremediation was possible, the question was posed whether phytovolatilization of TCE from the poplars could potentially impact human health or the environment. The following were the findings of this research. The removal of TCE by poplars is highly variable. This thesis presented four case studies in which poplars are being used to clean-up TCE contaminated groundwater, the data from three (Carswell AFB, Argonne National Laboratory, and Aberdeen Proving Grounds) of which phytoremediation appears to be successful and one case study (Kitsap Naval Base) where limited hydraulic control is occurring but no real indication of other phytoremediation mechanisms. Hydraulic control and degradation within poplar tissue are the leading containment and removal mechanisms in greenhouse and field studies. Hydraulic control was observed in all of the studies that monitored groundwater uptake by the poplars. Hydraulic control, rhizosphere biodegradation and microbial degradation, phytodegradation, and phytovolatilization are known to occur with poplars through the uptake of TCE contaminated groundwater, but the magnitude in which these processes remove TCE is still contested. Microbial degradation in young poplars is not significant, although it may be a significant degradation pathway in mature poplars, as evidenced by the Carswell AFB plantation. TCE and its metabolic products have been observed in tree tissue. Poplars are capable of releasing measurable quantities of TCE to the atmosphere via the transpiration process; however, the quantity of TCE that is volatilized is not significant enough to pose a health or environmental risk. Further, photodegradation and dilution help to quickly degrade and dilute the TCE.

This thesis also presented three case studies that involved pump-and-treat remediation that utilized air strippers. Air strippers are efficient at removing aqueous phase TCE from water, although the TCE is merely transferred to the atmosphere. No destruction or degradation of the TCE occurs as a result of the air stripping process unless emission controls (such as granular activated carbon) are added to the towers. The case studies exemplified the initial efficiency of TCE removal from water, but in all cases this efficiency diminished overtime.

As I have shown, there is not a one-size-fits-all remediation technique that can be used at every site that grapples with TCE contaminated groundwater. This is because there are so many variables that must be taken into account when it comes to finding an appropriate cleanup technique and there are trade-offs that must be weighed. The trade-offs include many of the issues addressed in this chapter such as aesthetics, public acceptance, and lack of long-term data. For example, if phytoremediation was chosen over air stripping the project may be more aesthetically pleasing, more cost effective, and ecologically sound; however you would not be able to rely on long-term historical data to exemplify the efficiency of this treatment method (though evidence is now suggesting that even pump-and-treat technologies can not reach clean-up goals). Instead, one would have to rely on short-term field, greenhouse, and laboratory data. Furthermore, there are no performance parameters that regulators can look to, to measure performance of the phytoremediation system. Time of cleanup is also a trade-off because of the inability to accurately predict the length of time required for cleanup and because the ability for trees to phytoremediate relies on the time required for tree growth. In contrast, if air stripping was chosen over phytoremediation operations and maintenance may be more predictable, there is a greater volume of historical use of this method, and it is known to remove TCE from groundwater; however, this method is costly, requires vast amounts of energy, can require decades of treatment, and evidence is showing diminishing efficiency returns overtime such that cleanup levels cannot be met.

The conditions at each site must be characterized and a remediation program be designed based on the results of the characterization. Given this, neither phytoremediation nor air stripping is a technique that is flexible enough to work everywhere. Notwithstanding, phytoremediation offers a low cost alternative to traditional remediation methods and is also associated with high levels of public acceptance and compatibility with ecological restoration [100]. As long as site conditions are acceptable, phytoremediation using poplars is a more desirable option for groundwater remediation, when these two factors are considered.

It is difficult to say that one method is overall better than the other. Poplars are better for treating TCE contaminated groundwater than air strippers if energy consumption, byproducts and waste, public perception, ecological restoration, and cost are concerns. But if the contamination is very high (ppm range) or contaminant mass reduction is desired in a short period of time, air strippers may be more effective because of their ability to rapidly strip TCE from water and they are not affected by high contamination concentrations. Air strippers may also be more effective at sites where there is not a large land base where trees could be planted or in.

6.1 Data Gaps and Further Research

Several data gaps were identified through researching this subject area. Most prominent was the lack of data on long-term use of poplars used for phytoremediation. This is partly due to the science of phytoremediation being fairly new but the other component is that there is a lack of funding to further research the effectiveness after three to five years of use. It is difficult to say if phytoremediation is a superior remediation alternative when there is a lack of long-term data. As Newman (2007) pointed out, after site owners and regulating agencies have seen that the trees are indeed helping to degrade and contain the contamination, there is a lack of interest (and money) to continue the thorough monitoring. Furthermore the limited data that is collected at these sites on a quarterly and yearly basis is not comprehensive enough to publish. Without this data, it can only be speculated that poplars continue to improve their effectiveness at treating TCE plumes until they reach maturity. But can it conclusively be said that poplars <u>do not</u> reach a point where their efficiency drops off or they reach an asymptote? Furthermore, there have not been any field scale phytoremediation sites that have been implemented long enough to show that poplars can remove enough TCE from groundwater to reach clean-up goals, so it is currently unknown if this is even possible.

Along the same lines, more research should be conducted on the microbial degradation in the rhizosphere of poplar plants because the existing data (what little there is) indicates that measurable degradation really only occurs once the poplars have matured, and this was only shown in one case study. It may be important to focus research efforts in the field because it has been shown that research conducted in the laboratory, although valuable, does not necessarily accurately reflect the process that occurs in the field.

Currently the number of field scale phytoremediation sites that have been thoroughly documented in publicly available articles and reports is limited to a few (the most prominent of which were addressed in Chapter 4). There are other sources that list many other sites where poplars have been planted for phytoremediation, but there is little follow-up documentation. I propose that since phytoremediation is a newer technique that has not gained 100% regulatory acceptance due to the lack of data that more field scale sites should be evaluated and documented. This is especially important as more data are indicating that there is a discrepancy between the results established in laboratories as compared to the results gathered in field studies. The conflict here arises because laboratory studies have identified different phytoremediation mechanisms as the major method for TCE removal and degradation (phytovolatilization), than what has been observed at full-scale field sites (phytodegradation and hydraulic control).

Similarly, there are very few scientific publications from the late 1990's to 2000's that document the efficiency of air stripping. The bulk of peer reviewed journal articles discussing air stripping were published in the 1980's when the use of air strippers was beginning. Most of the documentation on this subject has been by the EPA. The reason for this is unknown. Perhaps it is because air stripping towers are not systems that can easily be set up for experimentation due to the prohibitive cost and the tasks involved with the process.

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