# Feasibility Study of Phytoremediation of Ethylene Dibromide (EDB) on Fuel Spill

by

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B.Eng. (Chemical)
National University of Singapore, 1998



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Submitted to the Department of Civil and Environmental Engineering in Partial Fulfillment of the Requirements for the Degree of

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#### **Abstract**

The Massachusetts Military Reservation (MMR) on Cape Cod has been extensively used by many military organizations. Indiscriminate disposal of petroleum wastes and chlorinated solvents has contaminated the soil and groundwater. Ethylene Dibromide (EDB) has been detected in concentrations above the state Maximum Contaminant Level (MCL) limit of 0.02 ppb in one of the groundwater plumes, Fuel Spill 28 (FS-28).

A pump and treat system using granular activated carbon (GAC) has been installed at the site as a quick interim action to prevent EDB from further contaminating the groundwater wells. Subsequent discovery of EDB in the surface and shallow water around the cranberry bogs prompted the authorities to install a shallow well pumping system directly on the cranberry bog to prevent EDB from further upwelling into the surface and shallow waters. The EPA has determined that the use of EDB-contaminated water for agricultural purposes presents an unacceptable risk to human health and environment.

Currently, GAC adsorption is considered the best available treatment method for EDB. The objective of this study was to evaluate the feasibility of implementing phytoremediation at FS-28, specifically to address EDB. Phytoremediation is the engineered use of plants to contain or remove contaminants in groundwater. A 70 ft  $\times$  70 ft square plot of 121 hybrid poplar trees was designed to be located above the Lower Baptiste bog. This plot of poplars can transpire between 9 – 92 % of the groundwater flow, and uptake 2 – 60 mg/day of EDB from the shallow groundwater. The estimated maximum aquifer drawdown created by these trees is 12 cm. However, this phytoremediation system cannot replace the pump and treat due to the large area and depth extent of EDB plume, due to limited depth plant roots can penetrate. On the other hand, we can optimize the pumping system by implementing phytoremediation, through a reduction or possible shutdown in the shallow well pumping system. This will translate to cost savings through longer GAC cycle life and lower pumping rate.

Thesis Supervisor: Philip M. Gschwend

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## 1 Introduction

The Massachusetts Military Reservation (MMR), located on the upper western part of Cape Cod, has been extensively used by many military organizations dating back to 1930s when the base was first built. The heaviest military activity was from 1940 to 1946 by the U.S Army, and from 1955 to 1972 by the U.S Air Force (AFCEE, 1997b). The uses of petroleum fuel products and industrial solvents, as well as the generation of hazardous waste material were at a peak during these periods. It was a common practice to dispose of such wastes in landfills and dry wells, and to use them at firefighter training areas. Contaminants such as fuels and solvents were released to the unsaturated soils and they created groundwater plumes of dissolved organic contaminants when they reach the water table.

#### 1.1 Context

In 1992, ethylene dibromide (EDB) was discovered in groundwater in the vicinity of the leading edge of another groundwater plume, Chemical Spill No. 4 (CS-4). Subsequent investigations delineated the extent of EDB and the plume was officially designated Fuel Spill No. 28 (FS-28).

EDB has been determined to be a carcinogen by the U.S. Environmental Protection Agency (USEPA) and has been determined in drinking water wells above the maximum contaminant levels (MCLs), better known as the drinking water standards. The maximum detected concentration of EDB in FS-28 was 18 ppb (AFCEE, 1999a), with the Massachusetts MCL set at 0.02 ppb. A single well extraction system using granular activated carbon (GAC) was implemented as a time critical action. Also, alternative water supplies were provided to the local residents whose drinking wells were affected.

Subsequent discovery of EDB in the surface waters of Coonamessett River led to the perception from cranberry owners and consumers that the cranberries were unsafe to consume and thus unmarketable. The USEPA, Massachusetts Department of Environmental Protection (DEP) and Massachusetts Department of Public Health (DPH) have determined that the use of contaminated surface and groundwater for agricultural uses presents an unacceptable risk to

public health and the environment. All the downstream cranberry bogs were separated and isolated from the river using berms constructed on either side of river. Shallow well points were constructed to extract the surface water for treatment and recent results indicated absence of EDB in the surface water samples with this combined system of single well and shallow well pump treatment.

#### 1.2 Problem Identification

The conventional treatment for contaminated groundwater is pump and treat, which is especially efficient in removing organic contaminants such as chlorinated solvents or hydrocarbon compounds, typically associated with military or manufacturing uses. Treatment of EDB contaminated water is achieved using granulated activated carbon (GAC), which is considered the best available treatment (National Primary Drinking Water Regulation). Several alternatives to the use of granular activated carbon adsorption have been studied. These include advanced oxidation, air stripping, reverse osmosis, and the use of polymeric resins. Mitterhofer (1998) provided comparisons of these technologies against granular activated carbon. Bridgeforth (1998) did a detailed analysis of an air stripping unit for removal of EDB and benzene, and a comparison with ultraviolet oxidation technology.

Besides conventional pump and treat, other possible remedial technologies are biological treatment (bioslurping, natural attentuation, and phytoremediation), and *in situ* physical and chemical treatment (air sparging, permeable reactive barriers, thermal enhancement). There are several advantages and limitations of these technologies, in which the details are available from the Ground Water Remediation Technology Analysis Center (GWRTAC) web site (http://www.gwrtac.org/).

However, air stripping and pump and treat using GAC are the only two remedial technologies found to be effective in EDB removal. Based on a study conducted by Environmental Science and Engineering (Beaudet, 1983), air stripping is 99% effective in removing EDB from water and pump and treat using GAC is considered 100% effective in EDB removal. GAC adsorption was chosen for the treatment system because of the low concentrations of EDB in the influent and the low MCL level of  $0.02 \,\mu g/L$  set by State of Massachusetts.

Phytoremediation is an emerging cleanup technology that is both low-cost and low-tech. It has numerous reported successes in laboratories and pilot studies, with several trial systems being currently conducted at USEPA Superfund sites. Though phytoremediation is not a panacea, in appropriate situations, it has several advantages that outweigh the conventional and harsher remediation technologies. A recent report conducted by researchers from University of Washington revealed ongoing laboratory and field studies of EDB phytoremediation, with initial observations and results indicating some successes (Gordon *et al.*, 1997b).

### 1.3 Objectives

The objectives of this study were to:

- Develop an understanding of the various mechanisms and processes of phytoremediation.
- Study the feasibility of EDB phytoremediation in FS-28.
- Understand the impact of the proposed phytoremediation system on the current site.

In order to meet these objectives, an in-depth literature review of phytoremediation was conducted. The transport mechanisms of EDB through plants were also studied to better understand the phytoremediation mechanisms. A thorough understanding of the FS-28 groundwater plume was necessary to implement the phytoremediation system. Available information was summarized from previous Master theses (Bridgeforth, 1998; Mitterhofer, 1998), MMR reports (ABB-ES, 1995 and 1996; AFCEE, 1997a; 1997b; 1998; 1999a; 1999b and 1999c) and MMR web-site (http://www.mmr.org/).

## 1.4 Scope

The ensuing sections present the following information:

- Section 2, *Background Information*, provides background information about Cape Cod and MMR.
- Section 3, *Current Site Conditions at FS-28*, describes the extent of EDB contamination in FS-28, the previous remedial and investigation activities, suspected source areas, concerns of cranberry owners, geologic and hydrogeologic settings and the current remedial actions.
- Section 4, Feasibility Study of Phytoremediation of EDB on FS-28, presents an indepth literature review of phytoremediation, its advantages and limitations, and cost and performance comparison.
- Section 5, *Implementation Plan*, gives a detailed analysis of the proposed phytoremediation system on FS-28 and its estimated cost.
- Section 6, *Conclusions*, summarizes the results of this feasibility study.

## 2 MMR Background Information

The following subsections provide background information about the Massachusetts Military Reservation; its history, hydrology and hydrogeology. They also provide a brief description of the contamination present at the military and explain the need to remediate the aquifer.

## 2.1 Setting and Description

The Massachusetts Military Reservation, previously known as Otis Air Force Base, is located on the upper western part of Cape Cod, Massachusetts. It encompasses approximately 22,000 acres (30 square miles) within the towns of Bourne, Sandwich, Mashpee and Falmouth in Barnstable County. The MMR consists of facilities operated by the U.S. Coast Guard, the Army National Guard, the U.S. Air Force, Air National Guard (ANG), Veterans Administration, and the Commonwealth of Massachusetts.

MMR is comprised of four principal functional areas (AFCEE, 1997a):

- <u>Cantonment Area</u>: This southern portion of the reservation is the most actively
  used section of the MMR. It occupies 5,000 acres and is the location
  administration, operational, maintenance, housing, and support facilities for
  the base. The Otis Air Force Base facilities are located in the southern portion
  of the Cantonment Area.
- Range Maneuver and Impact Area: This northern part of the MMR consists of 14,000 acres and is used for training and maneuvers.
- <u>Massachusetts National Cemetery</u>: This area occupies the western edge of the MMR and contains the Veterans Administration Cemetery support facilities.
- <u>Cape Cod Air Force Station (AFS)</u>: The 87-acre section is at the northern portion of the Range and Maneuver and Impact Area and is known as the Precision Acquisition Vehicle – Phase Array Warning System.

A majority of the facilities at the MMR are located in the southern portion, while the northern portion consists of several firing ranges.

## 2.2 Climate and Hydrology

The climate in western Cape Cod is temperate, with annual temperatures ranging from 19 to 81 degrees Fahrenheit (°F). Proximity to the Atlantic Ocean results in mitigated temperature extremes. The coldest month is February, with daily temperature ranging from an average minimum of 23°F to a maximum of 38°F. July is the warmest month, with daily lows of 63°F to daily highs of 78°F (ANG, 1995). Wind speeds typically range from 9 to 12 miles per hour (mph), with storm velocities of 40 to 100 mph.

Cape Cod receives an average rainfall of 47.8 inches per year (ANG, 1995). The precipitation is distributed fairly evenly throughout the year, although a slightly higher portion of the precipitation occurs in winter months (Le Blanc *et al.*, 1986). The one-year/24-hour rainfall event in Cape Cod is 2.7 inches.

Due to the highly permeable sand and gravel deposits prevalent on Cape Cod, surface water runoff is less than 1% of the total precipitation. Approximately 55% of the total precipitation is returned to the atmosphere via evaporation or transpiration. The remaining 45% infiltrate to recharge the groundwater (Le Blanc *et al.*, 1986).

Although groundwater provides the main source of water for Cape Cod, approximately 4% of Cape Cod is covered by surface-water bodies. These surface-water bodies, mainly intermittent streams or kettle holes, receive a net charge of approximately 18 inches per year from direct precipitation (ANG, 1995).

## 2.3 Hydrogeology and Topography

The following topographic and hydrogeologic information on Cape Cod is summarized from E.C. Jordan (1989). The geology of western Cape Cod was shaped during the Wisconsin period, 85,000 to 7,000 years B.P. (Before Present), of the Pleistocene epoch, with the advance and retreat of two glacial lobes that resulted in glaciofluvial sedimentation. To the north and west, the Buzzards Bay and Sandwich Moraines are composed mostly of glacial till. South is the Mashpee Pitted Plain, an outwash plain

containing poorly sorted, fine to coarse grained outwash sands overlying finer-grained till and marine sediment.

This lower layer of fine sediment has a hydraulic conductivity that is as much as five times less than that of the upper outwash layer, so that ground water flow occurs mostly through the permeable upper layer. Seepage velocity within the sand and gravel outwash is estimated between 1.0 and 4.6 feet per day, with virtually no vertical flow. The entire plain is dotted with numerous kettle holes, bodies of water that resulted when large blocks of glacial ice embedded in the sediment melted. These ponds are maintained mostly by groundwater recharge and runoff.

The topography of the area can be classified as a broad, flat, glacial outwash plain, dotted by kettle holes and other depressions, with marshy lowlands to the south, and flanked along the north and west by recessional moraines and irregular hills. Remnant river valleys cross the Mashpee Pitted plain from north to south, while to the north and west Buzzards Bay and Sandwich Moraines lend a higher degree of topographic relief.

## 2.4 Site History

Since 1911, a wide variety of activities has been conducted on the MMR, including troop development and deployment, fire fighting, ordinance development, testing and training, aircraft and vehicle maintenance, and fuels transport, and storage. Operational units at the MMR included the U.S. Air Force, U.S. Navy, U.S. Army, U.S. Marine Corps, U.S. National Guards, U.S. Army National Guards, and U.S. Coast Guard. From 1955 to 1970, a substantial number of surveillance and air defense aircraft operated out of the ANG portion of the reservation. Since that time, the intensity of the operations has decreased substantially.

The heaviest military activity occurred from 1940 to 1946 by the U.S. Army, and from 1955 to 1972 by the U.S. Air Force. During these periods, large amount of petroleum and solvent wastes were disposed into landfills and dry wells, and used in fire fighting areas. As a result, contaminants were released to the unsaturated and saturated zone.

#### 2.5 Soil and Groundwater Contamination at MMR

Soil and groundwater investigations and remediation efforts were initiated with the discovery of detergents in a public water supply well in Falmouth in 1978. The United States Geological Survey (USGS) immediately began conducting groundwater investigations, and soon identified a groundwater plume extending south of the wastewater treatment plant and into the Ashumet Valley. Subsequently, the ANG established an Installation Restoration Program (IRP) at Otis ANG Base. In 1989, the MMR was named a Superfund site by the Environmental Protection Agency.

Since 1985, investigations at the MMR have revealed 78 contaminated soil and groundwater sites. As of September 1996, the ANG and regulators concluded that 31 of the 78 sites at the MMR pose no threat to the public and the environment and therefore require no further action. From the results of those investigations, seven major groundwater plumes have been identified:

- Fuel Spill-12 (FS-12)
- Fuel Spill-28 (FS-28)
- Chemical Spill-4 (CS-4)
- Chemical Spill-10 (CS-10)
- Landfill-1 (LF-1)
- Ashumet Valley
- Storm Drain-5 (SD-5)

## 2.6 Importance of Remediating the Contaminated Aquifer

Water resources at Cape Cod and MMR are used for the following purposes:

- Public water supply for drinking and recreational uses
- Agricultural use (cranberry, strawberry and vegetable)
- Industrial and commercial use
- Habitat for a wide variety of fish and wildlife

Contamination in any of those areas will pose a potential risk to human health. As groundwater is an important source of public water supply, for drinking water and recreational users, and for industrial and commercial users, the utmost priority is to ensure there is no contamination in any of the groundwater supply wells. The Sagamore Lens, the largest lens of the Cape Cod Aquifer, provides drinking water to over 70,000 homes and businesses in six towns. The Massachusetts Department of Environmental Management (1994) reported that during the off season in 1990, an average of 12.5 million gallons per day of water was supplied from the lens.

Groundwater and surface water in MMR are also used for agricultural purposes – for irrigation, frost control and harvesting in cranberry, strawberry and vegetable. Section 3.7 gives a detailed description of the groundwater and surface water uses in cranberry operations.

## 3 Current Site Conditions at Fuel Spill 28 (FS-28)

In December 1992, a groundwater sampling event was conducted to determine the downgradient extent of another groundwater contaminant plume, Chemical Spill 4 (CS-4) (Figure 3.1). EDB was detected in a monitoring well at concentrations above the federal drinking water Maximum Contaminant Level (MCL) of 0.05 µg/L. Subsequently, several investigations were conducted to delineate the extent of the plume and to pinpoint a source area. The plume was officially designated FS-28 in November 1996 (AFCEE, 1997a).

The FS-28 plume has been divided into the upper, middle, and lower study areas. The current remedial efforts have been concentrated on the lower study area, which contains the toe of the plume (Figure 3.2).

#### 3.1 Location of FS-28

The upgradient extent of the FS-28 plume, as currently mapped, is located in the Crane Wildlife Management Area, which is south of MMR in the town of Falmouth. As shown in Figure 3.2, the plume has a north-south orientation, bordered on the east by Coonamessett Pond, on the west by Deep Pond, and extends to a point south of Hatchville Road in Falmouth. The leading edge of the plume is located between Sandwich and Sam Turner Roads, north of Thomas B. Landers Road. The plume axis at the toe is coincident and parallel with the Coonamessett River, which flows south from the western arm of Coonamessett Pond to a tidal estuary, Great Pond, south of Route 28 in Falmouth (AFCEE, 1997a).

#### 3.2 FS-28 Plume Characteristics - Areal Extent

The FS-28 (EDB) plume extends from the Crane Wildlife Management Area north of Route 151, flows under the western portion of Coonamessett Pond, and terminates in the cranberry bogs surrounding the Coonamessett River. Figure 3.3 shows the lower blown-up part of FS-28 plume and the locations of the cranberry bogs surrounding the plume.

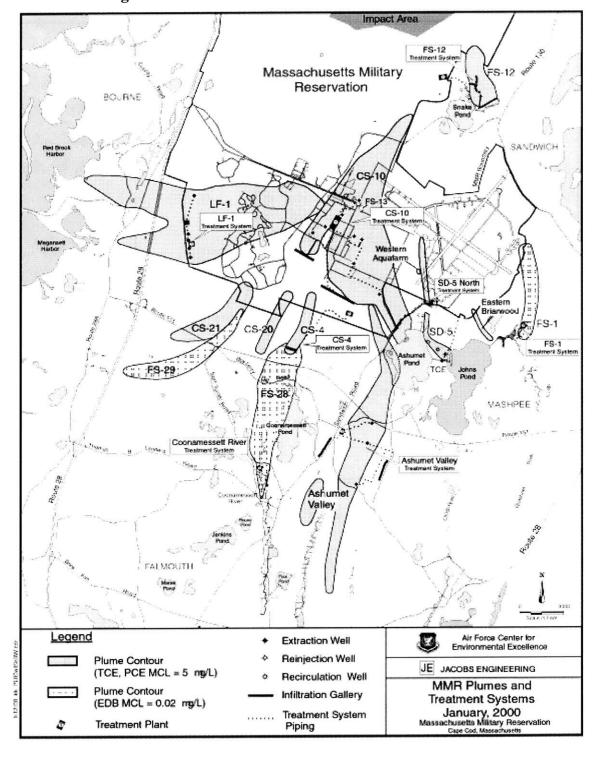


Figure 3.1 Location of Groundwater Plumes in MMR

(Source: MMR Installation Restoration Program - Plume Maps, available at http://www.mmr.org/cleanup/maps.htm)

Rouse 151 FS-28 Deep Plume Coonamessett Pond FS-28 Treatment Plant Thomas B. Landers Custow Bubbler Pipe Coonamessett River Air Force Center for Environmental Excellence Legend Plume Contour ( EDB MCL = 0.02 mg/L) JE JACOBS ENGINEERING Plume is under 1000 FS-28 Plume Coonamessett Pond by 100 feet January, 2000 Massachusetts Military Reservation Cape Cod, Massachusetts Bog Note: Plume underflows pond

Figure 3.2 Location of Fuel Spill (FS) 28 Groundwater Plume

(Source: MMR Installation Restoration Program - Plume Maps, available at http://www.mmr.org/cleanup/maps.htm)

The highest concentration of EDB in the FS-28 plume – 18 μg/L – was detected in a monitoring well near the extraction well (69EW0001) located south of Hatchville Road; concentrations decrease significantly to the north. AFCEE (1999a) reported that the maximum concentration detected just north of Hatchville Road was 14 μg/L, and the maximum concentration just south of the western arm of Coonamessett Pond was 4.9 μg/L. Between the western arm of Coonamessett Pond and Route 151, concentrations continue to decrease to the north. The highest concentration of EDB detected just north of the western arm of Coonamessett Pond was 3.1 μg/L, and the highest concentrations detected between Route 151 and Boxberry Hill Road was 0.025 μg/L. The plume contains approximately 11.7 kg of EDB within approximately 4.4 billion gallons of groundwater, based on 3-D contouring of analytical data (AFCEE, 1999a and 1999b).

North of Route 151, the FS-28 plume is laterally and vertically discontinuous at elevations ranging from –20 to –220 feet mean sea level (ft msl). The trailing edge of the FS-28 plume of the plume is difficult to define as the concentrations are generally close to the EDB detection limit of 0.004 µg/L. The northern most detection of the EDB plume is located approximately 1000 feet south of the MMR boundary. In the area between Coonamessett Pond and Route 151, EDB has been detected generally between the elevations of –30 and –190 ft msl. On the immediate south of the western arm of Coonamessett Pond, the FS-28 plume lies from –85 to –220 ft msl, and stays relatively deep until it passes under Hatchville Road. There is no conclusive evidence that EDB comes into contact with the bottom of Coonamessett Pond as none of the 45 water samples or 10 sediments samples collected from Coonamessett Pond in 1998 contained detectable concentrations of EDB (AFCEE, 1999a).

Groundwater containing EDB flows at a rate ranging from 0.02 to 0.2 feet/day in silty sands, and from 0.2 to 2 feet/day in outwash sands (AFCEE, 1997b). Numerical simulation models have predicted that the discharge location of the plume is the Coonamessett River (AFCEE, 1998). These models indicated that, in general, most of the EDB migrates to the surface waters of Coonamessett River north of Sandwich Road. The remaining portion of the plume continues to migrate in the subsurface, very close to the

river, eventually surfacing at points along the length of the river north of Great Pond (AFCEE, 1998).

Extensive surface water and groundwater sampling has been conducted in the Coonamessett River and associated cranberry bogs since October 1996. Previous studies have indicated that the EDB plume upwells in the upper part of the Lower Baptiste cranberry bogs and Broad River. Currently, this EDB-contaminated water has been found to emerge to the surface in and south of Broad River, and north of the Adams and Augusta Bogs. Once the contamination reaches the surface, it flows downstream in the river system and the concentrations generally decrease with downstream distance (AFCEE, 1999b).

#### 3.3 Source Areas

The FS-28 source investigation was primarily a search of the MMR Administrative Records for information about sites and activities that may have contributed in full or in part to the FS-28 EDB groundwater plume during the period from 1930s to the 1970s. Investigations were conducted by Jacobs Engineering to study previous releases, including the dates, volumes, location and chemical constituents (AFCEE, 1997a). The study areas were broken up into: non-EDB sources, limited/partial EDB sources, partial EDB sources, significant EDB, and full EDB sources. The various source categories were based on several criteria, including site history, historical usage of motor fuels, aviation gasoline, and pesticides, aquifer characteristics, and geomorphology.

Because EDB was a common additive in the fuels used at MMR base, the investigations focused on areas where motor fuel and aviation gases were stored, dispensed and possibly disposed. The investigations concluded that the FS-28 (EDB) plume is a detached plume; it was not produced by a single source but rather by a combination of sources over a period of 30 to 40 years (AFCEE, 1997a).

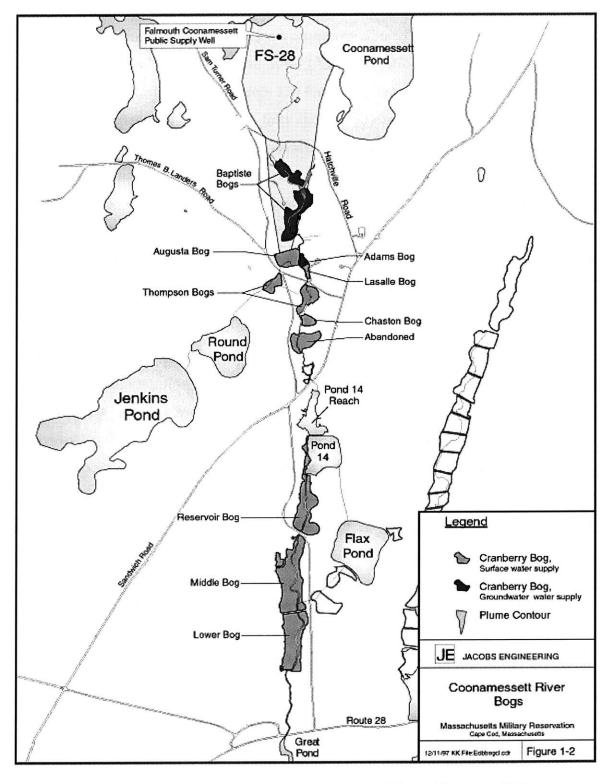


Figure 3.3 Location of FS-28 Plume and Cranberry Bogs

(Source: MMR Installation Restoration Program - Plume Maps, available at http://www.mmr.org/cleanup/maps.htm)

## 3.4 Geologic Setting

Data from previous investigations indicate the middle and lower study areas of FS-28 are underlain with glacial outwash sediments composed of tan, fine to coarse sand with lesser amounts of silt and gravel (less than 10%) (ABB-ES, 1995 and 1996). These sands are relatively well sorted to approximately 120 feet below mean sea level (msl), and become more poorly sorted below this depth. Silty and gravelly zones lie within the sand, ranging from one to ten feet in thickness. Underlying the outwash is a thin glacial till unit, containing an increased number of gravelly sand and silty sand lenses (to about 170 feet msl) (ABB-ES, 1996). Below 170 feet msl, fine and coarse sands can be found with little gravel, little silt, and trace cobbles. An occasional sand lens and silty sand lens is present over the bedrock surface. The top of the granite bedrock has been encountered at several locations at elevations of 220 to 243 feet below msl (AFCEE, 1997a).

## 3.5 Hydrogeologic Setting

A single groundwater flow system underlies western Cape Cod, from the Cape Cod Canal to Barnstable and Hyannis. This sole source aquifer, referred to as the Sagamore Lens, provides Upper Cap Cod's only potable source of water. This aquifer is unconfined (i.e., in equilibrium with atmospheric pressure) and is recharged by infiltration of precipitation. Recharge is approximately 1.6 feet/year, with seasonal variations producing fluctuations in water table of 1 to 3 feet. Groundwater flow is radial from the recharge mound (AFCEE, 1997a).

AFCEE (1997a) had determined the hydraulic conductivity using slug tests and also estimation from grain size analyses. For the slug test analyses, individual hydraulic conductivity ranged from 0.074 to 180 ft/day. Some of the wells could not be tested due to rapid oscillations in water level recovery, and these oscillation-type responses tend to occur in zones of high hydraulic conductivity. For grain size analyses, the estimated hydraulic conductivity ranged from 1.0 to 490 ft/day, with the highest value obtained from sample that was 170 – 175 below ground surface (AFCEE, 1997a).

Using an average horizontal hydraulic gradient of 0.002 ft/ft and a porosity of 0.24, the average linear velocity determined was 0.25 to 2.5 ft/day for outwash sands with hydraulic conductivity, K between 30 and 300 ft/day. For siltier sand, with K values between 3 and 30 ft/day, the average linear velocity ranges from 0.025 and 0.25 ft/day.

Based on a pumping test conducted at the Coonamessett Public Water Supply Well (CWSW), the full thickness of the outwash aquifer at the site has a transmissivity of approximately 86,000 to 100,000 ft/day (AFCEE, 1997a). Also, from the pumping test, the aquifer response to hydraulic stress indicates that the outwash aquifer is essentially unconfined, with a specific yield of 0.2. The vertical to horizontal anisotropy ratio in the area of the CWSW well screen is low, suggesting that silty layers do not have significantly lower vertical hydraulic conductivity than the silt free layers.

## 3.6 Surface Water Hydrology

Measurements by AFCEE and the U.S. Geological Survey (USGS) indicate that the Coonamessett River does not gain much water (and occasionally loses water) along the reach from its origination at Coonamessett Pond to where it crosses Hatchville Road and enters the cranberry bogs (AFCEE, 1999c). Once the river enters the bog, the river gains a significant amount of water from groundwater discharge. This recharge of water is coincident with a strong upward gradient near the river. South of Thomas B. Landers Road, the river continues to gain approximately 1 cubic foot per second (cfs) with every 1000 feet of river reach, with over 15 cfs of flow where the river becomes inter-tidal (AFCEE, 1999c).

Throughout the river system, the river flow is controlled by weirs and culverts managed by the cranberry owners and town officials who manage fish migration. South of Sandwich Road, the river flows through an abandoned cranberry bog which has developed over several decades into a reservoir called Pond 14 (Figure 3.3). On the downstream side of Pond 14, a dam is used to control water flow to the downstream river and bogs.

#### 3.7 Groundwater and Surface Water Uses

Groundwater and surface water resources in this area provide the drinking water for the surrounding communities and also provide a habitat for a variety of fish and wildlife in the area. AFCEE (1998) provided a description of the ecological setting of Coonamessett River and Pond, detailing the habitat types, land use, and vegetation, bird, fish, insect, mammals, and other animal species thriving in the community.

Additionally, approximately 60 acres of cranberry bogs south of Hatchville Road are operated on the Coonamessett River (AFCEE, 1998). Table 3.1 shows a list of bogs on the River system that may be potentially affected by EDB contaminated groundwater or surface water. Below is a summary of the cranberry operations (AFCEE, 1998 and 1999c).

Cranberry bogs are typically flooded in late November to early December to prevent freezing damage to the cranberry vines and again in the fall for harvesting. During the flooding, the Coonamessett River is dammed up, raising the water level from 0.5 to 3 feet over the area of the cultivated bogs. Upward vertical gradients are reduced under flooded conditions, which keeps the groundwater from moving into the bogs. In the spring, the irrigation of cranberry bogs begins near the middle of April when the night temperatures are anticipated to be below 32°F. For frost control, water is sprayed on the vines at the first sign of frost and this practice continues as needed until mid-June. From mid-June to October, the fields are irrigated as needed from 5 a.m. to 7 a.m. to provide at least 2 inches of water on the crop per week. Typically, spray irrigation is conducted three times during the week. During the fall, the bogs are harvested either dry or wet.

With the exception of the Augusta Bog, which is supplied by its own reservoir, and the Upper Baptiste Bog, which is supplied by clean water from the treatment plant, irrigation wells are used to supply water for spray irrigation (Figure 3.3). AFCEE has installed 10 irrigation wells in the bogs surrounding the Coonamessett River to replace the surface water sumps which were previously used in 1997 and 1998.

Table 3.1 Potentially Affected Bogs on the Coonamessett River

Index	Parcel Description	Owner	Est. Acreage (acres)	Bog Active as of Oct., 1996 <sup>1</sup>	Potentially Affected by EDB	Isolated from River	Method of Harvesting
E1	Upper Baptiste	Town of Falmouth	0.5	Yes	No	No	Dry
E2	Upper Baptiste	Town of Falmouth	1.5	Yes	No	No	Dry
E3	Upper Baptiste	Town of Falmouth	1.5	Yes	Yes	No	Dry
E4	Lower Baptiste	Town of Falmouth	6.6	Yes	Yes	No	Dry
F	Adams	Adams	1.05	Yes	Yes	No	Dry
G1	Augusta	Augusta	4.8	Yes	Yes	Yes	Wet
G2	Augusta	Augusta	1.8	Yes	Yes	Yes	Wet
Н	Lassalle	Lassalle	1.5	Yes <sup>2</sup>	Yes	Yes	Wet
I1	Thompson (West)	Town of Falmouth	1.91	Yes	Yes	Yes	Dry
I2	Thompson (East)	Town of Falmouth	3.13	Yes	Yes	Yes	Dry
J	Chaston	Chaston	1.5	Yes	Yes	Yes	Wet
Α	Reservoir	Town of Falmouth	7.84	Yes	Yes	Yes	Wet
Bl	Middle	Town of Falmouth	13	Yes	Yes	Yes	Wet
B2	Middle	Town of Falmouth	0.6	Yes	Yes	Yes	Wet
С	Lower	Town of Falmouth	10.6	Yes	Yes	Yes	Wet
D1	Flax	Town of Falmouth	2.4	Yes	Yes	Yes	Wet
D2	Flax	Handy	3	Yes	Yes	Yes	Wet
	Total Acr	60.98					

(Source: AFCEE, 1998)

Other agricultural crops that could be affected by the surface water contamination are strawberries and vegetables. Before installing irrigation wells, the farmer of these crops drew surface water from pond 14 (Figure 3.3) for frost protection and irrigation. In 1996, the farmer utilized approximately one million gallons of water during the six-month growing season. Frost control is typically conducted in mid-May for strawberries when the air temperature drops below 44°F. Routine irrigation continues, as needed, during the growing season to supplement rainfall (AFCEE, 1999c).

<sup>&</sup>lt;sup>1</sup>Date EDB discovered in groundwater adjacent to the Coonamessett River.

<sup>&</sup>lt;sup>2</sup> Active bog in terms of operation permitted, but not productive in terms of harvesting.

## 3.8 Environmental Agency and Cranberry Grower Concerns

EDB is the primary contaminant of concern in the FS-28 plume; it is also the most prevalent organic compound detected in all the samples in FS-28 plume. The maximum concentration of EDB detected was at 18 μg/L in samples of deep groundwater just south of Hatchville Road. Other volatile organic compounds detected in samples collected from monitoring wells are trichloroethylene (TCE), tetrachloroethylene (PCE), toluene, chloroform, carbon tetrachloride, and methylene chloride. For shallow water samples, only toluene and 1,2-dichloroethene were detected. However, the volatile organic contaminants concentrations in all those samples are below MCL limits (AFCEE, 1997a).

The EDB concentrations in shallow groundwater and surface water are not as high as those in the deep groundwater. In addition, the concentrations in the shallow groundwater are higher than the concentrations in the surface water where EDB is discharging to the surface. The concentrations of EDB in the Coonamessett River decrease downstream. The highest concentration of EDB detected in the surface water and shallow groundwater are  $0.36 \mu g/L$  and  $3.9 \mu g/L$ , respectively (AFCEE, 1998).

The EPA has classified EDB as a probable human carcinogen of medium carcinogenic hazard (Group B2), with an inhalation unit risk estimate of  $2.2 \times 10^{-4}$  (µg/m³)<sup>-1</sup> and a drinking water unit risk estimate of  $2.5 \times 10^{-3}$  (µg/L)<sup>-1</sup>(USEPA IRIS). The EPA has also calculated a provisional Reference Concentration (RfC) of 0.0002 mg/m³ for EDB (USEPA Office of Air Quality Planning and Standards). This RfC value provides a reference point to gauge the potential effects. However, exceedance of this value does not necessarily imply adverse health effects; but as the amount and frequency of exposures exceeding RfC increase, the probability of adverse health effects also increases.

The EPA, Massachusetts Department of Environmental Protection (DEP) and Massachusetts Department of Public Health (DPH) have determined that exposure to EDB-contaminated surface and ground waters for agricultural purposes presents an unacceptable risk to public health and the environment. Also, cranberry owners are

concerned about the public's perception that their crops are contaminated and therefore, unmarketable, even if their irrigation and harvesting waters are below the state drinking water standard for EDB of  $0.02 \,\mu\text{g/L}$ .

## 3.9 Previous and Ongoing Actions Taken

Since the discovery of EDB in FS-28 plume in 1993, several monitoring and remedial activities have been conducted to mitigate the risk of exposure of EDB in the overall protection of human health and environment. The following sections summarize the previous activities so as to provide an understanding of the rational behind the current treatment system.

#### 3.9.1 Summary of Previous Actions

Past monitoring and remedial actions included the following (ABB-ES, 1995 and 1996; AFCEE, 1997a; 1997b; 1998; 1999a; 1999b and 1999c):

- Installed thirty monitoring wells in the vicinity of the river coupled with sampling and analysis to better define the distribution of EDB.
- Installed a wellhead carbon filtration system for the Coonamessett Water Supply Well (CWSW) to protect Falmouth's water supply from EDB contamination.
- Conducted a private well sampling and analysis program for residents in the area of the EDB plume.
- Supplied bottled water and providing information on EDB contamination to residents in the Hatchville community.
- Provided alternative supply of water to private residents and one business in the Falmouth community.
- Collected air samples for EDB analysis in the vicinity of Broad River where the highest surface water concentrations have been found.
- Installed an eight-inch diameter extraction well (69EW0001) within the area of highest EDB concentration as a time critical removal action. Over 680 million gallons

- of water have been treated and discharged into Coonamessett River since the extraction treatment system has been operating in October 1997.
- Tested 250 surface water samples from the Coonamessett River, Round Pond and Deep Pond. No EDB was found in the two ponds
- Conducted two water level surveys in 1996.
- Completed shellfish residue study in 1997 where shellfish was collected from Green pond. No EDB was detected.
- Implemented non-time-critical removal actions consisting of physical separation of contaminated river from cranberry bogs, supplying clean water to all agricultural users of the Coonnamessett River, and addition of shallow well to the existing treatment system.
- Installed 10 irrigation wells in the bogs surrounding the Coonamessett River to replace the surface water sumps which were previously used.
- Completion of a Remedial Investigation and Feasibility Study for the Southwest Operable Unit in 1999 where preferred remedial alternatives were identified.
- Completion of a study of the impact of EDB contaminated water on cranberries by the Kansas State University. Report concluded that EDB was weakly sorbed to the outer wax layer of the fruit. Washing EDB tainted fruits with deionized water reduced the levels of EDB by 64 - 75%.

#### 3.9.2 Current Treatment System

The current remedial activities (Figure 3.4) are the continual operation of the system treating water from 69EW0001 and the shallow well points, and continued maintenance of the CWSW wellhead protection system. In addition, the use of earthen berms and vinyl sheet piles to physically separate the contaminated river from the cranberry bogs, and supplying uncontaminated water to the northern bogs on the Coonamessett River will be maintained (AFCEE, 1999a; 1999b).

The objectives of the treatment system are to:

 Prevent or reduce potential residential exposure to groundwater contaminated with EDB above 0.02 ppb.

- Prevent EDB contamination of surface water of Coonamessett River so as to ensure the water is safe for agricultural use.
- Prevent worker contact and child and adult wader contact with the Coonamessett
   River water containing unacceptable concentrations of EDB.
- Prevent or reduce ingestion of fish exposed to Coonamessett River water containing unacceptable concentrations of EDB.

The extraction well (69EW0001) has been in operation since October 1997 where the extracted groundwater has been treated in a granular activated carbon (GAC) system and discharged into the Coonamessett River. This eight-inch extraction well is screened from 160 to 220 feet below ground surface, and intercepts the part of the FS-28 plume containing the highest concentrations of EDB. This extraction well pumped in the range of 600 to 740 gpm in the first one and a half years. Figure 3.4 shows the location of the extraction well and shallow well points.

Shallow groundwater is extracted using a well point installed in the lower Baptiste bogs. This well point system consists of a group of closely spaced wells connected to a header pipe or manifold and pumped by suction lift. A central pump lifts water from each well by producing a partial vacuum in the header and the riser pipes. This shallow well system was designed to intercept the shallow water while not de-watering or impacting groundwater upwelling in the adjacent bog channel.

A typical well point consists of a 2-inch steel pipe installed to a depth of 13 ft below ground surface with a 2.3-foot or 3.0-foot screen connected to a PVC header system. There are a total of 204 well-points, which the size and shape of the capture zone can be modified. Currently, the treatment rate is 750 gpm, with 400 gpm from the single extraction well and 350 gpm from the shallow well points. From the well-point vacuum extraction pump, the water is discharged into an 800-gallon steel tank where it is pumped to the treatment plant building.

Granulated activated carbon (GAC) is used as the primary treatment technology. This system includes two 20,000-pound carbon vessel operated in series. Both the effluent from the single extraction well and shallow well are combined such that the pressures exiting the treatment vessel are equal. The treatment plant has removed an estimated 4.6 pounds of EDB (AFCEE, 1999b).

The treated water is discharged onto the eastern side of the Upper Baptiste bogs. The effluent discharge pipe is designed in a way such that the treated water flows into a vertical riser called a bubbler, constructed of an 18-inch diameter corrugated metal pipe. This is to increase the levels of dissolved oxygen in the treated water. The discharge system is flexible as it was designed to allow treated water to be discharged at six alternate locations. Remote discharge is available in the Adams bog, Augusta bog, Augusta bog, Chaston bog, and the East Thompson bog.

Results so far (AFCEE, 1999c) indicate that the current system is performing satisfactorily and effectively capturing the EDB-contaminated groundwater. There was no EDB detected in the surface water of the Coonamessett River and surrounding cranberry bogs. In addition, this combined pumping system (single well and shallow well) did not create any adverse drawdown effects in the surface water and groundwater surrounding the site.

Coonamessett Pond Treatment System -69EW0001 Discharge Location Broad River Little Shallow Well-Point Extraction System Pump House Coonamessett River Legend JE JACOBS ENGINEERING Well-Points Not Pumping Bogs FS-28 Well-Points Pumping \*\*\*\* Extraction, Treatment, and Pipeline Discharge System Berm 300 Massachusetts Military Reservation Cape Cod, Messachusetts FS-28 Plume Scale in Feet 10/13/99 mm Fle...FS28IASM-2.dwg Figure 2-2

Figure 3.4 Location of FS-28 Treatment System

Source: AFCEE, 1999c

## 4 Feasibility Study of EDB Phytoremediation on FS-28

In considering the feasibility of EDB phytoremediation, we need to have an understanding of the mechanisms behind it. This section aims to describe the various processes of phytoremediation. The advantages and disadvantages, along with a performance and cost comparison of phytoremediation will be presented.

## 4.1 Literature Review - Introduction to Phytoremediation

Phytoremediation (the prefix *phyto*- means *plant*) is the engineered use of plants for *in situ* remediation of contaminants in soil, sediments, sludges and groundwater (Miller, 1996; Schnoor, 1997; USEPA, 1998). Phytoremediation can be used for both organic and inorganic (including heavy metal) contaminant cleanup. This technology uses plants' natural abilities to degrade or break down, or contain and stabilize, the contaminants by acting as filters or traps.

## 4.2 Phytoremediation Processes

There are six phytoremediation processes that are currently being field tested for contaminant cleanup (USEPA, 1998; Schnoor, 1995 and 1997). Figure 4.1 illustrates the processes that are relevant to EDB phytoremediation.

Plant transpiration

Plant transpiration

Plant uptake

Biodegradation in the rhizosphere

Root absorption

Contaminants

Figure 4.1 Phytoremediation Processes

## 4.2.1 Phytotransformation

Phytotransformation is the uptake of organic and inorganic nutrient contaminants from soil and groundwater and the subsequent transformation by plants. Contaminants are degraded through metabolic processes within the plant, or external to the plant through the effects of compounds (such as enzymes) produced by the plants.

The direct uptake of chemical into the plant through roots depends on uptake efficiency, transpiration rate, and the concentration of chemical in soil water (Burken and Schnoor, 1996). Uptake efficiency, in turn, depends on physical-chemical properties, chemical speciation, and the plant itself. Transpiration is one of the key variables that determines the rate of chemical uptake and it depends on plant type, leaf area, nutrients, soil moisture, temperature, wind conditions and relative humidity.

Briggs *et al.* (1982) first reported a predictive relationship for the uptake of a compound as a function of the compound's physical-chemical properties using barley plants. Briggs *et al.* (1982) related the log  $K_{ow}$  (octanol-water partition coefficient) of the organic compounds to the transpiration stream concentration factor, TSCF (Shone and Wood, 1972). The TSCF is a measure of the concentration in the transpiration stream (xylem sap) divided by the bulk solution concentration in contact with the root tissues. TSCF values were determined for various organic compounds and a maximum value of 0.8 was determined at a log  $K_{ow}$  value of 1.8.

The determining process for compound translocation is the interaction between the compound and root surface. This is because the chemical must pass through the symplast of the endodermis (innermost layer of the cortex that forms a sheath around the vascular tissue of roots) to be translocated from the roots (Trapp *et al.*, 1994).

The empirical relationship for TSCF and log  $K_{ow}$  will vary for different plant species and for each contaminant. Burken and Schnoor (1998) determined a maximum TSCF at log  $K_{ow}$  value of 2.5 for hybrid poplars. Translocation from roots to shoots is optimal for chemicals with log  $K_{ow} = 1$  to 2, in which translocation may increase with transpiration (McFarlane *et al.*, 1987).

Soils may pose a potential problem for plants because of competing processes of sorption to soil organic matter. Therefore, the log  $K_{ow}$  for maximum TSCF may be shifted down to favor more polar molecules (Cunningham *et al.*, 1996). The removal of soil water by transpiration may also induce the movement, by unsaturated flow, of organic compounds dissolved in the soil water (water moves by unsaturated flow from wetter to drier areas in soil). This mass transport process may draw contaminants to the plants from areas outside the root zone, making them available for uptake.

After the organic chemical is translocated, the plant may store the chemical and its fragments into plant structures via lignification (covalent bonding of chemical into lignin of the plant); or it can volatilize, metabolize, or mineralize the chemical completely into carbon dioxide and water. Nellesen and Fletcher (1993) pointed out that the ratio of uptake/accumulation, translocation, adhesion, and biotransformation of xenobiotic are environmentally important because these influence the amount and nature of the food chain contamination.

Several laboratory and pilot studies have been conducted to determine the end metabolites of various contaminants. Trichloroethylene (TCE) is metabolized by poplar trees to trichloroethanol, trichloroacetic, and dichloroacetic acids (Gordon *et al.*, 1997; Newman *et al.*, 1997 and 1999). 2,4,6-trinitrotoluene (TNT) was found to be transformed by poplar trees to 4-amino-2,6-dinitrotoluene (4-ADNT), 2-amino-4,6-dinitrotoluene (2-ADNT) and other unidentified polar compounds (Thompson *et al.*, 1999).

Another form of phytotransformation is *phytovolatilization*, whereby the *contaminant or its metabolites* are released to the atmosphere. This process occurs as water and organic nutrients are taken up by the growing plants. TCE was reported to transpire through the leaves of cypress trees (Nietch and Morris, 1999) and poplar trees (Newman *et al.*, 1997). Studies done using salt marsh cordgrass (Ansede *et al.*, 1999) and broccoli, Indian mustard, sugar beet and rice (Zayed *et al.*, 1998) indicated that selenium was metabolized to a relatively harmless gas demethylselenide (DMeS) that was subsequently volatized to the atmosphere.

### 4.2.2 Rhizosphere Biodegradation

Rhizosphere bioremediation is the use of vegetation to enhance microbial degradation of organic contaminants in the root zone or rhizosphere (Anderson *et al.*, 1993; Shimp *et al.*, 1993). This technology is also known as *phytostimulation* or *plant-assisted bioremediation or rhizodegradation*. Anderson (1997) has identified five possible mechanisms for enhanced degradation of organic contaminants in the root zone.

#### 4.2.2.1 Increased Microbial Biomass

In the rhizosphere soil, there are more microorganisms compared to non-vegetated soil which results in higher availability of substrate. This translates to an increase in the degradation rate for the contaminant. Recent studies illustrated that increased microbial biomass through plants enhanced the degradation of ethylene glycol (Rice *et al.*, 1997) and perchlorate (Nzengung *et al.*, 1999).

#### 4.2.2.2 Increased or Synergistic Microbial Activity

The plant root zone is able to foster interactions of microbial communities at the molecular, physiological, and ecological levels to achieve chemical biotransformations (Lappin *et al.*, 1985). This increased or synergistic microbial activity may provide the spectrum of degradative enzymes, each of which may be required for mineralization but may not be present in a single microbial strain.

## **4.2.2.3** *Increased Microbial Diversity*

Vegetation provides a suitable habitat for a diverse population of microorganisms. This may enhance microbial degradation because of a key group or family of organisms (Liu *et al.*, 1991) that acts together. Generally, the rhizosphere is colonized by a predominantly Gramnegative bacterial community that has some important metabolic capabilities for degrading xenobiotic chemicals. Glutathione-S-transferase (an enzyme responsible for the conjugation of xenobiotics in mammals, plants and microorganisms) is active in 36 species of Gramnegative rhizosphere bacteria (Zablotowicz *et al.*, 1995).

#### 4.2.2.4 Root Exudates as Structural Analogs

Root exudates contain organic acids (e.g., citric and acetic acids) that may react with EDB in soil or groundwater. Most importantly, root exudates include enzymes such as nitroreductase and dehalogenase that may degrade organic compounds containing nitro groups (e.g. TNT, other explosives) or halogenated compounds (e.g. chlorinated hydrocarbons, pesticides).

Certain plant species can produce large amounts of exudates that enhance the growth of microbial degradation, and at the same time, have the ability to degrade the contaminant. Donnelly *et al.* (1994) reported that certain phenolic compounds in root exudates could support growth of polychlorinated biphenyl (PCB) degrading bacteria, and the organisms retained their ability to metabolize PCBs. A study conducted by Fletcher and Hegde (1995) on 17 different plant species revealed that red mulberry (*Morus rubra*) was capable of producing large amounts of root phenolics such as flavonoids and coumarin.

#### 4.2.2.5 Cometabolism

The presence of various root exudates makes the rhizosphere suitable for cometabolism of chemical contaminants. EDB may be degraded by rhizosphere organisms with root exudates as the primary substrate source.

# 4.2.3 Phytoextraction

Phytoextraction refers to the uptake and translocation of *metal* contaminants in the soil by plant roots into the aboveground portions of the plants such as shoots and leaves. In EDB phytoremediation, this is not relevant as we are dealing with organic contaminant.

# 4.2.4 Phytostabilization

Phytostabilization is the use of plants to immobilize contaminants in soil and groundwater through absorption and accumulation by roots, adsorption onto roots, or precipitation into the root zone of plants (rhizosphere). This process not only reduces the mobility of the contaminant to the groundwater or air, it also reduces the bioavaliability for entry into the food chain.

#### 4.2.5 Rhizofiltration

Rhizofiltration is the adsorption or precipitation onto plant roots or absorption into the roots of contaminants that are in solution surrounding the root zone. This process is similar to phytostabilization, but the plants are used primarily to address contaminated groundwater rather than soil.

# 4.2.6 Hydraulic Control - Riparian Corridors, Buffer Strips and Vegetative Covers

Plants whose roots can reach deep into the water table and establish a dense root mass can take up large quantities of water. These plants act as hydraulic pumps to contain or control the migration of subsurface water by decreasing the tendency of surface contaminants to move towards the groundwater.

Riparian corridors, buffer strips and vegetative covers incorporate aspects of phytotransformation, phytovolatilization, and rhizosphere bioremediation to control, intercept, or remediate contamination entering a river or groundwater plume. Riparian (*riparian means located on the bank of a river*) corridor refers to the use of plants along a stream or river-bank, while buffer strips are applied around the perimeter of landfills. These systems are applied to prevent contamination from spreading into surface water and/or groundwater. Vegetative cover uses plants in waste landfills to control erosion and minimize seepage of water that could percolate through a landfill forming contaminated leachate.

# 4.3 Advantages & Disadvantages of Phytoremediation

Phytoremediation technology has shown tremendous promise as a low cost cleanup technology for a wide variety of pollutants and sites. However, there are several limitations and disadvantages that make regulators and engineers favor other remediation technologies.

Table 4.1 summarizes some of the advantages and disadvantages of phytoremediation along with comments (Schnoor *et al.*, 1995; Miller, 1996; Schnoor, 1997, Chappell, 1998; Harrigan, 1999).

 Table 4.1a
 Advantages of Phytoremediation

Advantages of Phytoremediation	Comments
in situ	Contaminated groundwater or soil do not have to be pumped or excavated to above ground for treatment
Passive	Once trees are planted, contaminants in soil or groundwater will be contained, reduced or degraded with little or no external remediation activities performed except monitoring of plume and trees.
Solar Driven	Uptake of water, along with contaminants, is due to photosynthesis; no pumping required.
10 - 20 % lower costs than mechanical treatments	Conventional methods such as pump and treat, soil removal and washing are much more expensive.
Faster cleanup rate compared to natural attenuation	Engineered use of appropriate species of plants, with deliberate planting density and pattern to remediate a contaminated site compared to natural attentuation where no actions are taken.
Generate less secondary wastes	Compared to other conventional methods, no contaminated fluids will be produced and retreated.
High public acceptance	Aesthetic appearance, with enhancement to surrounding natural habitat.
Soils remain in place and are usable following treatment	Once contaminants are cleaned up, site is restored to "original" conditions for commercial or public uses.

 Table 4.1b
 Disadvantages of Phytoremediation

Disadvantages of Phytoremediation	Comments
Limited to shallow soils, groundwater and wetlands only	Plant roots can penetrate up to about 10-15 feet below ground surface. However, a new planting technology called TreeMediation (Nyer and Gatliff, 1996; Harrigan, 1999) allows tree roots to extend up to 40 feet.
High concentrations of contaminants can be toxic to plants	The toxic threshold levels of contaminants and their plant metabolites must be determined before phytoremediation can be applied.  Phytoremediation cannot be applied to sites with high levels of contaminants if no appropriate plant species are available.
Toxicity and bioavailability of plant	Treatability studies have to be performed for
metabolites are not known	specific plant species and contaminants.

Slower than conventional mechanical treatments	Remediation performance is dependent on plant's growth and activity.
For organic contaminants, only effective for moderately hydrophobic types	Extremely hydrophobic (log $K_{ow} > 3$ ) contaminants become bound to the root interface or organic portion of soil while low hydrophobicity (log $K_{ow} < 0.8$ ) will pass by root system without any uptake.
Potential for contaminants to enter food chain through animal consumption	Toxic contaminants and its metabolites that are translocated to the stems, leaves or fruit, can be passed up the food chain through animals.
Site specific	Phytoremediation is extremely site specific and performance varies for different plant species at different locations for different contaminants.
Unfamiliar to regulators	Relatively new technology with little performance data due to long remediation time.

# 4.4 Performances and Costs Comparisons of Phytoremediation

Currently, there are numerous reported successes of laboratory studies for various plant species and contaminants in phytoremediation. However, there is lack of conclusive field performance data. This is chiefly due to the time involved in phytoremediation, and partly to its unknown performance standards that make regulators favor other conventional methods. Even though there are several pilot scale projects reported in place (Schnoor *et al.*, 1995; Chappell, 1997; Schnoor, 1997; USEPA, 1998; http://www.phytokinetics.com), these projects are in preliminary or mid stages, with only a few successfully completed. In addition, the performances of these phytoremediation systems are site specific and may not be applicable to other contaminated sites.

In addition to performance data, accurate cost data are difficult to predict for new technologies compared to other conventional, established technologies. Since phytoremediation involves the planting of trees or grasses, it is by nature inexpensive compared to other technologies that involve the use of large scale, energy-consuming equipment.

Phytoremediation costs will vary depending on treatment strategies, desired remediation goals (containment versus removal) and location of contaminated site. For example, phytoextraction

that requires plant harvesting and metals recovery or disposal will be more expensive compared to other phytoremediation technologies.

Nyer and Gatliff (1996) provide a five-year cost comparison of phytoremediation using hybrid poplars in relation to conventional pump and treat technology for a 1-acre site with an aquifer 20 feet deep. Their results are reproduced in Table 4.2. Costs common to both technologies were not included. Table 4.3 shows some phytoremediation activity costs listed by two companies. These figures provided in the tables below are extremely site specific and are estimates of potential costs.

Table 4.2 Five-Year Cost Comparison of Phytoremediation by Hybrid Poplar Trees versus Conventional Pump and Treat (Nyer and Gatliff, 1996)

•	Phytotransformation		
	Design and Implementation	\$50,000	
	Monitoring Equipment		
	Capital	\$10,000	
	Installation	\$10,000	
	Replacement	\$ 5,000	
	5-Year Monitoring		ĺ
	Travel and Administration	\$50,000	
	Data Collection	\$50,000	
	Reports (annuals)	\$25,000	
	Sample Collection and Analysis	\$50,000	
	TOTAL	<i>\$250,000</i>	
•	Pump & Treat ( 3 wells and Reverse Osmosis S	System)	
	Equipment	\$100,000	
	Consulting	\$ 25,000	
ĺ	Installation and Construction	\$100,000	
	5-Year Operation		
	Maintenance	\$105,000	
	Operation (electricity)	\$ 50,000	
	Waste disposal	\$180,000	
	Waste disposal liability	\$100,000	
	TOTAL	<u>\$660,000</u>	

Table 4.3 Cost Estimates from Ecolotree and Applied Natural Science of Poplar Tree Remediation System (Chappell, 1997)

Ecolotree		
Activity	Cost	
Installation of trees at 1450 trees/acre	\$ 12,000 to \$15,000	
Predesign	\$ 15,000	
Design	\$ 25,000	
Site Visit	\$ 5,000	
Soil Cover and Amendments	\$ 5,000	
Transportation to Site	\$ 2.14 /mile	
Operation and Maintenance	\$ 1,500/acre with irrigation	
	\$ 1,000/acre without irrigation	
Pruning (not yearly)	\$ 500	
Harvest (during harvest season) \$ 2,500		
Applied Natural Science		
Activity	Cost	
TreeMediation program design and	\$ 50,000	
implementation		
Monitoring Equipment		
Hardware	\$ 10,000	
Installation	\$ 10,000	
Replacement	\$ 5,000	
Five-Year monitoring		
Travel and Meetings	\$ 50,000	
Data Collection	\$ 50,000	
Annual Reports	\$ 25,000	
Sample Collection and Analysis	\$ 50,000	

# 4.5 Phytoremediation of EDB

Currently, the best available treatment for EDB contaminated groundwater is granular activated carbon (GAC) adsorption (National Primary Drinking Water Regulations). While other technologies such as advanced oxidation using ultra-violet/ozone or air stripping are applicable for EDB removal, these technologies have certain disadvantages. Advanced oxidation using ultra-violet and ozone or hydrogen peroxide does not show consistent performance due to possible turbidity problem and UV tube casing fouling. In air stripping operations, there is problem of column fouling, which reduce overall efficiency and capacity. In addition, there is added requirement of off-gas treatment (incineration or GAC treatment)

and concerns in meeting regulatory discharge limits. These increase the operating costs relative to purely GAC treatment using pump and treat.

Phytoremediation, which is a low cost and low-tech remediation technology, has proven successes in remediating organic contaminants in laboratory and pilot studies. These organic contaminants include chlorinated solvents (TCE, PCE), petroleum hydrocarbons (BTEX), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), explosives, and pesticides.

However, there is a dearth of published data or studies on EDB phytoremediation, with the exception of an EPA report of on-going studies using Koa plant in Hawaii for remediation of EDB, dibromochloropropane (DBCP) and dichloropropane (DCP) (Gordon *et al.*, 1997b). This section examines the basic physical, chemical, and biological properties of EDB in order to assess its bioavailability to plant roots and the possible mechanisms of phytoremediation.

## 4.5.1 Background Information

The following sub sections provide a general description of ethylene dibromide, along with its regulatory history, and its sources and occurrences.

#### 4.5.1.1 General Description (Chemical Abstract Service, CAS # 106-93-4)

Ethylene dibromide (1,2-dibromoethane) is a clear, colorless, non-flammable liquid at room temperature with a mild, sweet odor. At a concentration of 10 parts per million in air, the average person can detect ethylene dibromide. Other synonyms or trade names are EDB, glycol dibromide, Bromofume, Dowfume W 85, Aadibroom, EDB-85, Nefis, Pestmaster, Kopfume, Soilbrom and Soilfume (National Primary Drinking Water Regulations).

#### 4.5.1.2 Regulatory History

Ethylene dibromide was first detected in groundwater in Hawaii in 1980 (Oki and Giambelluca, 1987). By late 1983, it was reported that trace amounts of EDB were detected in grains, grain products and in groundwater in Florida, Georgia, California, South Carolina, New York, Wisconsin, Washington, Massachusetts, Connecticut, and Hawaii (ATSDR,

1992). With the widespread discoveries of EDB in groundwater drinking wells and the evidence of its toxicity to humans, the use of EDB as a soil fumigant was banned in 1983. By early 1984, all registered agricultural uses of EDB were phased out as a result of the EPA determination that agricultural uses of EDB presented an "imminent threat" to the health of humans.

The Maximum Contaminant Level (MCL) for EDB in drinking water, set by various states, varies from 0.001 ppb to 0.1 ppb (Pignatello and Cohen, 1990). The federal EPA MCL in drinking water is 0.05 ppb or 0.00005 mg/L while in Massachusetts, the state drinking water MCL is 0.02 ppb (US Air Force-IRP, 1998).

#### 4.5.1.3 Anthropogenic Sources

Ethylene dibromide has been produced in the United States since the 1920s. It was used widely as a fumigant on more than 40 crops until 1983. Out of the 127,000 MT (280 million lb) of EDB produced in 1983, agricultural usage was estimated to be about be 7%, which is 9,000 MT (20 million lb). When used as a soil fumigant, EDB was injected directly as a liquid into the soils for the control of nematodes, with smaller amounts used as a fumigant of grain and fruit (Weintraub *et al.*, 1986). In 1984, the EPA banned the use of EDB as a soil and grain fumigant (ATSRD, 1992).

Ethylene dibromide was also used as a lead scavenger in leaded gasoline and aviation fuel. About 93% (260 million lb) of EDB produced in 1983 were used as an additive. EDB constitutes approximately about 0.03% by weight of gasoline containing 1.1g lead/gal (Weaver *et al.*, 1988)

Besides the two above main applications in the past, EDB is currently used in the treatment of felled logs for bark beetles, termite control, control of wax moths in beehives, spot treatment of milling machinery and for Japanese beetle control on ornamental plants. In addition, EDB is also used as an intermediate for dyes, resins, waxes and gums (ATSDR, 1992).

The occurrences of EDB in groundwater or soil are mainly due to leaking underground storage tanks (LUST) of leaded gasoline and leachate from soil as EDB is extremely water-soluble. From 1983 to 1993, according to the Toxics Release Inventory, EDB releases to land totaled 2,267 lbs, and water releases totaled 2,554 lbs. These releases were primarily from facilities classified as petroleum refineries (National Primary Drinking Water Regulation).

# 4.5.2 Physical and Chemical Properties of EDB

The physical and chemical properties relevant to the fate and transport of EDB are presented in Table 4.4.

Table 4.4 Physical and Chemical Properties of EDB relevant to its Environmental Fate

Property	Value
Formula	BrCH <sub>2</sub> CH <sub>2</sub> Br
Molecular Weight	187.88
Boiling Point	131.6 ℃
Melting Point	9.97 °C
Density	2.178 g/cm <sup>3</sup>
Vapor Pressure	7.7 mm Hg at 20 °C
	10.8 mm Hg at 25 °C
Water Solubility	3, 370 mg/L at 20 °C
	4, 250 mg/L at 25 °C
Henry's Law Constant, K <sub>H</sub> (Dimensionless)	0.0246 at 20 °C
	0.0345 at 25 °C
Octanol-Water Partition Coefficient, log Kow	1.93
Diffusion Coefficient in Dry Air, Dair	0.0708 cm <sup>2</sup> /s at 20 °C
	$0.0813 \text{ cm}^2\text{/s at } 25 ^{\circ}\text{C}$
Diffusion Coefficient in Water, Dwater	1.0 X 10 <sup>-5</sup> cm <sup>2</sup> /s at 25 °C
Bioconcentration Factor, log BCF (Dimensionless)	0.301 - 0.778

(Source: Adapted from Pignatello and Cohen, 1990)

EDB is fairly water-soluble and therefore, tends to be transported along with groundwater. However, despite its relatively high water solubility and volatility, EDB has been found to persist in soils and groundwater for up to 20 years (Pignatello *et al.*, 1987; Steinberg *et al.*, 1987; Sawhney *et al.*, 1988). Sorption of EDB by soil constituents retards both vapor and aqueous phase transport of EDB and plays a crucial role in affecting the persistence of EDB in the environment. The  $K_d$  and  $K_{\infty}$  of EDB vary from 0.25 to 5 L/kg and 12 to 134 L/kg, respectively, for soils ranging from sandy loam to peaty loam (Pignatello and Cohen, 1990). One possible reason for EDB persistence in fumigated soil is that EDB is encapsulated within soil aggregates. The entrapped EDB must diffuse through the long and tortuous paths among the micropores before reaching the water surrounding the aggregates (Pignatello *et al.*, 1987; Steinberg *et al.*, 1987).

## 4.5.3 EDB Availability to Plant Roots

As discussed in Section 4.2.1, plant uptake of a chemical depends on the uptake efficiency, transpiration rate, and the concentration of chemical in soil water. Uptake efficiency, in turn, depends on physical-chemical properties, chemical speciation, and the plant itself. The ability of a plant to take up a chemical from the soil and groundwater and translocate it to its shoots is described by the chemical's root concentration factor (RCF). The RCF is a measure of the root concentration of a contaminant divided by the concentration in the external bulk solution (Shone and Wood, 1972). It is important to estimate the mass of contaminant of sorbed to the roots in phytoremediation as it is an indication of whether the contaminant will be translocated to above-ground portions (stems, leaves) and be degraded or transpired or just merely sorbed to the roots.

Predictive relationships between RCF, TSCF and the chemical water solubility,  $\log K_{ow}$  were developed for various compounds to determine their optimal  $\log K_{ow}$  (Briggs *et al.*, 1982; Burken and Schnoor, 1998). These relationships will be presented in Section 5.3. EDB appears to be readily taken up through plant roots as its  $\log K_{ow}$  value falls within the optimum range of 0.5 - 3.0 reported by Schnoor *et al.* (1995). As a result, phytoremediation appears to be a viable option for treating EDB contaminated groundwater.

## 4.5.4 Toxicity of EDB to Human Beings and Animals

EDB is extremely toxic to humans; exposure to high concentrations of EDB through inhalation, ingestion, or skin contact can result in death (USEPA Office of Air Quality Planning and Standards). Changes in the liver and kidney have been noted in humans who died from ingestion of EDB. The chronic effects of exposure to EDB have not been well documented in humans, but animal studies indicate that chronic exposure to EDB may result in toxic effects to the liver, kidney and testis, irrespective of the route of entry. The LC<sub>50</sub> for rat is determined to be 14,300 mg/m<sup>3</sup> (Registry of Toxic Effects of Chemical Substances). Limited data also indicated that long term exposure to EDB could impair reproduction by damaging sperm cells in the testis (ATSDR, 1992).

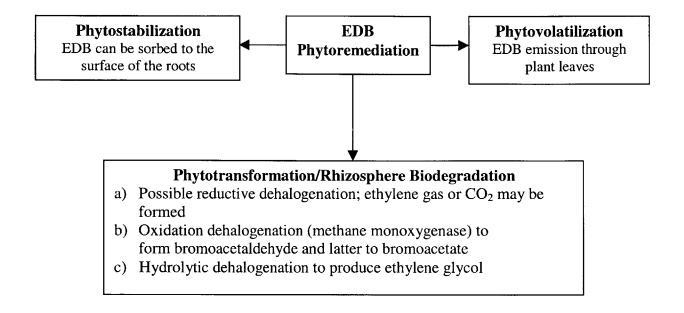
The main focus of health concern has been the potential of EDB as a carcinogen. EPA considers EDB to be a probable human carcinogen and has ranked it in EPA's Group B2 (USEPA IRIS). Numerous studies have been conducted to assess the toxicological effects of EDB on animals, with a detailed review of the toxicological effects presented by Alexeeff *et al.* (1990).

# 4.5.5 Possible Mechanisms of EDB Phytoremediation

The mechanisms of phytoremediation are generally inferred from results of laboratory and field studies, and greenhouse studies. The concentration of contaminant and its metabolites will be determined at various portions of the plant - root, shoot, stem, and leaf, after a period of time (one or two growing season). In greenhouse studies, the possible emission of volatile gases will be studied for phytovolatilization mechanism.

One possible way to determine the mechanisms of EDB phytoremediation is make a comparison with the possible enzymatic microbial pathways and degradation products of EDB. This is valid because different species of poplar trees contain numerous enzymes, in addition to microorganisms present in the rhizosphere, some of which may possibly degrade EDB. Pignatello *et al.* (1990) gave a detailed report of the EDB microbial and abiotic transformation pathways and products. Figure 4.2 illustrates the possible phytoremediation mechanisms of EDB.

Figure 4.2 Possible Phytoremediation Mechanisms of EDB



## 4.6 Analysis of Failure Modes

Contingency plans must be in place to ensure the success of the phytoremediation system, especially when we are dealing with a natural system of flora and climate. There are several events that can cause failure of plants that should be assessed and preemptive measures must be in place to tackle these problems efficiently. These failures include killing frost, wind storms, animals (deer and beaver etc.), diseases or infestation (fungus, insects) and latent toxicity. Additional funds have to be apportioned into plant replacement, pest control, and possible fencing to ensure a viable and effective planting system.

# 5 Implementation Plan

Schnoor (1997) has specified several basic design considerations that are essential to the success of phytoremediation. Due to paucity of laboratory, pilot and field data and studies on EDB phytoremediation, the following design parameters are proposed criteria for the implementation.

#### **5.1** Plant Selection

There are several key variables taken into consideration in the selection of plants for EDB phytoremediating. An understanding of the phytoremediation mechanism(s) involved would enable us to select the appropriate plant species. In most cases, the plants that are used on contaminated field sites have been extensively tested in laboratory studies with considerable successes.

Poplar (*Populus*), as shown in Figures 5.1, belongs to the Willow (*Salicaceae*) family of deciduous trees found in north temperate and arctic regions (Little, 1996). It is chosen for EDB phytoremediation for the following reasons:

#### **5.1.1** High Evapotranspiration Rate

Poplars, which are phreatophytic plants, are able to extend their roots to the water table and pump from the upper layer of the saturated zone. Due to high evapotranspiration rates, a large plot of poplar trees is able to cause a significant drawdown or cone of depression in the water table as illustrated in Figure 5.2. This will retard the flow of EDB plume and at the same time, remediate the site.

Results from a phytoremediation field site in Aberdeen, Maryland indicated an estimated 0.1 meter depression in the water table after a year of planting hybrid poplar trees (Compton *et al.*, 1998). For a stand of 5-year old poplar trees at density of 1,750 poplars/acre under warm arid conditions of eastern Washington State, a drawdown of 140 cm/year was created (Gordon *et al.*, 1997a).

Figure 5.1a Hybrid Poplar Cutting

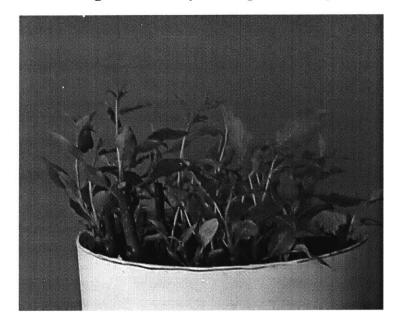


Figure 5.1b Young Poplar Tree

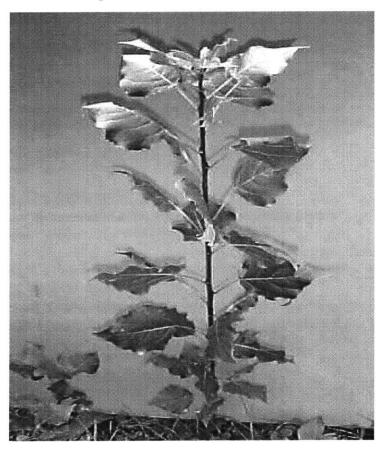


Figure 5.1c Rows of Poplar Trees



Figure 5.2 Depression of Water Table due to High Evapotranspiration Rate of Poplar

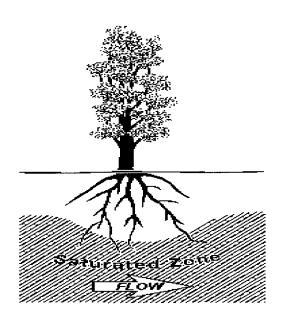


Table 5.1 provides some estimates of evapotranspiration rates of hybrid poplars obtained through laboratory and field studies. These values are site specific and dependent on tree age and species, time and day of the year, and amounts of solar radiation. They vary from 6 L/tree for a young tree to 200 L/tree for a five-year old poplar.

**Table 5.1** Estimates of Evapotranspiration Rates by Hybrid Poplars

Evapotranspiration Rates	Source	
100 -200 L/day/tree for 5 year old trees	Newman et al., 1997	
100 L/day/tree for a 5 year old tree under optimal conditions	Stomp et al., 1994	
3.33 L/day in spring, 6.78 L/day in summer, and 48.9 L/day in fall	Compton et al., 1998	

#### **5.1.2** Presence of Degradative Dehalogenase Enzyme

Studies have been conducted on the degradation processes and pathways of various contaminants (chlorinated solvents, TNT, BTEX, herbicide) through poplar uptake. Newman *et al.* (1997) suggest that TCE metabolism in poplars is similar to the mammalian breakdown of TCE, based on the production of similar TCE metabolites in both plants and mammals. This hypothesis seems plausible as many of the enzyme systems, such as cytochrome P-450 oxygenases and glutathione S-transferases, involved in the mammalian metabolism of TCE are also found in plants (Cunningham *et al.*, 1996).

Hybrid poplars also contain a dehalogenase enzyme that is able to breakdown halogenated alkanes and alkenes (Chappell, 1997). Dehalogenase will react with TCE (via oxidative pathway) and CCl<sub>4</sub> (via reductive pathway) to give the ultimate end product of CO<sub>2</sub>. Schnoor *et al.* (1995) reported that the half live of hexachloroethane in hybrid poplar is 50 hours.

#### **5.1.3** Nativity of the Plant Species

Plants that are indigenous to the site would be able to withstand the climatic conditions and local parasites or pathogens.

Little (1996) reported that poplar trees are generally found in moist or wet soils, along stream banks, flood plains and sandbars. Mears (manager of Segal Ranch; personal communication, 2000) reported that hybrid poplars are able to thrive in the same climatic conditions as the dominant plant species in FS-28. The dominant species of tress along the Coonamessett River are red maple (*Acer rubrum*) and pitch pine (*Pinus rigida*) with red maple and willow (*Salix spp.*) found in the understory layer (AFCEE, 1998b).

#### **5.1.4** Favorable Growth Factors

There are more than 30 hybrids of poplars to choose from in which these hybrid species have superior genetic traits than the parent species. Poplars are chosen due to their high growth yield (3 to 5 meters/year) and long life span (40+ years).

# 5.1.5 Widely Used Plant Species for Phytoremediation

Hybrid poplars have been widely tested in laboratory and pilot studies and used successfully in various contaminated sites for cleanup. Table 5.2 shows several site locations and contaminants where hybrid poplars have been used for remediating contaminated groundwater or soil.

Table 5.2 Locations of Sites where Hybrid Poplars are employed

Name and Location	Type of Contaminant	Type of Treatment	Source
Aberdeen Proving	TCE and	Interception and	Compton et
Ground, Maryland	tetrachloroethene in	containment; enhanced	al., 1998
	groundwater	natural destruction	
Edward Sears	Solvents in	Interception and	Chappell 1998
Property; New	groundwater	containment; enhanced	
Gretna, NJ		natural destruction	
Solvents Recovery	Chlorinated volatile	Biological "pump and	Phytokinetics
Systems of New	organic compounds	treat" system	Inc.,
England Superfund			www.phytokineti
Site, Southington,			cs.com
Connecticut			
Chevron-Ogden,	TPH (Total petroleum	Interception and	Phytokinetics
Utah Site	hydrocarbon)	containment	Inc.,
			www.phytokineti
			<u>cs.com</u>

## 5.2 Treatability

It is important to perform treatability studies prior to design in order to ensure that the phytoremediation system will achieve the desired results. The phytotoxicity of the EDB and its metabolites, and transformation data are obtained in treatability studies.

Currently, there are no published literature or laboratory studies of toxicity assessments of EDB and its metabolites on hybrid poplars or any other plants. It is worth mentioning that most literature cited only the toxicity assessment of a single organic or inorganic contaminant with only a recent paper by Ferro *et al.* (1999) that assessed the toxicity effects of a volatile organic mixture on poplar trees.

A proposed sequence of phytotoxicity assessment will be *hydroponic studies*, followed by *small pot studies* with soils from the site in *greenhouse* to final *plot studies*. Samples of contaminated groundwater in FS-28 should be used in hydroponic studies to assess the toxicity effects on the hybrid poplars. Different concentrations of EDB itself should also be employed to understand the transformation process where the roots, shoots, stems and leaves will be harvested for metabolite analysis and mass balance closure.

Another important consideration for treatability studies is the potential release of EDB through plant leaves to the atmosphere by phytovolatilization. Fate calculations in the atmosphere for EDB and other toxic volatile organic compounds such as benzene and TCE must be determined to ensure that the levels do not exceed state or government regulatory levels.

A recent paper by Narayanan *et al.* (1999) studied the transpiration of TCE, vinyl chloride and carbon tetrachloride to the atmosphere by plants simulating various scenarios. They reported that these contaminants are very unlikely to exceed EPA standards under those scenarios.

# 5.3 Groundwater Capture and Transpiration

In designing an effective phytoremediation, we need to ensure that the plume that leaves the vegetation will not be evapoconcentrated. This is a potential concern especially for hydrophilic compounds as these contaminants are not readily taken up plants. The TSCF and RCF are related to the logK<sub>ow</sub> through the expressions (Burken and Schnoor, 1998):

$$= 0.756 \exp \left\{ -(\log K_{ow} - 2.50)^2 / 2.58 \right\}$$
 (1)

RCF (concentration in root/groundwater concentration)

$$=3.0 + 10^{0.65\log \text{Kow} - 1.57} \tag{2}$$

For groundwater remediation, a flow net diagram of the aquifer with concentration of the contaminant is required to estimate the eventual fate. The plot of trees can be grouped for consideration as an average withdrawal point and a simple capture zone calculation (Javandel and Tsang, 1986) can be applied to estimate whether the phytoremediation "pump" can be effective at entraining the plume of contaminants. The goal is to create a water table depression where contaminants will flow to the vegetation for uptake, degradation and transpiration.

The uptake rate of a contaminant is given by the equation:

$$U = TSCF \times T \times C \tag{3}$$

where U = uptake rate of contaminant, mg/day

TSCF = transpiration stream concentration factor, dimensionless

T = transpiration rate of vegetation, L/day

C = aqueous phase concentration in soil water or groundwater, mg/L

# **5.4** Planting Density and Pattern

There are several considerations taken into account in deciding the location, and the number of trees and planting pattern. The location of the phytoremediation system is constrained by the distance of the EDB plume from ground surface to the aquifer and the surrounding natural and human habitat. As mentioned in Table 5.1b, phytoremediation is limited to shallow groundwater (10-20 feet) even though a new proprietary planting technology called TreeMediation developed at Argonne National Laboratory can get poplar roots to reach to a depth of 30-40 feet below ground surface (Nyer and Gatliff, 1996; Harrigan, 1999). However, the EDB plume at FS-28 is at elevations ranging from -20 to -220 feet mean sea level (AFCEE, 1999c) and is migrating to the surface south of Hatchville Road, discharging in the Coonamessett River (AFCEE, 1997a).

Besides considering the depth of EDB plume, there are cranberry bogs located along both sides of the Coonamessett River (Figure 3.3) which prohibit any phytoremediation activities from being carried out directly on the bogs as that would damage the bogs owners' interests. Based on flow net diagrams (AFCEE, 1997a) of the depth of the EDB plume and the available land space and constraint, the proposed location will be between north of the Lower Baptiste Bogs (E4) and Broad River as shown in Figure 5.3.

For planting density and pattern, Schnoor (1997) proposed 1000 to 2000 trees per acre for hybrid poplars, with 2 feet between trees and 10 feet between rows for row conformation. In order for trees to have sufficient sunlight when the canopy is fully developed, the spacing between each tree can be increased to 6 - 10 feet depending on land availability. The distances of 10 ft between rows and 6 - 10 ft between trees also allow easy maintenance and removal of weeds, vines and grasses that will otherwise threaten the growth of trees. Chappell (1997) provided three cases of phytoremediation systems that are currently being implemented where the plot size ranged from 0.3 acre to 1.0 acre. The number of poplar trees ranged from 120 (0.3 acre plot) to 660 (1.0 acre).

Another factor in deciding the number of trees is the evapotranspiration rate of poplar trees and the overall impact on the water table created by the water uptake of poplars. As discussed

in Section 6.1.1, the evapotranspiration rate is dependent of the particular species of poplars, climate (temperature, relative humidity) and site conditions.

#### **5.5** Calculations and Results

Using a 7 ft  $\times$  7 ft spacing between each tree, the proposed design parameters are as follow:

Planting area =  $70 \text{ ft} \times 70 \text{ ft}$ Spacing b/w each tree = 7 ftNumber of rows = 11Number of trees = 121

Using an evapotranspiration range of 6 to 200 L/tree (Table 5.1), we can evaluate the total amount of water transpired by this plot of trees.

	<u>Minimum</u>	<u>Maximum</u>
Poplar evapotranspiration rate =	6 L/tree	200 L/tree
Amount of water transpired =	730 L/day	24,000 L/day

The transpiration stream concentration factor (TSCF) of EDB is given by equation (1) of Section 5.3. Using a log  $K_{ow}$  value of 1.93 (Table 4.4), the TSCF for EDB is:

$$TSCF = 0.67$$

The uptake rate of EDB from the trees can be determined from equation (3) of Section 5.3, based solely on the poplar's evapotranspiration rate. Assuming a uniform maximum EDB concentration (C) of 3.9  $\mu$ g/L within the width and depth of the plot (Section 3.8), from equation (3), the uptake rate of EDB or flux by poplar trees is:

Uptake rate of EDB, 
$$U = 2 \text{ mg/day}$$
 60 mg/day

In calculating the percentage of water transpired by trees in relation to the aquifer's volumetric flow, only the depth at which the plant roots penetrated to is used.

		<u>Minimum</u>	<u>Maximum</u>
Groundwater seepage velocity, U	=	0.02 ft/day	0.2 ft/day

Depth of aquifer = 20 ft
Width of plot area = 70 ft

Groundwater flowrate,  $Q_w = 28 \text{ ft}^3/\text{day}$  280 ft<sup>3</sup>/day

= 790 L/day 7900 L/day

**Percentage of water transpired** = Amount transpired by trees / GW flowrate

= 9 % 92 %

# **5.6** Contaminant Cleanup Time

The first order rate constant for uptake can be obtained from the contaminant uptake rate as follows (Schnoor, 1997):

$$k = U/M_0 \tag{4}$$

where  $k = \text{first order constant for uptake, year}^{-1}$ 

U = uptake rate of contaminant, kg/year

 $M_0$  = initial mass of contaminant present over plot of trees, kg

Using the maximum transpiration of T = 24,000 L/day and the volume of aquifer system V = 70 ft  $\times$  70 ft  $\times$  20 ft, the first order uptake constant is calculated as:

$$k = (TSCF \times T \times C)/(V \times C)$$

$$k = 6 \times 10^{-3} dav^{-1}$$

We can model the rate of loss of EDB from the groundwater or soil as a dispersive plug flow vessel with inflow, outflows and loss through plant uptake.

$$\delta C/\delta t = -U(\delta C/\delta x) - kC$$
 (5)

where U = groundwater seepage velocity, ft/day

C = EDB concentration at time t

At steady state, assuming groundwater flow U is constant throughout the phytoremediation system, equation (5) reduces to:

$$C(t) = C_0 \exp(-kt) \tag{6}$$

where  $C_0 = EDB$  concentration at inlet,  $\mu g/L$ 

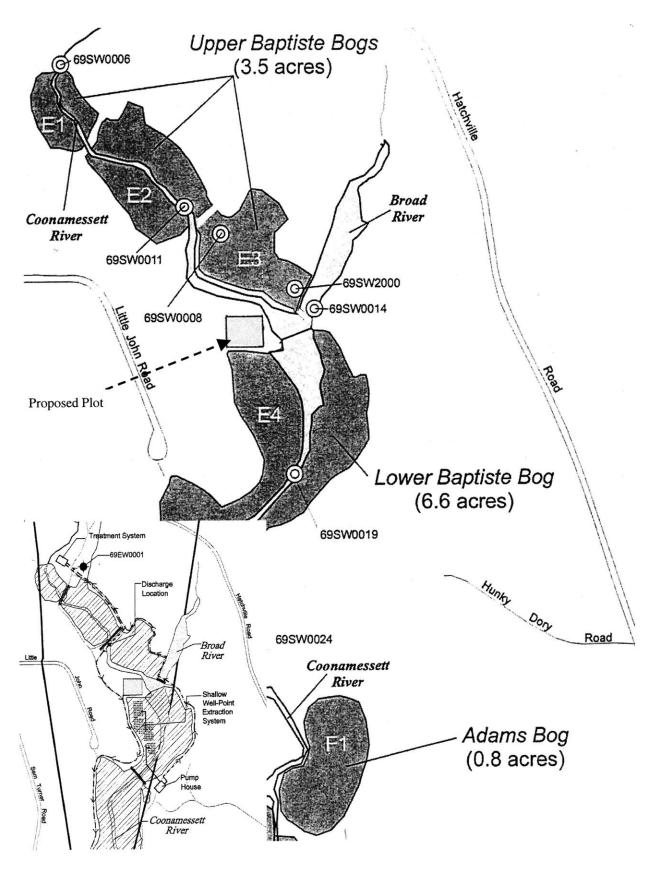
The time at the outlet of the phytoremediation system is given by:

t = 
$$x / U$$
, where  $x = 70$  ft (7)  
t = 350 days or 3,500 days

For an inlet maximum concentration of 3.9  $\mu$ g/L, the outlet concentration at these times are calculated from equation (6):

$$C = 0.5 \mu g/L$$
 or  $0 \mu g/L$ 

Figure 5.3 Location of Proposed Planting Area (Square Shaded Region)



# 5.7 Estimated Drawdown from Aquifer

The drawdown or depression of water table,  $s_w$  created by the plot of trees can be estimated using *Thiem* equation. In using *Thiem* equation, the plot of trees will be grouped together as a "pump", with the evapotranspiration rate equivalent to the well pumping rate. Steady state conditions are assumed which is applicable since the impact of water table is only appreciable after couple of growing seasons or when the trees have matured. Also, it is assumed that the changes in the saturated aquifer thickness are small compared to the total saturated depth.

*Thiem* equation for the drawdown,  $s_w$  is given by:

$$s_w = (Q_w/2\pi Kb) \ln (R/r_w)$$
 (8)

where  $s_w = drawdown$  at well radius, cm

 $Q_w$  = evapotranspiration rate of trees, cm<sup>3</sup>/day

K = hydraulic conductivity, cm/day

b = aquifer thickness, cm

R = radius of influence, cm

 $r_w$  = radius of vegetation plot, cm

The radius of influence, R is defined as the horizontal distance beyond which pumping of the well has little influence on the aquifer; that is; beyond R, no significant drawdown due to pumping is assumed to exist. R is given by:

$$R = b (K/2N)^{1/2}$$
 (9)

where R = radius of influence, cm

K = hydraulic conductivity, cm/day

N = annual recharge by precipitation, cm/year

Using an annual recharge, N= 49 cm/year (ABB-ES, 1992), a hydraulic conductivity, K = 9,140 cm/day (AFCEE, 1997a),  $r_w = 1,070$  cm (35 ft), b = 7,600 cm (250 feet), and  $Q_w = 24,000$  L/day, the values of R and  $s_w$  are:

$$R = 1.4 \times 10^{6} \text{ cm}$$

$$s_w = 12 cm$$

## 5.8 Agronomic and Maintenance

Agronomic and maintenance must be factored into the overall cost analysis of a phytoremediating system. Use of fertilizers might be required to stimulate growth of vegetation and at the same time, enhance growth of rhizosphere microbial bacteria. Nutrients include nitrogen, phosphorus and potassium from commercial fertilizer mixes, and carbon addition and soil conditioners such as aged manure, sewage sludge, compost and straw. The typical fertilizers application rates are 50 lbs phosphorus/acre and 100 lbs of nitrogen/acre per year (Schnoor, 1997).

Soil amendments such as pH adjustments through addition of lime or acid must be first tested in laboratory to ensure that the change in pH and addition of lime/acid do not affect plant uptake rate and quantity of contaminant.

Operation and maintenance (O&M) of the phytoremediating system is required and these include mowing, replanting, pruning, possible harvesting (for testing or disposal), vegetation monitoring for contaminants, and fertilizers use. Additional monitoring wells will be required, if necessary, to be installed up and down gradient of the vegetation plot.

#### 5.9 Estimated Cost

As noted in Section 4.4, phytoremediation costs are extremely site specific. However, it is useful to obtain a rough estimate of the cost based on other ongoing or previous phytoremediation systems. This estimated cost could be used for future budgeting, cost comparison, and feasibility study. The estimated setup cost of our phytoremediation system is scaled from Table 4.2, multiplied by a conservative factor of 2.

Table 5.3 Estimated Cost of FS-28 Phytoremediation System

FS-28 Phytoremediation System: 121 Hybrid Poplar Trees of 70 ft $\times$ 70 ft plot area			
Trees Installation	\$ 1,000		
Predesign	\$ 3,000		
Design	\$ 5,000		
Site Visit \$ 2,500			
Soil Cover and Amendments	\$ 1,000		

Operation and Maintenance (excluding	\$ 1,000
monitoring)	
TOTAL	\$ 13,500

#### 5.10 Discussion

Currently, the combined extraction treatment re-injection system (single well and shallow well) using GAC treatment system is performing satisfactorily as no EDB has been detected in the surface waters near the cranberry bogs. Even though phytoremediation can possibly remediate EDB (the possible EDB phytoremediation mechanisms are phytotransformation, phytovolatilization, rhizosphere bioremediation and phytostabilization), the phytoremediation system operating by itself cannot possibly and effectively remove all the EDB. There are two reasons for this:

- 1. the large depth extent of the EDB plume and
- 2. plant roots can only penetrate up to 40 feet below ground surface.

As described in Section 3.2, the EDB plume averages 100 feet below ground surface and it upwells to the surface in and south of Broad River, and north of the Adams and Augusta Bogs. As plant roots can only penetrate up to 40 feet below ground surface, this limits our phytoremediation system to areas near the cranberry bogs where tree roots can access the EDB plume. In addition, the availability of land space for phytoremediation needs to be fully explored as the surrounding land bank includes existing residential and other agricultural users (strawberry and vegetable owners).

One possible remediation scheme is to implement phytoremediation along with the current extraction treatment system, with a reduction or possible shutdown in the shallow well pumping rate (or along with an increase in single well pumping rate). The plot of trees may completely or partially replace the shallow well pumping system since the shallow well pumping system was implemented to prevent EDB contamination of the surface water for agricultural purposes. With sufficient trees planted above and around the cranberry bogs acting as a riparian barrier and remediating EDB concurrently, it may be possible to contain or prevent EDB from upwelling or surfacing into the Coonamessett River.

When phytoremediation is effectively implemented, this scheme of optimized pump rate will translate to overall cost reduction through savings in reduced pumping rate, longer GAC cycle life, and lower operation and maintenance costs.

# 6 Conclusions

The EDB plume in FS-28 is migrating further south towards the cranberry bogs. This EDB plume has upwelled into the surface water and tainted the cranberries in 1997. The EPA has determined that the use of EDB-contaminated water for agricultural purposes presents an unacceptable risk to human health. Since then, several remedial activities have been undertaken. The current treatment system consists of two pumping systems (single deep well and shallow well over the cranberry bogs) using GAC for treatment to contain and reduce the EDB levels. In addition, the cranberry bogs will continue to be physically separated by earthen berms and vinyl sheets, with alternative source of irrigation water being provided by AFCEE.

Currently, GAC adsorption is considered the best available treatment for EDB contaminated water. Phytoremediation is the engineered use of plants to cleanup contaminated groundwater, soil or sediments. It is an emerging low cost and low-tech remediation technology that has been applied successfully in several USEPA Superfund sites. It has shown promising successes in laboratory and pilot studies in remediating various organic and inorganic contaminants.

The objective of this thesis was to evaluate the feasibility of implementing phytoremediation in FS-28 to contain and remove EDB. Table 6.1 summarizes the proposed design parameters and the impacts of this phytoremediation system.

A square plot (70 ft  $\times$  70 ft) of 121 hybrid poplar trees is proposed to be located above the Lower Baptiste Bog. This proposed phytoremediation system is unable to replace the current treatment system due to the large area and depth extent of the EDB plume. The tree roots can only penetrate up to a maximum depth of 40 ft and the EDB ranges from 20 to 220 ft below ground surface in FS-28. Also, there is space constraint due to surrounding cranberry bogs and residential communities.

One possible cost saving alternative is to implement phytoremediating along with the pump and treat system, but reduce or possibly shutdown the shallow well pumping system. It can be applied to open and free areas where the EDB is within 40 feet below ground surface, especially at regions near the cranberry bogs. The plot of trees planted above and around the cranberry bogs can contain and reduce the EDB, thereby preventing it from upwelling to the surface water.

**Table 6.1** Summary of Proposed Phytoremediation Parameters

#### **Planting Density and Pattern**

- Hybrid poplar trees
- Square plot of 70 ft  $\times$  70 ft
- Spacing between each tree 7 ft
- Number of trees 121

## **Impacts**

- 730 24,000 L/day of water transpired
- Evapotranspiration is 9 92% of groundwater flow
- 2-60 mg/day of EDB uptake into trees
- Maximum aquifer drawdown 12 cm

#### **Estimated Setup Cost**

• \$13,500

# 7 Bibliography

- ABB-ES. 1992 (October). Groundwater Remediation Strategy. Installation Restoration Project; MMR; Prepared for HAZWRAP; Portland, Maine. . 1995 (September). Draft Technical Memorandum Monitoring Well MW-1206Z Groundwater EDB Investigation. Installation Restoration Project; MMR; Prepared for HAZWRAP; Portland, Maine. \_. 1996 (December). Draft Technical Memorandum, Ethylene Dibromide Phase II Groundwater Investigation. Prepared for Air Force Center for Environmental Excellence/MMR Installation Restoration Program. Portland, Maine. AFCEE. 1997a (February). Draft Fuel Spill (FS-28) Plume Technical Decision Memorandum. FC-J23-35K78408-M17-0001. Prepared by Jacobs Engineering Group Inc. for AFCEEE/MMR. Installation Restoration Program, Otis Air National Guard Base, MA. . 1997b (June). Draft Final Fuel Spill (FS-28) Plume Action Memorandum. AFC-J23-35K78408-M17-0004. Prepared by Jacobs Engineering Group Inc. for AFCEEE/MMR. Installation Restoration Program, Otis Air National Guard Base, MA . 1998 (November). Final Engineering Evaluation, Cost Analysis, and Execution Plan for Caonamessett River FS-28 Bog Separation Project. AFC-J23-35-Q85009-M1-0002. Prepared by Jacobs Engineering Group Inc. for AFCEEE/MMR. Installation Restoration Program, Otis Air National Guard Base, MA. . 1999a (May). Final Southwest Operable Unit (SWOU) Remedial Investigation. AFC-J23-35Q86101-M14-0006. Prepared by Jacobs Engineering Group Inc. for AFCEEE/MMR. Installation Restoration Program, Otis Air National Guard Base, MA \_. 1999b (September). Draft Proposal Plan for the FS-28 and FS-29 Plumes in the Southwest Operable unit. AFC-J23-35Q86101-M25-0005. Prepared by Jacobs Engineering Group Inc. for AFCEEE/MMR. Installation Restoration Program, Otis Air National Guard Base, MA. \_. 1999c (October). FS-28 Interim Action Start-Up Monitoring Report. AFC-J23-35S19002-M17-0004. Prepared by Jacobs Engineering Group Inc. for AFCEEE/MMR. Installation Restoration Program, Otis Air National Guard Base, MA
- ANG, 1995 (April). Ashumet Valley Ground Water Operable Unit Draft Remedial Investigation Report Vol. 1. Air National Guard; Otis Air Force Base, MA.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1992. *Toxicological Profile for 1,2-Dibroethane*. U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanat, GA.

- Alexeeff G.V., Kilgore W.W., and M.Y. Li. 1990. *Ethylene Dibromide Toxicology and Risk Assessment*. *In* Reviews of Environmental Contamination and Toxicology. (Ed. George, W.W.) 112: 49-122.
- Anderson T.A., Guthrie E.A., and B.T. Walton. 1993. *Bioremediation in the Rhizosphere*. Environmental Science & Technology. 27(13): 2630-2636.
- Anderson T.A. 1997. Development of a Phytoremediation Handbook: Considerations for Enhancing Microbial Degradation in the Rhizosphere. 1997 AAAS Fellowship Abstract.

  <a href="http://es.epa.gov/ncerqa\_abstracts/fellow/aaas/rumbold.html">http://es.epa.gov/ncerqa\_abstracts/fellow/aaas/rumbold.html</a>
- Ansede, J.H., Pellechia P.J., and D.C. Yoch. 1999. Selenium Biotransformation by Salt Marsh Cordgrass Spartina alterniflora: Evidence for Dimethyselenoniopropionate Formation. Environmental Science & Technology. 33(12): 2064-2069.
- Beaudet, B.A. 1983. Evaluation of Treatability of Ethylene Dibromide and Dibromochloropropane by Activated Carbon and Packed column Air Stripping. USEPA Contract No. 68-01-6494, Work Assignment No. 8. Environmental Science and Engineering, Inc., Gainesville, Florida.
- Bridgeforth, S E. 1998. Groundwater Treatment Technologies: Air Stripping vs UV/Oxidation. Master of Engineering Thesis. Department of Civil and Environmental Engineering, MIT.
- Briggs, G.G., Bromilow, R.H. and A.A. Evans. 1982. *Relationships between Lipophilicity and Root Uptake and Translocation of Non-Ionized Chemicals by Barley*. Pesticide Science. 13: 495-504.
- Burken, J.G. and J.L. Schnoor. 1996. *Phytoremediation: Plant Uptake of Atrazine and Role of Root Exudates*. Journal of Environmental Engineering ASCE. 122(11): 958-963.
- Compton, H.R., Haroski, D.M., Hirsh, S.R., and J.G. Wrobel. 1998. *Pilot Scale Use of Trees to Address VOC Contamination*. In Bioremediation and Phytoremediation Chlorinated and Recalcitrant Compounds; Wickramanayake G. B and R.E. Hinchee Editors. The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, California; pp 245-256.
- Burken, J.G. and J.L. Schnoor. 1998. Predictive Relationships for Uyptake of Organic Contaminants by Hybrid Poplar Trees. Environmental Science & Technology. 32(21): 3379-3385.
- Chappell, J. 1997. *Phytoremediation of TCE in Groundwater using Populus*. Status Report Prepared for the U.S. EPA Technology Innovation Office. <a href="http://www.clu-in.org/remed1.htm">http://www.clu-in.org/remed1.htm</a>

- Cunningham, S.D., Anderson, T.A., Schwab, A.P., and F.C. Hsu. 1996. *Phytoremediation of Soils contaminated with Organic Pollutants*. Advances in Agronomy. 56: 55-114.
- Donnelly, P.K., Hegde, R.S., and J.S. Fletcher. 1994. *Growth of PCB-Degrading Bacteria on Compounds from Phytosynthetic Plants*. Chemosphere. 28(5): 981-988.
- Ferro, A. M., Kennedy J., Kjelgren R., Rieder J. and S. Perrin. 1999. *Toxicity Assessment of Volatile Organic Compunds in Poplar Trees*. International Journal of Phytoremediation. 1(1): 9-17.
- Fletcher, J.S., and R.S. Hegde. 1995. Release of Phenols by Perennial Plant-Roots and their Potential Importance in Bioremediaion. Chemosphere. 31(4): 3009-3016.
- Gordon, M.P., Choe, N., Duffy, J., Ekuan, G., Heilman, P., Muiznieks, I., Newman, L.A., Ruszaj, M., Shurleff, B.B., Strand, S.E., Wilmoth, J. 1997a. *Phytoremediation of Trichloroethylene with Hybrid Poplars*. In Phytoremediation of Soil and Water Contaminants. Kruger, E.L., Anderson T.A., and J.R. Coats Editors. American Chemical Society Symposium Series 664. Orlando, Florida; pp 177-185.
- Gordon, M.P., Strand, S., and L.A. Newman. 1997b. *Final Report: Degradation of Environmental Pollutants by Plants*. USEPA Grant No. R822329. Department of Biochemistry, University of Washington Medical School. <a href="http://es.epa.gov/ncerqa/final/gordon.html">http://es.epa.gov/ncerqa/final/gordon.html</a>
- Harrigan Kate, 1999. A Special Report A Growth Spurt for Phytoremediaiton. Pollution Engineering. 31(13): 24-26.
- Javandel, I. and C.F. Tsang. 1986. *Capture Zone Type Curves A Tool for Aquifer Cleanup*. Groundwater. 24(5), 616-625.
- Lappin, H. M., Greaves, M.P., and J.H. Slater. 1985. Degradation of the Herbicide Mecoprop [2-(2-methyl-4-chlorophenoxy) propionic acid] by a Synergistic Microbial Community. Applied and Environmental Microbiology. 49(2):429-433.
- LeBlanc, Dennis, John H. Guswa, Michael H. Frimpter, and C.J. Londquist. 1986. Groundwater Resources of Cape Cod, Massachusetts. USGS, HA-692.
- Little, E. L., 1996. National Audubon Society Field Guide to North American Trees; Eastern Region. Alfred A. Knopf, Inc, New York.
- Liu, C.M., McLean, P.A., Sookdeo, C.C., and F.C, Cannon. 1991. Degradation of the Herbicide Glyphosate by Members of the Family Rhizobiaceae. Applied and Environmental Microbiology. 57(6):1799-1804.
- Massachusetts Department of Management, 1994. Water Resources of Cape Cod, Water Use, Hydrology, and Potential Changes in Groundwater Levels. October.

- McFarlene, J.C., T.P Fleeger, and J. Fletcher. 1987. Transpiration Effect on the uptake and Distribution of Bromacil, Nitrobenzene, and Phenol in Soybean Plants. Journal of Environmental Quality. 16(4): 372-376.
- Miller, R., 1996. *Phytoremediation: Technology Overview Report*. Groundwater Remediation Technologies Analysis Center. http://www.gwrtac.org/html/tech\_over.html#PHYTOREM
- Mitterhofer, Cordula. 1998. Evaluation of Granular Activated Carbon Adsorption to Remediate Ethylene Dibromide Contamination at Fuel Spill-28 at the MMR. Master of Engineering Thesis. Department of Civil and Environmental Engineering, MIT.
- Narayanan, M., Erickson L.E., and L.C. Davis. 1999. Simple Plant-Based Strategies for Volatile Organic Pollutants. Environmental Progress. 18(4): 231-242.
- National Primary Drinking Water Regulations. *Technical Factsheet on Ethylene Dibromide*. Office of Ground Water and Drinking Water, US EPA <a href="http://www.epa.gov/ogwdw000/dwh/t-soc/edb.html">http://www.epa.gov/ogwdw000/dwh/t-soc/edb.html</a>
- Nellessen, J.E. and J.S. Fletcher. 1993. Assessment of Published Literature Pertaining to the Uptake Accumulation, Translocation, Adhesion and Biotransformation of Organic Chemicals by Vascular Plants. Environmental Toxicology and Chemistry. 12(11): 2045-2052
- Newman, L., Strand, S.E., Domroes, D., Duffy, J., Ekuan, G., Karscig, G., Muiznieks, I.A., Ruszaj, M., Heilman, P., and M.P. Gordon. 1997. *Uptake and Biotransformation of Trichloroethylene by Hybrid Poplars*. Environmental Science & Technology. 31(4): 1062-1067.
- Nietch, C.T., and J.T.Morris. 1999. Biophysical Mechanisms of Trichloroethene Uptake and Loss in Baldcypress Growing in Shallow Contaminated Groundwater. Environmental Science & Technology. 33(17): 2899-2904.
- Nyer, E.K. and E.G. Gatliff. 1996. *Phytoremediation*. Ground Water Monitoring and Remediation. 16(1): 58-62.
- Nzengung, V.A., Wang, C., and G. Harvey. 1999. *Plant Mediated Transformation of Perchlorate into Chloride*. Environmental Science & Technology. 33(9): 1470-1478.
- Oki, D.S. and T.W. Giambelluca. 1987. DBCP, EDB and TCP Contamination of GroundWater in Hawaii. Ground Water. 25(6): 693-702
- Pignatello J.J., Sawhney B.L. and C.R. Frink. 1987. EDB-Persistence in Soil. Science. 236 (4804): 898-898.

- Pignatello, J.J. and S.Z. Cohen. 1990. Environmental Chemistry of Ethylene Dibromide in Soil and Groundwater. In Reviews of Environmental Contamination and Toxicology. (Ed. George, W.W.) 112:1-47.
- Rice, P.J., Anderson T.A., and J.R. Coats. 1997. Evaluation of the Use of Vegetation for Reducing the Impact of De-icing Agents. In Phytoremediation of Soil and Water Contaminants. Kruger, E.L., Anderson T.A., and J.R. Coats Editors. American Chemical Society Symposium Series 664. Orlando, Florida; pp 162-176.
- Robinson, B.H., Brooks, R.R., and B.E. Clothier. 1999. Soil Amendments Affecting Nickel and Cobalt Uptake by Berkheya coddii: Potential Use for Phytomining and Phytoremediaiton. Annals of Botany. 84: 689-694.
- Sawhney B.L., Pignatello J.J., and S.M. Steinberg. 1988. Determination of 1,2-Dibroethane (EDB) in Field Soils Implications for Volatile Organic Compounds. Journal of Environmental Quality. 17(1): 149-152.
- Schnoor, J.L., Litch, L.L., McCutcheon, S.C., Wolfe, N.L. and L.H. Carreira. 1995. Phytoremediation of Organic and Nutrient Contaminants. Environmental Science & Technology. 29(7): 318A-323A.
- Schnoor, J.L., 1997. *Phytoremediation: Technology Evaluation Report.* Groundwater Remediation Technologies Analysis Center. <a href="http://www.gwrtac.org/html/tech\_eval.html#PHYTO">http://www.gwrtac.org/html/tech\_eval.html#PHYTO</a>
- Shimp, J.F., Tracy, J.C., Davis, L.C., Lee, E., Huang, W., Erickson, L.E. and J.L. Schnoor. 1993. Beneficial Effects of Plants in the Remediation of Soil and Groundwater contaminated with Organic Materials. Critical Reviews in Environmental Science & Technology. 23: 41-77.
- Shone, M.G.T. and A.V. Wood. 1972. Journal of Experimental Botany. 23, 141.
- Steinberg S.M., Pignatello J.J., and B.L. Sawhney. 1987. Persistence of 1,2-Dibromoethane in Soils Entrapment in Intraparticle Micropores. Environmental Science & Technology. 21(12): 1201-1208.
- Stomp, A.M., Han, K.H., Wibert, S., Gordon, M.P., and Cunningham, S.D. 1994. *Genetic Strategies for Enhancing Phytoremediation*. Annals of the New York Academy of Science. 721:481-491.
- Thompson, P.L., Ramer, L.A., and J.L. Schnoor. 1998. *Uptake and Transformation of TNT by Hybrid Poplars*. Environmental Science & Technology. 32(7): 975-980.
- Trapp, S., McFarlene, C., and M. Matthies. 1994. *Model of Uptake of Xenobiotics ino Plants Validations with Bromacil Experiments*. Environmental Toxicology and Chemistry. 13(3): 413-422.

- US Air Force-IRP. 1998. Fuel Spill 28 Groundwater Plume. Massachusetts Military Reservation (MMR) Fact Sheet #98-10. http://www.mmr.org/cleanup/fs28fact.htm
- U.S. Environmental Protection Agency (USEPA), 1998. A Citizen's Guide to Phytoremediation. EPA/542/F-98/011. Office of Solid Waste and Emergency Response, August 1998. <a href="http://clu-in.org/products/citguide/phyto2.html">http://clu-in.org/products/citguide/phyto2.html</a>.
- U.S. Environmental Protection Agency (USEPA). *Integrated Risk Information System (IRIS)* on 1,2-Dibroethane. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment. <a href="http://www.epa.gov/ngispgm3/iris/subst/0361.htm">http://www.epa.gov/ngispgm3/iris/subst/0361.htm</a>
- U.S. Environmental Protection Agency (USEPA). *Ethylene Dibromide*. Office of Air Quality Planning and Standards. <a href="http://www.epa.gov/ttnuatw1/hlthef/ethyl-di.htm">http://www.epa.gov/ttnuatw1/hlthef/ethyl-di.htm</a>
- U.S. Department of Health and Human Service. Registry of Toxic Effects of Chemical Substances. National Toxicology Information Program, National Library of Medicine, Bethesda, MD. 1993.
- Weaver, M. Fisher, Cohen S.Z., and J.J. Pignatello. 1998. Environmental Chemistry of Ethylene Dibromide. Agricultural Impacts on Groundwater Conference. DesMoines, Iowa.
- Weintraub, R.A., Jex G.W., and H.A. Moye. 1986. Chemical and Microbial Degradation of 1,2-Dibromoethane (EDB) in Florida Groundwater, Soil and Sludge. American Chemical Society Symposium Series. Washington, D.C. 315: 294-308.
- Zablotowicz, R.M., Hoagland, R.E, Locke M.A., and W.J. Hickey. 1995. Glutathione-S-Transferase Activity and Metabolism of Glutathione Conjugates by Rhizosphere Bacteria. Applied and Environmental Microbiology. 61(3):1054-1060.
- Zayed, A., Lytle, M.C., and N. Terry. 1998. Accumulation and Volatilization of Different Chemical Species of Selenium by Plants. Planta. 206:284-292.