EVALUATION OF GRANULAR ACTIVATED CARBON ADSORPTION TO REMEDIATE ETHYLENE DIBROMIDE CONTAMINATION AT FUEL SPILL 28 AT THE MASSACHUSETTS MILITARY RESERVATION

by

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B.S., Civil and Environmental Engineering
University of California at Berkeley, 1995

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

MASTER OF ENGINEERING
in Civil and Environmental Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 1998

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Abstract

The Massachusetts Military Reservation (MMR) is a Superfund site located on Cape Cod, Massachusetts. Military activities at the MMR have resulted in several groundwater plumes consisting of mostly chlorinated solvents and petroleum hydrocarbons. Ethylene Dibromide (EDB) was identified as the main contaminant in one of the groundwater plumes, Fuel Spill (FS) 28. Fuel Spill 28 has recently contaminated the cranberry bogs located south of the MMR, close to the town of Falmouth. An estimated total of $1 million was spent to destroy the tainted cranberry crop from 1997 and to reimburse the farmers.

As an interim action, a pump-and-treat system using granular activated carbon (GAC) has been installed at the site to prevent exposure of the residents to EDB, to contain the EDB plume, and to prevent the plume from further contaminating the economically important cranberry bogs. The use of granular activated carbon is currently considered the best available treatment (BAT) method for EDB. Unfortunately, breakthrough of EDB occurred after only 69 days of operation; the bed-life was originally estimated to range from 210 to 540 days. This unexpected need for changeout and reactivation of the carbon beds adds significant costs to the system.

The objective of this study was to evaluate the use of granular activated carbon adsorption at Fuel Spill 28. Possible explanations for the pre-mature breakthrough were explored using isotherm data developed by Calgon Carbon Corporation and a number of simple analytical models. The possible explanations that were investigated include overestimation of carbon bedlife, desorption, backwashing, bacterial growth, competitive adsorption, and pre-loading due to total organic carbon. Based on the analysis performed, it can be concluded that the carbon bedlife was likely overestimated. Using the advection dispersion equation resulted in carbon bedlives ranging from about 60 days to 130 days (accounting for dispersion). Other calculations that ignore the effects of dispersion, such as the equilibrium column model, resulted in an over-estimate of the carbon bedlife; calculations which were derived directly from the isotherm data significantly overestimated the bedlife. The findings of this study also showed that other factors may have affected the carbon bedlife as well. While pre-loading and competitive adsorption may be feasible explanations at FS-28, no conclusion could be drawn due to insufficient data collected at the site. Desorption following the backwashing event and bacterial growth, however, are likely contributing factors to the pre-mature breakthrough.

Thesis Supervisor: Dr. Harry Hemond
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ACKNOWLEDGEMENTS

I would first like to thank my advisors Prof. Harry Hemond and Prof. Phil Gschwend for their intelligence, patience and enthusiasm. Special thanks to Prof. Hemond for being encouraging when it seemed like this thesis was never-ending. I also want to thank Trish Culligan for her support and guidance when I needed it most.

My deepest and warmest gratitude goes to Prof. Dave Marks who always had an open door for us. You are just one of a kind ! I'd also like to thank Jackie and Muriel for being support and Cynthia Stewart who has definitely eased the work-load by being flexible when necessary.

I would also like to thank Pete Shanahan and especially Bruce Jacobs for their ideas and continuing support. Special thanks also to Ed Pesce, Tom Zsymoniak at Jacobs Engineering, Laura Foster at Jacobs Engineering, Bill Naylor at Norit, and Mark Stenzel at Calgon Carbon Corporation for the information and suggestions.

Many thanks to Ricardo and his wife Marie-Jose (you guys mean a lot to me !), Amparo, Peter and Janani, Sharon, Ana, Jerry, Thu, and Vitto for their positive attitude, continous support and friendship. I will really miss you guys a lot and hope you will visit whereever I may be! Special thanks to Derrick who shared those very long nights with us in the MENG room and saved my life with Gummy Bears. You all made my life here at MIT not only more fun, but also more meaningful.

Thanks to my long-distance friends, especially Kristi, Cheri, Gabi, Nancy, Amy, Karen, Mika, Ron, and Scott who have been there in the past and have helped me grow into what I am today. Sorry you can't be here for this graduation ! Thanks also to Steve Crane and Jacky Bowen for their guidance over the past years.

Charles, thanks so much for everything – I couldn't have made it without your help and support ! I will never be able to thank you for all you did for me !

Special thanks also to Marilee and Tim. I am indebted for all you have given to me. You have helped me overcome rough times and have encouraged my every endeavor. Love you !

Finally to my family, my Dad who has been there for financial and moral support and my brother and his family who have helped me see that there is more to life than studying. My love also goes out to my Mom – I wish you could have lived to see me graduate from MIT and share this moment with me. You instilled the strength and determination in me which allowed me to come this far. Thanks !

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1. INTRODUCTION

Historically, the Massachusetts Military Reservation (MMR), located on the upper western part of Cape Cod, was used as a military reservation by the Army, the Navy, and the Air National Guard (ANG). Past releases of hazardous materials have resulted in widespread contamination of both soil and groundwater in the reservation. Documented sources of contamination comprise former motor pools, landfills, fire-fighting training areas, and drainage structures such as dry wells. Wastes generated from these activities include oils, solvents, antifreeze, battery electrolytes, paint, waste fuels, metals, and dielectric fluids from transformers and electrical equipment (E.C. Jordan, 1989). Several major groundwater plumes have been found to be migrating from these source areas and have been defined during extensive investigations of the area.

1.1 Context

One of the major groundwater plumes, Fuel Spill (FS-28), has recently contaminated the cranberry crops located south of the MMR, close to the town of Falmouth. The U.S. Environmental Protection Agency (USEPA), Massachusetts Department of Environmental Protection (MADEP), and Massachusetts Department of Public Health (MA DPH) have determined that the use of contaminated surface and groundwater for agricultural purposes presents an unacceptable risk to public health and the environment. Additionally, the groundwater contamination from FS-28 has also affected local water supplies, resulting in the closure of private drinking water wells and the associated need for alternative water supplies. Tourism is one of the main sources of income at Cape Cod during the summer months. Therefore, the perception of risk from untreated groundwater plumes might hinder economic growth on the Cape and result in lost revenues. For these reasons, it is important to treat the contaminated groundwater in order to reduce chemical concentrations in the aquifer to "acceptable" levels both for regulatory agencies as well as the public.

As an interim action, a pump-and-treat system was installed downgradient of the hotspot concentration at FS-28 in October 1997. Currently, the groundwater, which is contaminated with ethylene dibromide (EDB), is being extracted and treated with granular activated carbon (GAC); the treated water is being discharged to nearby surface water bodies. This interim action has been implemented as a time-critical action to: 1) prevent the exposure of the residents in the Town of Falmouth to EDB, 2) to contain the EDB plume, and 3) to prevent the plume from further contaminating the cranberry bogs.

1.2 Problem Identification

Most sites that involve contaminated groundwater use pump-and-treat systems to achieve cleanup goals. Typically, conventional pump-and-treat systems extract relatively large volumes of water with relatively low contaminant concentrations. Because of the geologic complexity and slow rates of contaminant desorption and dissolution, these systems typically displace many pore volumes of aquifer water to flush out the contamination. Conventional pump-and-treat systems are therefore inherently inefficient for removing contaminants from the subsurface (Daniel, 1993).

Alternatives for the remediation of EDB-contaminated groundwater have not been as thoroughly researched as those for the other more common contaminants, such as the chlorinated solvents or hydrocarbon compounds, typically associated with military sites. A permeable reactive wall, developed by the University of Waterloo, could provide a remedial alternative to the current pump-and-treat system at FS-28. Based on laboratory experiments, zero-valent iron, which is the reactive medium in the permeable wall, readily degrades EDB. However, because the FS-28 plume is very deep at its point of highest concentration, installation of a reactive wall may be cost-prohibitive.

Treatment of the contaminated water being extracted by the pump-and-treat system is currently achieved with GAC, which is considered the best available treatment (BAT) method for EDB. Although the system only went into operation in October 1997, a carbon changeout occurred in February 1998, after breakthrough was detected in the lead carbon canister following 69 days of operation; the carbon bedlife was originally estimated to range from 210 to 540 days. The need for changeout (and reactivation) of the carbon beds after an unexpectedly short period of operation will greatly add to operation and maintenance costs of the system unless the situation can be improved.

1.3 Objectives

The focus of this study was to answer the following questions:

- What are the mechanisms of GAC adsorption ?
- What could be some of the reasonable explanations for the early breakthrough occurring at the FS-28 treatment system ?
- Can the current pump-and-treat system be improved by using different types of adsorptive media or by altering operating conditions ?

In order to answer these questions, a thorough understanding of the FS-28 groundwater plume was necessary. Available background information was summarized from previous reports and from contacts with Jacobs Engineering. To conduct an in-depth evaluation of the current treatment system, it was also important to understand the dominant fate and transport mechanisms of EDB.

1.4 Scope

The ensuing sections present the following information:

- Section 2, *Background Information,* provides background information about Cape Cod and the MMR and also discusses why aquifer restoration at the Cape is important.
- Section 3, *Current Site Conditions at Fuel Spill 28,* thoroughly describes the current site conditions of the FS-28 plume. This includes a description of the extent of

contamination, previously conducted investigations, suspected source areas, geologic and hydrogeologic settings, as well as the current remedial actions at the site.

- Section 4, *Fate and Transport Mechanisms of Ethylene Dibromide,* presents background information on the fate and transport mechanisms of EDB.

- Section 5, *Use of Granular Activated Carbon Adsorption for Hotspot Removal at Fuel Spill 28,* describes the GAC treatment technology and provides some possible explanations for the pre-mature breakthrough occurring at the system currently operating at FS-28.

- Section 6, *Suggested Improvements and/or Alternatives to Carbon Adsorption*, evaluates the use of alternatives to carbon adsorption and also provides some suggestions for improvements of the current system at FS-28.

- Section 7, *Conclusions*, provides the conclusions of this study.

2. BACKGROUND INFORMATION

The following sub-sections provide background information on Cape Cod and the Massachusetts Military Reservation, its history, population and land use. They also give a brief description of the contamination present at the military reservation and explain the importance of remediating the contaminated aquifer.

2.1 Cape Cod

2.1.1 Location

Cape Cod is located in southeastern Massachusetts, as shown in Figure 2-1. It is surrounded by Cape Cod Bay to the north, Buzzards Bay to the west, Nantucket Sound to the south, and the Atlantic Ocean to the east. Cape Cod is separated from the rest of Massachusetts by a canal.

2.1.2 Climate

The climate of western Cape Cod is temperate, with expected annual temperatures ranging from 19 to 81 degrees Fahrenheit (°F). Occasionally, seasonal extremes exceed these limits. Temperatures are commonly moderate due the proximity to the Atlantic Ocean and associated Gulf Stream. Wind speeds typically range from 9 to 12 miles per hour (mph), with storm velocities of 40 to 100 mph. The prevailing winds along Cape Cod are heavily influenced by the Atlantic Ocean and the Gulf Stream. From November through March, the prevailing winds arise from the northwest, whereas from April through October, the prevailing winds originate from the southwest (ANG, 1995).

2.1.3 Hydrology

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 the winter months (LeBlanc *et al.*, 1986). The one-year/24-hour rainfall event for 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 by plants. The remaining 45% infiltrate to recharge the groundwater (LeBlanc *et al.*, 1986).

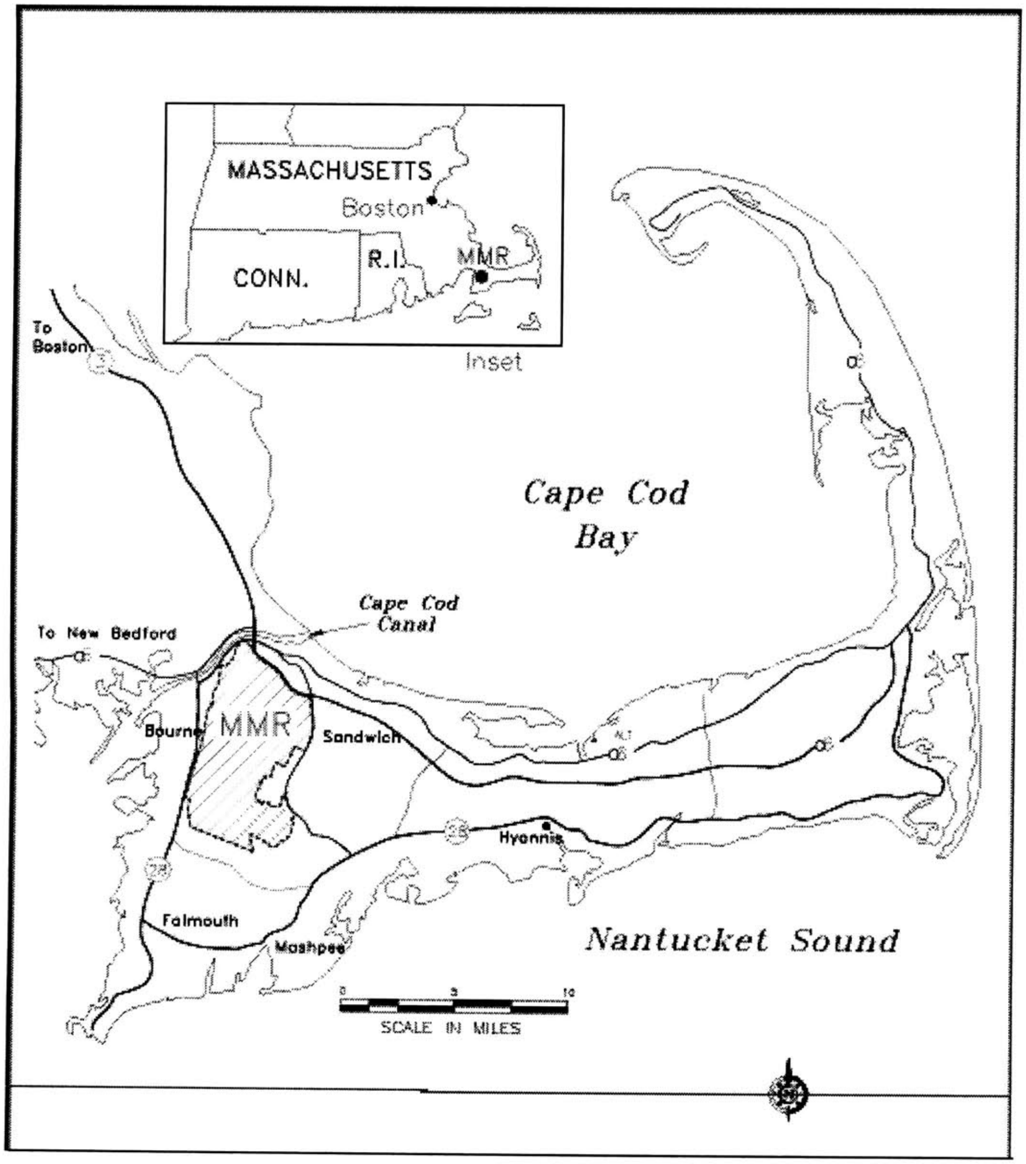

Figure 2-1: Location of Cape Cod and the Massachusetts Military Reservation

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

2.1.4 *Hydrogeology and Topography*

The geology of western Cape Cod was shaped during the Wisconsin period, 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. To the south is the Mashpee Pitted Plain, an outwash plain containing poorly sorted, fine- to coarse-grained outwash sands overlying finer-grained till and marine or lacustrine sediment. This lower layer of fine sediment has a hydraulic conductivity that is as much as five times lower than that of the upper outwash layer, so that groundwater flow occurs mostly through the permeable upper layer. Seepage velocity within the sand and gravel outwash is estimated to range from 1 to 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 kettle holes are maintained mostly by groundwater recharge (E.C. Jordan, 1989).

The topography of the area can be characterized 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 the west by recessional moraines and hummocky, irregular hills. Remnant river valleys cross the Mashpee Pitted Plain from north to south, while to the north and west the Buzzards Bay and Sandwich Moraines lend a higher degree of topographic relief (E.C. Jordan, 1989).

2.2 Massachusetts Military Reservation

2.2.1 *Setting and Description*

The MMR, 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 (Figure 2-1). The MMR consists of facilities operated by the U.S. Coast Guard, the Army National Guard, the U.S.

Air Force, ANG, Veterans Administration, and the Commonwealth of Massachusetts. Most facilities are located in the southern portion of the reservation. The northern portion consists of numerous firing ranges. The MMR is comprised of four principal functional areas (Jacobs, 1997c):

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

2.2.2 *History*

Since its origin in 1911, a variety of activities have been conducted on the MMR, including troop development and deployment, fire-fighting, ordinance development, testing and training, aircraft and vehicle operation and 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 Guard, U.S. Army National Guard (ANG), 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 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. The use of petroleum fuel products and industrial solvents was at a height during these periods; it was common practice for many years to dispose of such wastes in landfills and dry wells, and to use them at firefighting training areas. As a result, contaminants were released to the unsaturated zone.

2.2.3 *Land Use*

Land uses adjacent to the MMR include residential, commercial, recreational, agricultural, and wildlife management. Land use at the MMR is generally limited to supporting military training with some residential and recreational usage. Most of the daily activities occur in the southern portion of the reservation. In the northern portion of the reservation, approximately 80% of the total area is undeveloped scrub forest and fields. Most of this area is divided into firing ranges, but also serves as habitats for various indigenous and migratory wildlife. Civilian access to the entire area is strictly controlled and, for most areas, is completely prohibited because of the threat of unexploded ordnance.

The population of the towns adjacent to the MMR fluctuates significantly between winter (29,000) and summer (70,000) due to tourism. The permanent population of the MMR amounts to approximately 2,000 people, primarily in on-base housing maintained by the U.S. Coast Guard. Additionally, an estimated 800 non-residents are employed year-round within various Department of Defense (DOD) and other operations. Periodic activities associated with training military reserve personnel can increase the base population by several hundred to several thousand (Cape Cod Commission, 1996).

2.3 Soil and Groundwater Contamination at the MMR

The MMR is located on top of a recharge area that supplies water to all the towns surrounding the base. In 1978, the town of Falmouth detected detergents in a public water-supply well located south of the MMR wastewater treatment plant. The United States Geological Survey (USGS) immediately began conducting groundwater investigations and soon identified a groundwater plume extending south of the treatment plant and into 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 (MMRIRP, 1997c).

Between 1982 and 1985, investigations at the MMR revealed 73 contaminated soil and groundwater sites. Since 1985, five additional sites have been identified, bringing the total number of contaminated sites to 78. As of September 1996, the ANG and regulators concluded that 31 of the 78 sites at the MMR pose no threat to the public nor the environment and therefore require no further action (MMRIRP, 1997c). As a result of the investigations conducted at the base, 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)

In 1993, the ANG, in conjunction with the USEPA, MADEP, and various citizen groups, began addressing the groundwater plumes at the MMR. These groups worked in concert to develop a containment program that called for 100%, simultaneous remediation of the groundwater plumes. However, evaluation of the design in 1996 revealed that simultaneous containment was not possible without adversely impacting the ecosystems of Cape Cod due to excessive watertable drawdown. As a result, a Technical Review and Evaluation Team (TRET) was established to evaluate alternatives to the 100%, simultaneous containment design.

In May 1996, TRET concluded that the groundwater plumes would undergo a phased remediation approach (MMRIRP, 1997c). In July 1996, a Strategic Plan was published that outlined the Plume Response Project (PRP). This project defined the remedial action and construction schedule for each of the plumes at the site. However, the remedial action outlined in the PRP is merely an "interim action" (MMRIRP, 1997c). The PRP is not the final solution for the groundwater plumes, but rather a short-term solution preventing further contamination. The long-term solutions, ones that address the bodies of the plumes rather than their advancing fronts, are still under investigation.

2.4 Importance of Remediating the Contaminated Aquifer

Water resources at the Cape and the MMR are being used in a number of different areas, including:

- public water supply (drinking water and recreational uses)
- agricultural irrigation/cranberry cultivation,
- industrial and commercial use, and
- habitat for a wide variety of fish and wildlife.

Groundwater is an important source of public water supply, both for recreational uses as well as drinking water (Massachusetts Department of Environmental Management, 1994). The Sagamore Lens, the largest lens of the Cape Cod Aquifer, provides drinking water to over 70,000 homes and businesses in the towns of Sandwich, Falmouth, Mashpee, Barnstable, Bourne, and Yarmouth. In fact, the Cape Cod aquifer has been designated as a sole source aquifer by the USEPA, meaning that it is the only source of potable water for the residents, businesses, and visitors to the area. The MMR itself has a yearly population of about 2000 people while the population of the surrounding towns fluctuates between the winter and summer seasons. During the off season in 1990, an average of 12.5 million gallons per day were supplied from the lens (Massachusetts Department of Environmental Management, 1994). Twice as much water is needed during the summer months due to tourism.

Groundwater is also used for irrigating agricultural crops at Cape Cod. Cranberry bogs are most affected by the groundwater and surface water contamination due to the flooding practices described in Section 3. The other agricultural crops which are affected by the contamination include strawberries and vegetables. Approximately one million gallons of water were used in 1996 during the six-month growing season (Jacobs, February 1997b).

3. CURRENT SITE CONDITIONS AT FUEL SPILL (FS) 28

In 1992, EDB was discovered in groundwater in the vicinity of the leading edge of the Chemical Spill No. 4 (CS-4) plume (Figure 3-1). Since 1992, several investigations were conducted to delineate the extent of the plume and to pinpoint a source area. The plume was officially designated as FS-28 in November of 1996 (Jacobs, 1997b). Based on an isoconcentration contour of 0.02 μg/L (inferred from currently available field investigation results), the plume is roughly 9,000 feet long, has a maximum width of 3,000 feet and varies in thickness up to 100 feet (MMRIRP, 1997a). EDB is the primary contaminant of concern (COC) in the FS-28 plume.

The FS-28 plume area has been divided into the upper, middle, and lower study areas. The current remedial efforts are concentrated on the lower study area, which contains the toe of the FS-28 plume (shown in Figure 3-1). Therefore, the following sections refer to the lower study area of the FS-28 plume.

The FS-28 groundwater plume was not included as part of the Record of Decision (ROD) for Interim Action (Stone & Webster, 1995) which addressed six of the groundwater plumes emanating from the MMR. A remedial investigation study for the Southwest Operable Unit (SOU) is currently underway to more accurately define the nature and extent of the EDB plume, to identify other possible areas of contamination, and to conduct extensive water and sediment testing of the Coonamessett Pond, Deep Pond, and the Broad and Coonamessett Rivers, which are those water bodies closest to the FS-28 groundwater plume (MMRIRP, 1998).

3.1 Location of FS-28

The upgradient extent of the FS-28 plume is located in the Crane Wildlife Management Area, in the town of Falmouth. As shown in Figure 3-2, the plume has a north-south orientation and is bounded 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 narrow and is located upgradient of Thomas Landers Road. The plume axis at the toe generally parallels and is coincident with the Coonamessett River (Jacobs, 1997a).

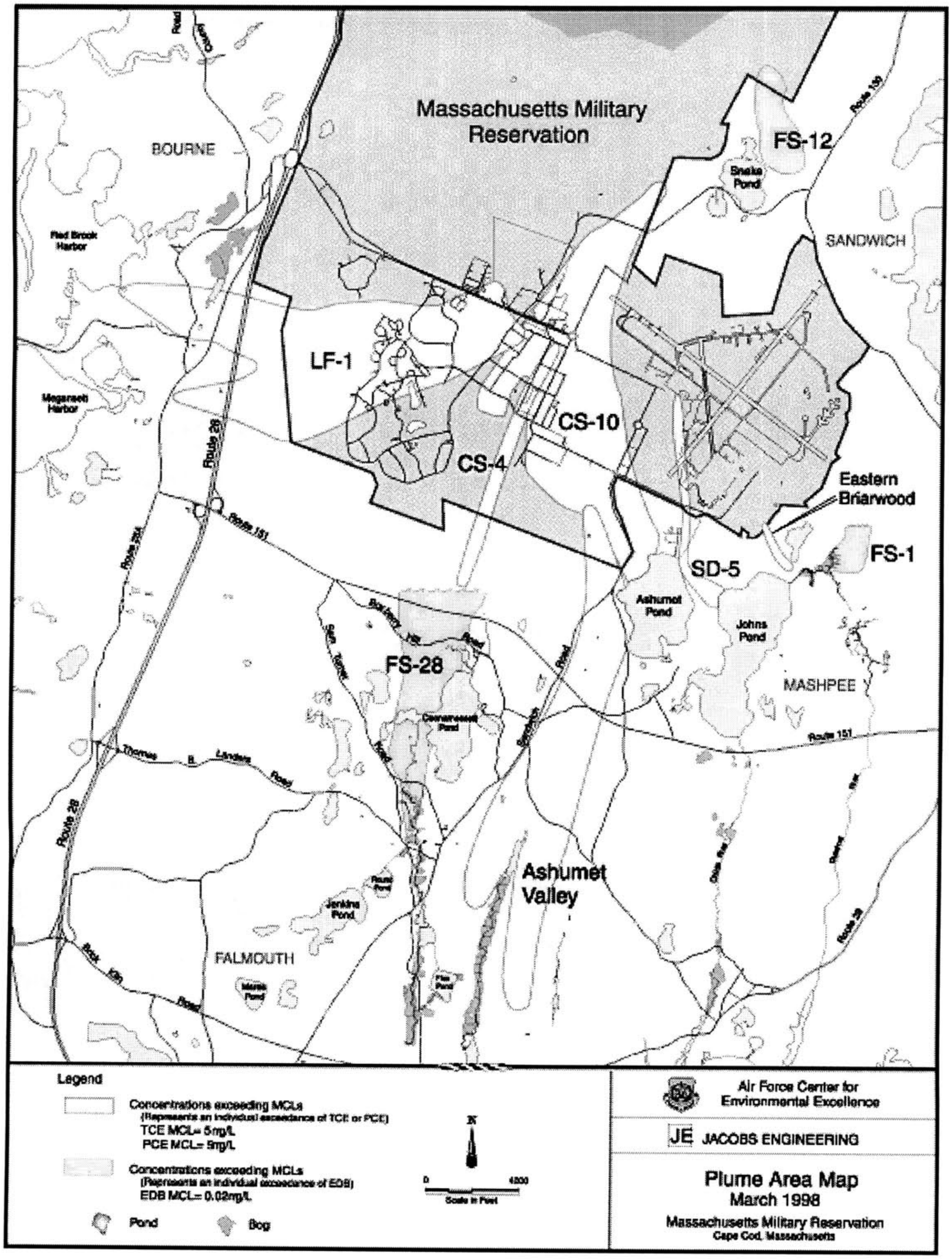

Figure 3-1: Location of the Groundwater Plumes at the MMR

(MMRIRP, 1998)

3.2 Previous Field Investigations

During a field investigation conducted at the toe of the CS-4 plume by ABB Environmental Services (Jacobs, 1997a) in April 1993, the presence of a deep EDB plume was confirmed in the vicinity of the CS-4 extraction well fence. In 1995, ABB-ES conducted another field investigation to define the downgradient extent of the EDB plume. During this investigation, EDB was found upgradient of the extraction well fence and also in the underlying silt-clay unit. At the request of the Installation Restoration Program (IRP), monitoring wells were installed in the vicinity of Falmouth's Coonamessett Water Supply Well (CWSW). When EDB was detected in the deep groundwater samples, the search for the downgradient extent of the FS-28 plume extended further south.

An EDB Remedial Investigation/Feasibility Study (RI/FS) Data Gap Sampling Field Program was conducted by Jacobs in 1996 to determine the downgradient extent of the EDB plume and to assess whether EDB may be entering the Coonamessett Pond or the CWSW (Jacobs, 1997a). During the field program, EDB was detected at higher than previously measured concentrations north of Hatchville Road. Additionally, it was also detected at the top of the water table and in surface water samples collected from a cranberry bog at the Coonamessett River.

3.3 Extent of Ethylene Dibromide Contamination

Streamflow data indicates that there is significant discharge from the aquifer to the river between Hatchville Road and Thomas Landers Road (Jacobs, 1997a). The FS-28 plume appears to be migrating to the surface waters of the Coonamessett River, wetlands, and cranberry bogs shown in Figure 3-3. The area of discharge to the surface water seems to be confined to within a few hundred feet of the Coonamessett River Channel and can be inferred from surface water and shallow groundwater results. Various numerical models indicate that the remainder 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. Based on modeling results, it is also assumed that the plume is effectively captured in the river valley. The leading edge of the plume is considered to be at monitoring well 69MW1300, south of monitoring well 69MW1284 shown in Figure 3-4 (Jacobs, 1997b).

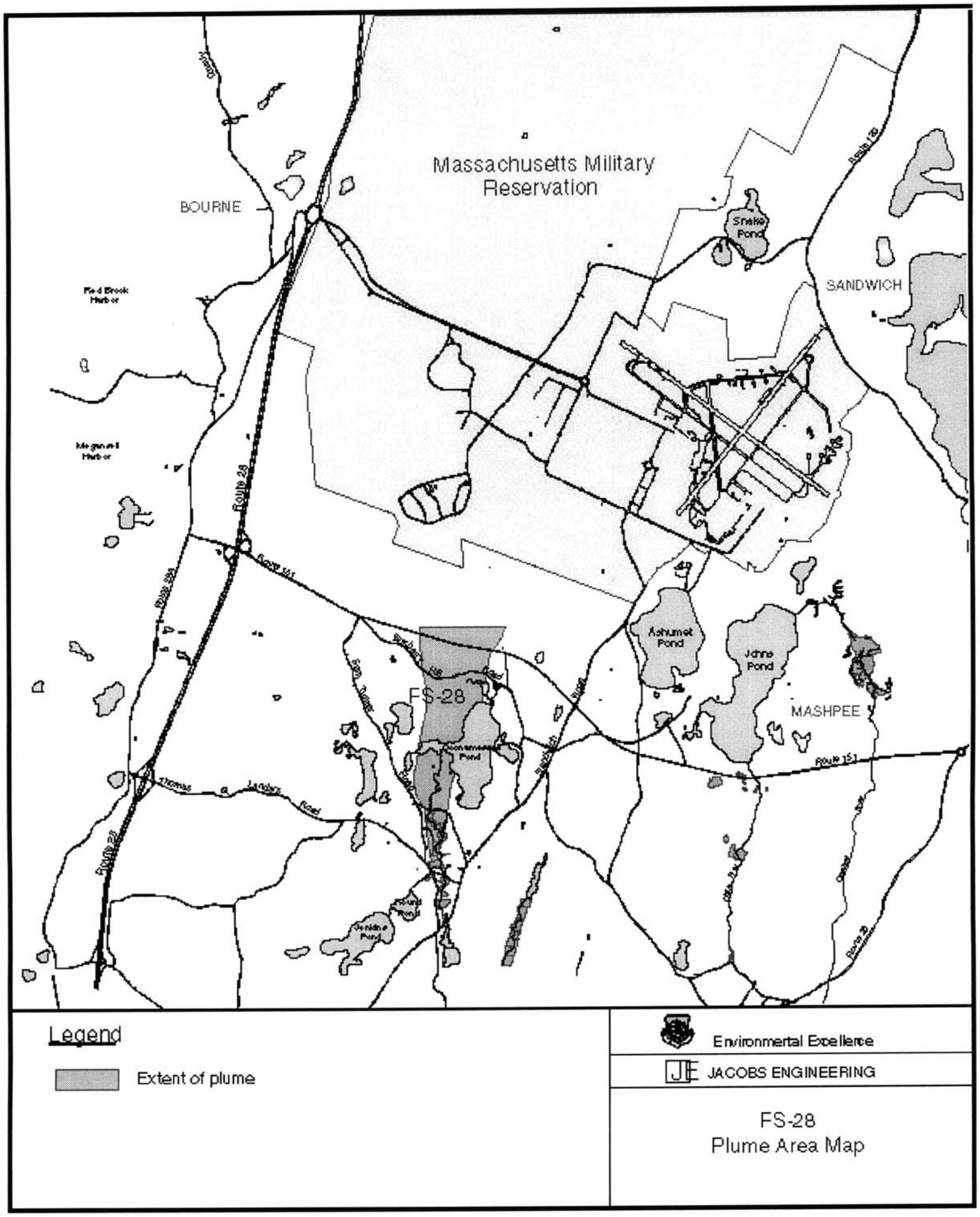

Figure 3-2: Location of the FS-28 Groundwater Plume

(MMRIRP, 1998)

The highest concentration of EDB (11 µg/L) was detected in deep groundwater samples collected from monitoring well 69MW1284A. As shown in Table 3-1, the concentrations of EDB in the shallow groundwater and surface water are not as high as those in deep ground water (ranging in concentration from 0.005 µg/L to 4.1 µg/L in shallow groundwater and from 0.010 µg/L to 0.096 µg/L in surface water). As expected, concentrations in the shallow groundwater are higher than the concentrations in the surface water where the EDB is discharging to the surface. This distribution pattern is consistent with the conceptual model in which EDB concentrations decrease after reaching the surface due to natural attenuation. EDB was not detected in the sediment samples collected from the Coonamessett River, which could be attributed to the concept that EDB might be undergoing natural attenuation, specifically reductive dehalogenation in the anaerobic sediment of the river. At the CWSW site, EDB has been detected at concentrations of 0.23 µg/L in samples collected from an adjacent well screened approximately 195 feet below the bottom of the supply well screen (Jacobs Engineering, 1997b).

Table 3-1: Summary of EDB Detections in the Lower Study Area at FS-28

	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)
Deep Groundwater	0.016 (69MW1300A)	11.0 (69MW1284A)
Shallow Groundwater	0.005	4.1
Surface Water	0.010	0.096
Coonamessett Sediment	ND	ND

(Source: Jacobs, 1997a)
J - Is a qualifier that indicates that the value is estimated
ND - Not Detected
µg/L - Micrograms per Liter

Notes:
1) The maximum values from off-site and field analytical laboratory data are reported here.
2) The current MCL for EDB in Massachusetts is 0.02 µg/L.

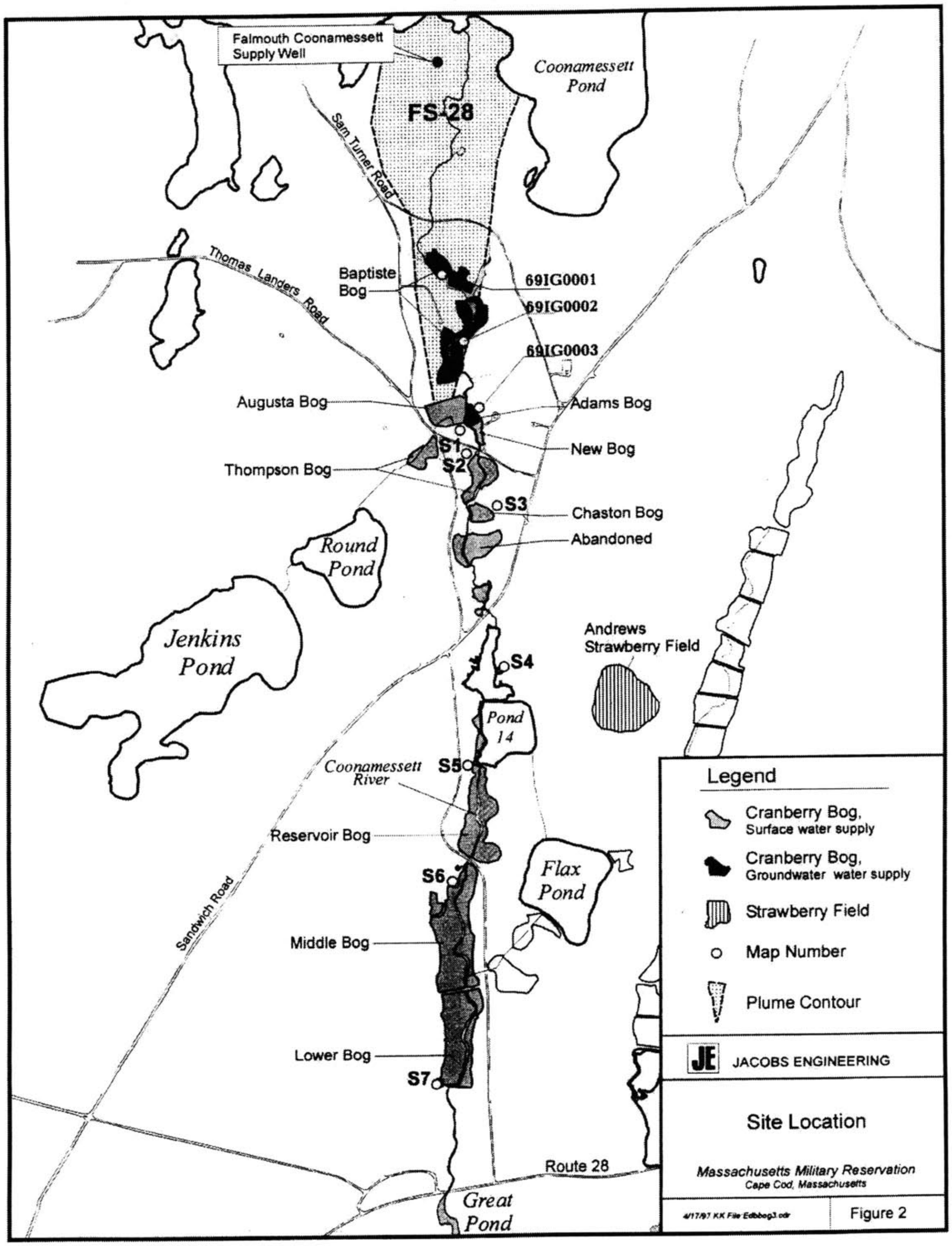

Figure 3-3: Locations of Cranberry Bogs Potentially Affected by the FS-28 Groundwater Plume

(Source: Jacobs, 1997b)

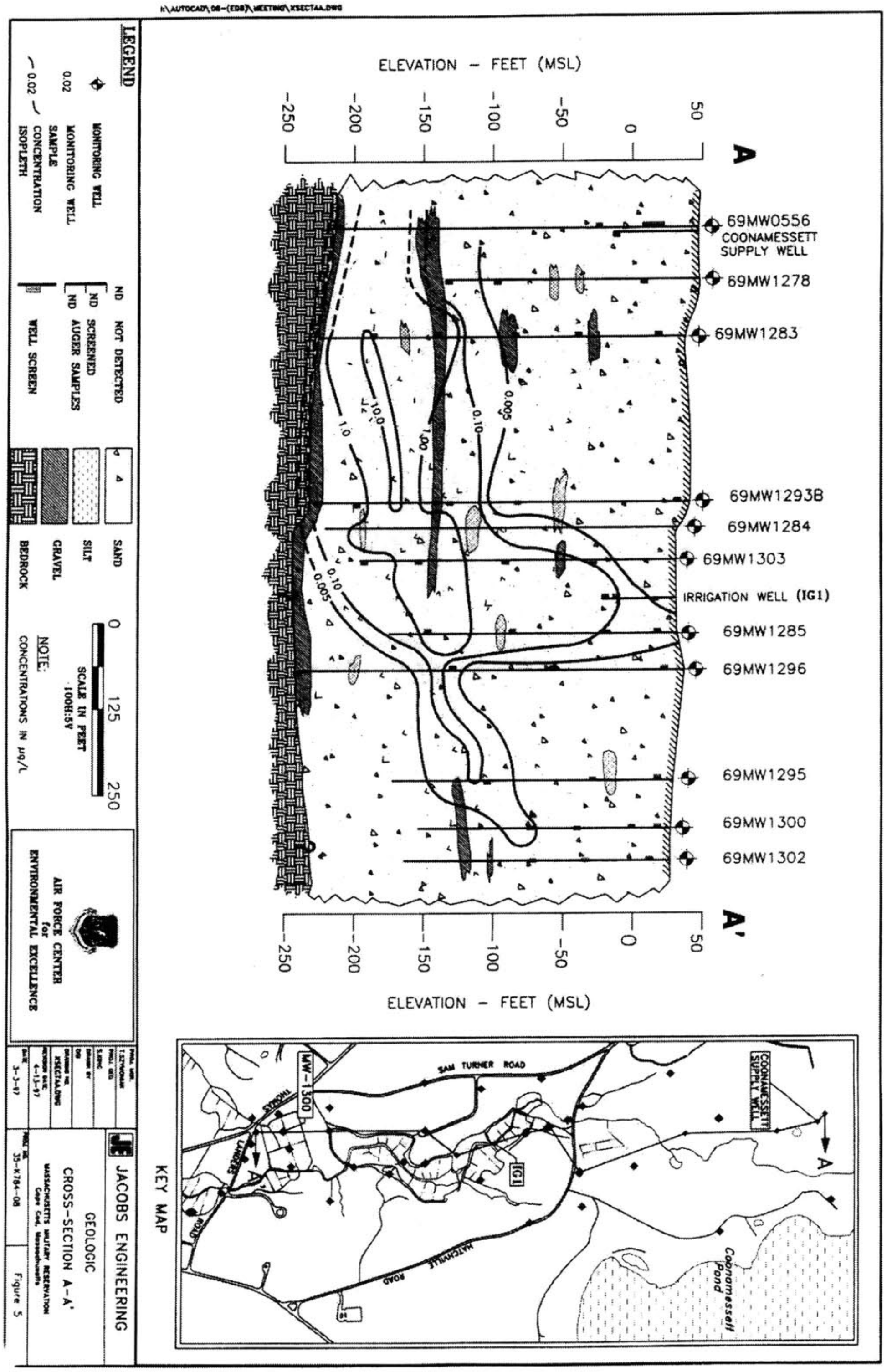

Figure 3-4: Vertical Extent of Contamination at FS-28

(Source: Jacobs, 1997b)

3.4 General Chemistry of Groundwater at FS-28

As shown in Table 3-2, trichloroethylene (TCE), tetrachloroethene (PCE), toluene, chloroform, carbon tetrachloride, and methylene chloride were detected in the samples collected from the monitoring wells in the lower study area of FS-28. The only other compounds detected in shallow groundwater samples included toluene and 1,1-dichloroethylene (1,1-DCE). These volatile organics may be associated with the FS-28 plume; however, a strong correlation has not been established.

Background manganese concentrations appear to be slightly higher in the area and low concentrations of semivolatile organic compounds (SVOCs) were detected in three wells. Manganese or SVOCs are not considered to be contaminants of concern for this groundwater plume (Jacobs, 1997b).

3.5 Source Areas

At this time, a definite source of the FS-28 plume at the MMR has not been established and it is likely that no definite source area can be linked to the plume. Appendix A of the Draft Fuel Spill (FS-28) Plume Technical Decision Memorandum (Jacobs, 1997a) identified a number of sites upgradient of FS-28 that could realistically be responsible for the plume.

During the investigation conducted by Jacobs Engineering, previous releases (including the dates, volumes, location, and chemical constituents) were investigated. Study areas were broken up into: non-EDB sources, limited/partial EDB sources, partial EDB sources, significant EDB sources, 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. Additionally, confirmed spillage of fuels and associated laboratory analyses were also considered.

Jacobs Engineering concluded that FS-28 was not produced by a single source; rather, a combination of upgradient multiple sources is responsible for the EDB plume (Jacobs, 1997a).

Table 3-2: Chemistry of Deep Groundwater at FS-28

Compound	Maximum Concentration (µg/L)	Minimum Concentration (µg/L)	Frequency of Detection	Max. Contaminant Level (MCL) (µg/L)
Dissolved Metals				
Aluminum	40 J	ND	5/21	200
Arsenic	ND	ND	0/21	50
Barium	5.8 J	ND	17/21	2,000
Boron	43.7 J	ND	4/5	-
Cadmium	1.6 J	ND	2/21	5
Calcium	7,560	1,280	21/21	-
Chromium	3.7 J	ND	2/21	100
Copper	9 J	ND	14/21	1,000
Iron	1,110	ND	8/21	300
Lead	22.3	ND	13/21	5
Magnesium	2,990	887	21/21	-
Manganese	184	3.5 J	21/21	50
Mercury	0.69	ND	2/21	2
Nickel	3.2 J	ND	4/21	100
Potassium	1,840	644 J	16/21	-
Silver	1.7 J	ND	1/21	100
Sodium	14,600	5,280	21/21	-
Vanadium	ND	ND	0/21	-
Zinc	28.4	ND	20/21	5,000
Anions				
Bromide	0.47	ND	15/21	-
Choride	12 J	7.8	21/21	-
Diss. Orthophosphate	0.069 J	0.02	9/9	-
Fluoride	0.2	ND	11/14	-
Nitrate as N	1.2	ND	17/20	-
Nitrite as N	0.01	ND	2/20	-
Phosphorus, Total	ND	ND	0/7	-
Sulfate	9.6	ND	21/21	-
VOCs				
Carbon Tetrachloride	0.43 J	0.28 J	-	.5
Chloroform	1.30	0.3	-	-
Methylene Chloride	0.80	0.80	-	5
Tetrachloroethylene	0.26 J	0.26 J	-	5
Toluene	15.00	0.081 J	-	150
Trichloroethylene	1.10	0.20 J	-	5
SVOCs				
Bis(2-E.) phthalate	25.00	25.00	-	-
Isopropylbenzene	0.73	0.73	-	-
General Parameters [a]				
D. O. (mg/l)	16.84	0	-	-
Turbidity (NTU)	250.8	0	-	-
pH	8.69	4.76	-	-
Temperature (°C)	13.28	9.72	-	-

(Source: summarized from Jacobs Engineering, 1997b)

"-" Not applicable or not available

J - Estimated Value

Notes:

[a] General Parameters were obtained from monitoring field sampling parameters

D.O. - Dissolved Oxygen
NTU - Nephelometric Turbidity Unit
SVOC - Semivolatile Organic Compound
VOC - Volatile Organic Compound

Due to the presence of EDB in the western and eastern lobes of CS-10 and the presence of preferential pathways for contaminant migration at CS-10, this plume was identified as the only significant source area. Jacobs also concluded that cranberry bogs, farms, and golf courses are not potential sources as pesticides other than EDB were used. Additionally, other study areas (including CS-4) were identified as partial sources for FS-28. These sites had a history of motor fuel and aviation gasoline spills containing EDB and displayed moderately favorable aquifer characteristics (Jacobs, 1997a).

3.6 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. Additionally, approximately 68 acres of agricultural crops south of Hatchville Road are irrigated from either groundwater wells or surface water. Table 3-3 presents a summary of the agricultural water usage for the affected cranberry bogs. The other agricultural crops include strawberries and vegetables. The farmers of these crops draw surface water from Pond 14 for frost protection and irrigation. Approximately one million gallons of water were used in 1996 during the six-month growing season (Jacobs, 1997a).

Table 3-3: Summary of Agricultural Water Usage

Parcel Description	Crop	Water Source	Required Flowrate (gpm)
Baptista Bog	Cranberry	GW	800
Auguste Bog	Cranberry	SW	600
Adams Bog	Cranberry	GW	100
New Bog	Cranberry	SW	150
Thompson Bog	Cranberry	SW	420
Chaston Bog	Cranberry	SW	100
Andrews	Strawberries	SW	800
Reservoir Bog	Cranberry	SW	650
Middle Bog	Cranberry	SW	1,200
Lower Bog	Cranberry	SW	900

(Source: Jacobs, 1997b)

Notes:

GW – Groundwater

SW – Surface Water

gpm – gallons per minute

The cultivated bogs are typically flooded in late November to early December to prevent frost damage to the cranberry vines. Due to an unusually warm winter, bogs were flooded in 1997/1998 from mid-December to mid-February. During flooding, the Coonamessett River is dammed up, raising the water level from 0.5 to 2 feet over the area of the cultivated bogs. Upward vertical gradients are reduced under flooded conditions, keeping the groundwater from flowing into the bogs (Jacobs, 1997a).

In 1998, the irrigation of the cranberry bogs began in early spring using treated water from the treatment plant. For frost control, spray irrigation has been conducted and will continue as needed until mid-June. From mid-June to October, the fields will be irrigated as needed to provide at least 2 inches of water on the crop per week. During the fall, the bogs are harvested either dry or wet.

3.7 Geologic Setting

Previous investigations indicate that the FS-28 middle and lower study areas are underlain by glacial outwash sediments composed of tan, fine to coarse sand with lesser amounts of silts and gravel (less than 10%). The sands are relatively well-sorted to approximately 120 feet mean sea level (msl), and become 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). 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. Bedrock has typically been encountered at elevations ranging from 220 to 243 feet msl (Jacobs, 1997a).

3.8 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 is the Upper Cape Cod's only potable water source. The aquifer is unconfined and is recharged by infiltration and precipitation. Recharge is approximately 1.6 feet/year, with seasonal variations producing fluctuations in the water table of 1 to 3 feet. Groundwater flows out radially from the recharge mound (Jacobs, 1997a).

A value of 380 ft/day has been accepted as a representative value of average hydraulic conductivity for the outwash sands (on a regional scale) at the MMR (Tillman, June 1996). Using an average hydraulic gradient of 0.002 ft/ft and a porosity of 0.39, average linear velocities ranging from 0.25 to 2.5 ft/day can be calculated for the outwash sands (Jacobs, 1997b).

Vertical gradients at FS-28 range from almost horizontal flow (0.0003 ft/ft) to strongly upward flow (0.0039 ft/ft). Upward vertical gradients were observed along the western edge of the study area. Groundwater was observed seeping into the drainage ditches bordering the cranberry bogs. Artesian conditions were observed in the bogs.

Based on a pumping test conducted at the CWSW, the full thickness of the outwash aquifer at this site has a transmissivity of approximately 86,000 to 100,000 ft^2/day. Furthermore, aquifer response to pumping indicated 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 silt-free layers.

3.9 Current Modeling Efforts

The U.S. Geological Survey (USGS) is conducting studies in the vicinity of the FS-28 plume and has performed a particle tracking analysis to simulate the contaminant transport, especially as influenced by the Coonamessett Pond. Additionally, the USGS is conducting studies to date the age of the groundwater plume in the FS-28 study area, which might be beneficial in better identifying source areas.

Numerical modeling (using MODFLOW) was undertaken by Jacobs to evaluate the migration of the FS-28 plume, potential discharge locations, and remedial alternatives. MODFLOW was run under both flooded and non-flooded conditions in the cranberry bogs. To estimate travel times, hydraulic conductivity was approximated at 250 ft/day and effective porosity was estimated at 0.24. Jacobs predicted that the effective porosity was not likely to vary more than 20% in either direction and therefore, travel times ought to be within 20% of the estimated value as well. Plume migration was simulated with particle tracking using MODPATH. This model generates pathlines for ground-water flow from the MODFLOW output and captures the most significant transport – advection (Jacobs, 1997a).

Preliminary results for the modeling indicate that the Coonamessett River and the cranberry bogs present a strong sink for groundwater and plume discharge. Particle tracking indicates that the upper fringes of the FS-28 plume would discharge in 1998 immediately downstream of Hatchville Road, but the bulk of the deeper plume would not discharge significantly within the five-year time period simulated. If flooded conditions were maintained, the plume would generally travel farther; however, there would still be some discharge of the plume to the bogs between Hatchville and Thomas B. Landers roads. According to Jacobs, the irrigation wells, if operated at their maximum flowrates, could potentially have a significant influence on the long-term migration pathway of the plume. The irrigation wells, if used as capture wells, would only be able to capture the upper portion of the plume and could allow some of the plume to pass beneath. Due to the limitations of the model, an evaluation of the most leading part of the plume could not be conducted thoroughly (Jacobs, 1997a).

3.10 Time-Critical Actions

The EPA, DEP, and MA DPH have determined that the use of EDB-contaminated surface and groundwater for agricultural purposes represents an unacceptable risk to public health and the environment. An Action Memorandum (Jacobs Engineering, 1997b) has been prepared to serve as the primary decision document for the remedial action at FS-28. The proposed removal action is being implemented by the Air Force as a time-critical action to: 1) prevent the exposure of the residents of the Hatchville area in the Town of Falmouth to EDB, 2) to contain the EDB plume, and 3) to prevent the plume from further contaminating the cranberry bogs.

The Air Force Center for Environmental Excellence (AFCEE) has taken immediate actions to eliminate any exposure or potential exposure to EDB, including:

- Installation of a granular activated carbon wellhead treatment system at the CWSW and at the irrigation well screened in the EDB plume,
- Installation of an extraction well to intercept the deep portion of the EDB plume,
- Supply of bottled water to residents in the Hatchville community,
- Provision of an alternative water supply to the Falmouth community,
- Installation of irrigation wells outside the EDB plume, and
- Definition and monitoring of the plume.

3.11 Summary

The FS-28 plume was discovered in 1992 south of the CS-4 plume. The plume is roughly 9,000 feet long, has a maximum width of 3,000 ft and varies in thickness up to 100 feet. It has a north-south orientation and is bounded by Coonamessett Pond on the east, Deep Pond on the west, and Thomas Landers Road on the south. The leading edge of the plume is narrow and the axis of the plume generally parallels the Coonamessett River. Due to the significant discharge from the aquifer to the Coonamessett River, the FS-28 plume migrates to the surface water, wetlands, and cranberry bogs south of Hatchville Road. The area of discharge can be inferred from surface water and shallow groundwater results and seems to be confined to a few hundred feet of the Coonamessett River. Based on modeling, the leading edge of the plume is assumed to continue to the south to eventually surface again along the river north of Great Pond.

EDB is considered the only significant contaminant of concern at FS-28. The FS-28 plume area has been divided into the upper, middle, and lower study areas. The current remedial efforts are concentrated on the lower study area, which contains the toe of the FS-28 plume. To address remediation, the lower study area has been divided up into three major areas to be addressed:

- The hotspot area, which contains the 10 μg/L isoconcentration;
- The portion of the plume which upwells into the cranberry bogs; and
- The leading edge of the plume which continues to travel to the south.

Modeling of the current extraction well has shown that it is not possible to address all of these areas of contamination in one remediation scheme. In order not to disturb the ecology at the Coonamessett River, the extraction well is pumping at a maximum flowrate of 750 gpm. This pumping rate, however, will not capture the portion of the plume which surfaces in the cranberry bogs nor the leading edge of the FS-28 plume. It has been assumed that the leading edge of the plume will attenuate naturally (dispersion, hydrolysis, sorption, etc.) so that the concentrations downstream should not pose a threat to receptors. The following sections will address the remedial scheme at FS-28.

4. FATE AND TRANSPORT MECHANISMS OF ETHYLENE DIBROMIDE

Groundwater contamination results in an increased risk to human health and the environment as well as an economic threat to public water systems. As a result, it is important to restore the groundwater resources. In order to remedy groundwater contamination, it is necessary to understand the basic physical, chemical, and biological properties of the contaminants and to evaluate their governing fate and transport mechanisms. The purpose of this section is to review the available environmental chemistry of EDB in order to assess its fate in soil and groundwater. This section will also discuss the uses of EDB, its regulatory history, mobility, and persistence.

4.1 Background Information

4.1.1 General Description (CAS Number 106-93-4)

Ethylene dibromide, also known by the chemical names EDB, ethylene bromide, and 1,2-dibromoethane, is a non-flammable, colorless liquid with a mildly sweet odor. At a concentration of 10 parts per million (ppm) in air, the average person can detect EDB. Ethylene dibromide has been used as a fumigant and also as a fuel additive as outlined in the following sub-sections.

4.1.2 Regulatory History

Ethylene dibromide was first detected in groundwater in 1980 in Hawaii (Mink, 1981; Oki and Giambelluca, 1987). In 1982, it was detected in some Georgia farms wells and in the following year, EDB was found in groundwater in California and Florida (USEPA, 1983a). With the increasing incidence of EDB in groundwater and the combined evidence of this chemical's toxicity as well as its leaching potential, the USEPA issued an emergency order suspending the registration of EDB as a soil fumigant in September 1983 (USEPA, 1983b). The USEPA concluded that the use of EDB posed an imminent health hazard. The current maximum contaminant level (MCL) set in the United States is 0.05 μg/L; the MCL set by the State of Massachusetts is 0.02 μg/L.

4.1.3 *Toxicity*

Ethylene dibromide can be adsorbed via dermal, oral, and inhalation routes; with all of these exposures, it produces tumors in rats and mice. Ethylene dibromide is also a reproductive toxin, but is does not appear to be teratogenic. Limited information indicates that EDB can damage the liver and kidneys following extensive or prolonged exposure; however, few human poisonings have been reported from either acute or chronic exposure.

Initial risk estimates indicated that citrus fruit workers exposed to EDB had a 100% chance of contracting cancer. Revised estimates of occupational exposure indicated a lower risk, but the risk estimates still range from 1 to 40 excess cancer cases per 10,000 persons exposed (Alexeeff *et al.*,1990).

4.2 Uses of Ethylene Dibromide

The following sections describe the past uses of EDB as a soil fumigant and additive to gasoline and aviation fuel.

4.2.1 *Use of Ethylene Dibromide as a Fumigant*

The use of EDB as a pre-plant soil fumigant constituted over 90% of all agricultural uses in the U.S. and is undoubtedly the principal source of EDB groundwater contamination nationwide. By 1983, nearly 23 million lbs of EDB (as an active ingredient) were applied to about 400,000 ha of a variety of crops in the U.S., including citrus fruits, potatoes, tobacco, and tomatoes (Pignatello and Cohen, 1990). The heaviest application rates probably occurred in the Florida citrus groves.

When used as a soil fumigant, EDB was injected as a liquid directly into the soils. The relatively high vapor pressure led researchers to believe that EDB would readily volatilize in the soil and therefore, pesticide applicators were advised to seal the soil surface with water or an impervious cover which increased the potential for leaching (Weaver *et al.*, 1988).

4.2.2 *Use of Ethylene Dibromide as a Fuel Additive*

Ethylene dibromide was also used as a lead scavenger in leaded gasoline and aviation fuel. In 1983, an estimated 260 million lbs/year of EDB were used as an additive to gasoline (Weaver *et al.*, 1988). It is estimated that EDB constitutes approximately 0.03% by weight of gasoline containing 1.1 g of lead/gal (Weaver *et al.*, 1988). Hoag (1984) found an average EDB concentration of 178 ppm in leaded gasoline while unleaded gasoline has much lower concentrations of EDB, ranging from 0.1 to 7.2 ppm. Aviation gasoline is thought to contain twice as much EDB as leaded gasoline (Pignatello and Cohen, 1990). Underground Storage Tanks (USTs) are known to leak and some groundwater contamination resulted from these leaks or accidental fuel spills. If EDB is present in combination with other soluble gasoline constituents, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), the contaminant source is likely fuel.

4.3 Physical and Chemical Properties of EDB

In order to evaluate the governing fate and transport mechanisms, it is important to understand the physical and chemical characteristics. Table 4-1 below presents a summary.

Table 4-1: Physical and Chemical Properties of EDB

Property	Numerical Value
Formula	$BrCH_2CH_2Br$
Molecular Weight	187.88
Density	2.17 g/cm^3
Melting Point	9.79 °C
Boiling Point	131 °C
Vapor Pressure	10.8 mm Hg (25 °C) 7.7 mm Hg (20 °C)
Water Solubility	4,250 mg/L (25 °C) 3,370 mg/L (20 °C)
Henry's Law Constant, K_H	0.0345 (25 °C) 0.0246 (20 °C)
Octanol-Water Partition Coefficient, log K_{OW}	1.76 - 1.93
Soil Partition Coefficient, log K_{OC}	1.643 – 1.699
Diffusion Coefficient in Dry Air, D^{air}	0.0813 cm^2/s (20 °C)
Diffusion Coefficient in Water, D^{water}	1.0 x 10^{-5} cm^2/s (25 °C)
Bioconcentration Factor, log BCF	0.301-0.778

(Source: Pignatello and Cohen, 1990; Weaver *et. al.*, 1988, Mackay *et al.*, 1993; Montgomery, 1955)

As shown above, EDB is a low molecular weight compound. Solubility is one of the most important characteristics governing a chemical's fate. Because EDB is moderately soluble compared to other chemicals, it tends to be transported quickly through the aquifer. As shown in the table above, EDB does not have a high affinity for soils. Its soil/water distribution coefficient, K_d, has been reported to be less than 3 which is significant since Cohen *et al.* (1984) stated that pesticides with a K_d value of less than 5 have the potential to leach into groundwater if they are persistent.

It should be noted, however, that despite these low reported values of K_d, residual EDB can become trapped in soil micropores. As a result, K_d values from desorbing EDB from treated soil were extremely high (Weaver *et al.*,1988).

4.4 Fate and Transport of EDB

The following sections describe the pertinent fate and transport mechanisms of EDB. The fate of this chemical is governed by its physical and chemical properties as well as the chemical, physical, and microbiological processes in the aquifer.

4.4.1 Vadose Zone Transport

Mostly, transport of EDB in soil is governed by volatilization, advection, and dispersion. Other factors that will influence vadose zone transport, such as microbial degradation, sorption, and abiotic transformations are discussed in Section 4.4.2.1.

Volatilization

Because of its vapor pressure and Henry's Law Constant, a fraction of EDB will volatilize from the soil. The volatilization half-life of EDB was calculated by Jury *et al.* (1984) to be 0.4 days and 3.4 days at a soil depth of 1 cm and 10 cm, respectively.

Advection and Dispersion

Because of its density, EDB will move into the soil when applied or spilled at the surface. In the subsurface, EDB will degrade, dissolve in soil moisture, or diffuse into soil pore spaces. Vapor and liquid diffusion in the soil is controlled by Fick's Law and studies of EDB have shown that vapor diffusion (as opposed to liquid diffusion) will dominate until the water content becomes a high percentage of total porosity.

The advective mobility of a compound in soil will depend on the fraction that has partitioned into the liquid phase. Therefore, advection in the vadose zone is influenced by the water content and the organic content of the soil.

4.4.2 Saturated Zone Transport

Volatilization does not occur readily in groundwater. As mentioned above, EDB is moderately soluble in water. It travels slower than groundwater itself, but faster than most other volatile organics, including toluene and benzene. Since dissolved EDB does not change the density of water appreciably, an EDB-contaminated plume in an aquifer will move along the flow paths of bulk groundwater. The velocity, size, shape, and distribution of the plume will be subject to the influences of sorption and dispersion of the solute.

4.4.3 Other Controlling Mechanisms

The following sections discuss the effects of microbial transformations, sorption, and abiotic transformations which will also influence the fate of EDB.

Microbial Transformations

A review of available biodegradation data pertaining to EDB concluded that this chemical is biotransformed quite readily in the environment; lifetimes can be as short as several days in surface soils and as long as many months in aquifer materials (Pignatello and Cohen, 1990). Based on laboratory studies, EDB is degraded under all redox conditions, except possibly denitrifying. Products of microbial transformations include the bromide ion, carbon dioxide, and ethylene. It must be noted that there is no evidence of microbial degradation of EDB outside of laboratory experiments where EDB is the only available electron acceptor (Jacobs, 1997g). It should also be noted that, at high concentrations, EDB is toxic to bacteria. The portion of EDB entrapped in micropores of the soil is inaccessible to microbial degraders and chemical processes.

Sorption

Sorption can affect the transport of EDB both in the vadose as well as the saturated zone. Furthermore, degradation rates are also affected by sorption since organic compounds are less available for microbial attack in the "sorbed state".

As shown in Table 4-1, EDB does not have a high affinity for soils contradicting which contradicts the evidence that EDB was found in the topsoil of several agricultural sites at concentrations of up to 300 μg/Kg up to 19 years after the last known fumigation. This contradiction may be attributable to the concept of non-equilibrium sorption. This concept is not well understood; however, it is believed to result from slow kinetics, dominated by molecular diffusion. It has been suggested that sorption of a chemical is rate-limited by diffusion through the small pores between fine soil grains. The strong occlusion of EDB in the case-study mentioned above was thought to be a result of physical entrapment in the soil micropores.

Abiotic Transformations

There is increasing evidence that abiotic transformations may play a role in determining the subsurface fate of EDB. The most important processes involved are hydrolysis and reactions with sulfur nucleophiles. Photolysis is not discussed due to the limited penetration of sunlight in the soil column. Several studies have been conducted to investigate hydrolysis of EDB. All authors agree that under ambient, pure laboratory conditions, the hydrolysis half-life for EDB is at least two years and probably longer (Weaver *et al.,* 1988).

Ethylene dibromide is readily attacked by sulfur nucleophiles, most importantly hydrogen sulfide, which is a product of anaerobic microbial activity in the aquifer. Recent work of several researchers led to the conclusion that the reaction of EDB with sulfur nucleophiles can be highly competitive with neutral hydrolysis depending on ambient sulfide concentrations and that the transformation products from this reaction, i.e., alkyl sulfides, will differ from the neutral hydrolysis reaction products (Weaver *et al.*, 1988).

5. USE OF GRANULAR ACTIVATED CARBON ADSORPTION FOR HOTSPOT REMOVAL AT FUEL SPILL 28

As described in Section 3.11, from a technical perspective, the contaminated areas at FS-28 ought to be addressed in three "phases." The first phase should address removal and treatment of the highest concentrations (hotspot) within the plume. Phase 2 should address those parts of the plume that are not captured by the extraction well and upwell into the cranberry bogs and surface waters of the Coonamessett River; Phase 3 ought to verify that the leading edge of FS-28 does not pose a threat to downgradient receptors. This section will focus on the removal and treatment of the highest concentrations (hotspot) of the lower portion of the FS-28 plume.

5.1 Interim Remedial Action

As an interim action, one extraction well (69EW0001) has been installed in the northern portion of FS-28 (south of monitoring well MW1284A, shown in Figure 3-4) and has been extracting water at a flowrate of approximately 670 gpm. The extracted water is currently being treated with GAC and then discharged to nearby surface water bodies. Initial influent levels of EDB were at 4.7 μg/L; however, they leveled off to 0.8 μg/L during the treatment period. The interim treatment system went into operation on October 14, 1997. Breakthrough occurred in the lead canister on December 22, 1997, following only 69 days of operation and the carbon bed was changed out on February 10, 1998. The carbon bedlife was originally estimated to range from 210 to 540 days (Jacobs, 1998).

5.2 Final Remedial Action

A final remedial alternative has not been chosen for the lower study area at FS-28. A feasibility study will be conducted to determine which technology will address the overall and long-term objectives most efficiently.

5.3 Pump-and-Treat Technology

Between 1982 and 1992, about 73 percent of the cleanup at Superfund sites used pump-and-treat technology. At that time, however, the limitations of pump-and-treat systems were not fully recognized as large-scale studies of the effectiveness of pump-and-treat systems were not yet available. In 1989, the EPA conducted a review of 19 sites where pump-and-treat systems were operating and concluded that at none of these sites was the aquifer restored to drinking water standards (USEPA, 1989a,b,c). A review of 77 sites where the efficiency of pump-and-treat systems was studied by the National Research Council (NRC, 1994) concluded that pump-and-treat systems appear to be capable of restoring groundwater at sites with simple geology and dissolved contaminants; however, at most sites, the operation of the pump-and-treat system should be viewed as a long-term project, in which the system design is modified in response to improved understanding of the site conditions.

Only two remedial technologies, namely pump-and-treat using GAC and air stripping, have been found to reduce EDB significantly. Based on a study conducted by Environmental Science and Engineering (Beaudet, 1983), air stripping is 99% effective in removing EDB from water while pump-and-treat with GAC is considered 100% effective in removing EDB. Because of the low concentrations of EDB in the influent and the extremely low MCL set by the State of Massachusetts (0.02 μg/L), GAC adsorption was chosen as an interim action for the remediation at FS-28.

5.3.1 Effectiveness of Pump-and-Treat Systems

The effectiveness of a pump-and-treat system depends heavily on hydrogeologic and contaminant properties. Two types of contaminant characteristics can complicate groundwater cleanup significantly: 1) the tendency of the chemical to sorb to solid materials; this is not expected to pose a problem at FS-28, and 2) the tendency of organic contaminants to remain in the form of a non-aqueous phase liquid (NAPL). Heterogeneities of the soil further complicate the cleanup, as geologic complexities can affect the efficiency of the pump-and-treat system by causing tailing of the contaminant concentrations in the aquifer. Contaminant tailing has been observed with chlorinated solvents, and it has been found, that while the concentration of the contamination in the extracted groundwater declines, it never reaches zero, even after two or more plume volumes have been extracted. In the literature, tailing has been attributed to the presence of NAPLs, the effects of sorption, and heterogeneities in hydraulic conductivity (Domenico and Schwartz, 1990).

For EDB, however, pump-and-treat systems might be moderately effective as this technology is focused on where the bulk of the contaminant mass exists – the groundwater.

5.3.2 Cleanup with Pump-and-Treat Systems

To determine the feasibility of cleanup of the FS-28 hotspot with a pump-and-treat system, the following parameters need to be determined:

- Total estimated mass of EDB contamination,
- Vertical and horizontal extent of contamination,
- Configuration of the extraction system, and
- Estimated cleanup time.

5.4 Treatment with Granular Activated Carbon (GAC)

The use of carbon for its adsorptive qualities was known as early as 1550 B.C., when charcoal was utilized in the purification of medicines. Current industry is now taking advantage of GAC to remove a variety of organic compounds from water (Nyer, 1992). Activated carbon adsorption is regarded as the basis by which other technologies are measured. This section will review the basic mechanisms of carbon adsorption and provide some possible explanations for the early breakthrough at the FS-28 GAC treatment system.

5.4.1 Granular Activated Carbon

The adsorbent most frequently used in environmental applications is activated carbon. The following sub-sections will review the background information on the manufacture, types, characteristics, and regeneration of activated carbon.

5.4.1.1 Manufacture

Activated carbon is prepared by producing a char from various materials including almond, coconut, walnut hulls, woods and coal. The char is produced by heating the material to expel the hydrocarbons, but under conditions with insufficient air to sustain combustion. The char particle is then activated by chemical or steam activation. These processes develop a porous structure and creates a large internal surface area (Tchobanoglous and Burton, 1991). The use of different raw materials as well as processing allow for many different types of activated carbon, each differing in adsorption and regeneration characteristics.

5.4.1.2 Types

Activated carbon is available in three general forms: granular, pellets, and powder -- the application determines which form is most applicable. Carbon used in the gaseous-phase adsorption typically consists of the granular form. Generally, liquid-phase carbons are either powdered or granular and tend to have the same surface area as gas-adsorbing carbons, but have larger total pore volumes (Cheremisinoff and Cheremisinoff, 1993). Powdered activated carbon (PAC) is more commonly used in biological treatment systems.

5.4.1.3 Adsorbent Characteristics

Since adsorption is possible only in those pores that can be entered by molecules, the carbon adsorption process is dependent on the physical characteristics of the activated carbon and the molecular size of the adsorbate. Therefore, surface area and pore structures are two very important factors in the adsorption process. Examination of a microscopic cross-section of activated carbon reveals a porous structure with a large internal surface area. The following criteria have to be considered in the selection process of an appropriate adsorbent:

- Surface Area – the larger the surface area of the adsorbent, the higher the adsorption. Typically, bituminous carbon (Calgon Filtrasorb 300) has an internal surface area of approximately 1,000 m^2/g (USEPA, 1971).

- Bulk Density – a measure to determine carbon quantity. Typical bulk densities for Calgon Filtrasorb 300 ranges from 0.45 to 0.48 g/cm^3 (28 to 30 lb/ft^3)
- Pore volume – a measure to determine how readily a contaminant can be adsorbed; the pore volume is about 0.85 cm^3/g for Calgon Fitrasorb 300 bituminous carbon (Cheremisinoff and Cheremisinoff, 1993).
- Particle Size – the effective size of the Calgon Fitrasorb 300 bituminous carbon is 0.8-1 mm (Calgon Carbon Corporation, 1998).

5.4.1.4 Regeneration

Granular activated carbon can easily be regenerated by oxidizing the organic matter through heating. During this process, about 5 to 10 percent of the carbon is typically destroyed and must be replaced. Regenerated carbon is not as efficient as virgin carbon. One major disadvantage to PAC is that its regeneration has not been well defined (Tchobanoglous and Burton, 1991).

5.4.2 Theoretical Adsorption Theory

Adsorption is the process in which a soluble contaminant (the adsorbate) is removed from water by contact with a suitable solid interface (the adsorbent). The amount of adsorption on most surfaces is exceedingly small, but a number of porous solids with an unusually high surface area have been developed, including activated carbon, silica gel, and activated alumina. The two most important types of adsorption are: 1) physical adsorption and 2) chemical adsorption (Cheremisinoff and Cheremisinoff, 1993). Adsorption on activated carbon is of a physical nature. The adsorption process is thought to involve the following steps: macrotransport, microtransport, and sorption.

Macrotransport involves the transport of the adsorbate molecules to the liquid-adsorbent (solid) interface. Macrotransport may be the rate-limiting step in systems that have poor mixing, dilute concentrations of adsorbate, small particle sizes of adsorbent, and high affinity of adsorbate for adsorbents (Helfferich, 1962; Tillman, 1996). Microtransport describes the diffusion of the molecules through the micropore system of the GAC granule to the adsorption sites. It is this process that limits the overall transfer for those systems that have good mixing, large particle-size adsorbents, high concentrations of adsorbate, and low affinity of the adsorbent. Sorption describes the attachment of the organic molecule to the carbon itself. Generally, adsorption is favored by large, less soluble, less polar compounds. Saturated organics are also adsorbed easily, as are branched-chain organics (LaGrega *et al.*, 1994).

5.4.2.1 Adsorption Isotherms

Adsorption equilibrium is obtained when the rate of adsorption onto the solid phase equals the rate of desorption from the solid surface back to the water phase. A plot of the amount of the contaminant sorbed against the concentration of the contaminant in the water is termed the adsorption isotherm. The amount of contaminant that can be taken up by an adsorbent (expressed as weight of contaminant per unit weight of carbon) is referred to as the adsorption capacity, $(\frac{X}{M})$, and represents an equilibrium relationship between the contaminant adsorbed and the contaminant concentration remaining in solution. The adsorption capacity is a function of both the characteristics and concentrations of the contaminant as well as temperature.

There are several forms of isotherms, but most experimentally determined isotherms can be fit with a Freundlich model (Schwarzenbach *et al.*, 1993):

$$\frac{X}{M} = K \bullet (C_W{}^n) \qquad (1)$$

where $\frac{X}{M}$ = *mass of contaminant adsorbed [mg] per dry unit weight of carbon [g], also termed adsorption capacity for GAC*

C_W = *concentration of contaminant in solution after adsorption equilibrium is reached which is assumed to equal the influent concentration,* C_i *[mg/L]*

K, n = *are experimentally determined Freundlich constants at a given temperature, where K has units of [L/g]*

Adsorption isotherms are commonly used to determine carbon usage rates, the amount of carbon needed *[lbs]* to treat 1000 gallons of contaminated water. The mass of contaminant adsorbed in a carbon column can be determined by:

$$X = (C_i - C_e) \bullet V \tag{2}$$

where C_i = *influent concentration [mg/L]*
C_e = *effluent concentration [mg/L]*
V = *Volume of solution [L]*

The constants in the Freundlich isotherm can be determined by plotting $\frac{X}{M}$ versus C_W as follows:

$$Log\left(\frac{X}{M}\right) = log\,K + n\;log\,C_W \tag{3}$$

For solutions with dilute concentrations of contaminants, a straight line should be obtained with *K* as the intercept and *n* as the slope of the line. The value obtained for n for adsorption of most organic compounds by activated carbon is <1. Steeper-line slopes, i.e. when n is close to 1, indicate a high adsorptive capacity at high equilibrium concentrations that rapidly decreases at lower equilibrium concentrations covered by the isotherm. Relatively flat slopes, i.e. n is << 1, indicate that the adsorptive capacity is only slightly reduced at the lower equilibrium concentrations. As the Freundlich equation indicates, the adsorption capacity $\frac{X}{M}$ is a function of the equilibrium concentration of the solute; therefore, higher capacities are obtained at higher equilibrium concentrations (Faust and Aly, 1983).

Given an influent concentration, the theoretical adsorption capacity of the carbon for a particular contaminant can be determined using an adsorption isotherm. However, since this calculation is based on equilibrium conditions and since equilibrium conditions are rarely met in the field (contact times are typically too short), the adsorption capacity as determined from batch tests is generally overestimated. In the field, the carbon is not typically exhausted (i.e., not all adsorption sites are occupied) and, furthermore, the effects of biological activity present in the field are not seen with theoretical adsorption isotherms. Additionally, isotherm tests are typically conducted under steady state conditions, at constant pH, and with virgin carbon, which has a greater adsorption capacity than reactivated carbon. Column tests that simulate the actual operation of full-scale units (and influent concentrations) are therefore required to obtain realistic carbon usage rates for field operating conditions.

5.4.2.2 Multi-Component Influents

Most influents contain a mixture of contaminants and therefore the adsorption isotherms determined in the laboratory represent an ideal-case scenario. Because other contaminants may compete for adsorption sites, the adsorption capacity of any compound may be decreased. Several mathematical models have been developed that allow for a direct computation of the solute loading from known concentrations in the mixture. If the concentrations of the solutes in the mixture are low, no significant decrease is expected in the adsorption capacity (Tillman, 1996).

One of the models developed to describe multi-component adsorption behavior for contaminants at low concentrations (DiGiano, *et al.*, 1978; Tillman, 1996) can be described as follows:

$$\frac{X}{M}i = K'^{\left(\frac{n'-1}{n'}\right)} \bullet (K_i \bullet C_i^{n_i})^{1/n'} \bullet \left[\sum_N \left(\left(\frac{K_i}{K'} \right) \cdot C_i^{n_i} \right)^{\frac{1}{n'}} \right]^{n'-1} \qquad (4)$$

where $\frac{X}{M}i$ = *adsorption capacity of solute i [mg contaminant/g carbon]*

K', n' = *average of all* k_i *and* n_i *constants*

K_i, n_i = *Freundlich constants, describing single solute adsorption*

C_i = *concentration of solute i in the mixture [mg/L]*

N = *number of solutes in the mixture*

This model, developed by DiGiano, Baldauf, Frick, and Sontheimer (DiGiano *et al.*, 1978) is a simplification of the Ideal Adsorbed Solution (IAS) model which was originally developed by Radke and Prausnitz. The IAS model is based on a thermodynamic framework as it relies on the assumption that the adsorbed phase forms an ideal solution. It requires single-solute isotherms to be known which are then used with the initial concentrations of the contaminants to generate loading rates for multi-component solutions. The IAS model is mathematically more complicated, especially in systems that contain more than two components. The model described in equation *(4)* was derived from the same thermodynamic framework and a comparison between this model and the IAS model shows that the two models are in good agreement in a concentration range of less than 0.1 mmol/L (DiGiano *et al.*, 1978). Equation *(4)* can mathematically be reduced to the Freundlich equation for a single-component solution.

5.4.3 Design Criteria at FS-28

To determine the maximum usage from activated carbon, experimental analysis using actual influent concentrations is often necessary. Operating factors such as influent water characteristics, treatment facility configuration, and effluent requirements are controlling criteria in the selection of the appropriate carbon type and mode of application. The following criteria were evaluated during selection and design of the adsorption system for the FS-28 hotspot treatment.

5.4.3.1 Vessel Capacity and Arrangement

Carbon beds of 20,000 lbs have become a standard size, as the spent carbon from a single unit can easily be transported from the site in a single trailer. The two basic liquid-phase equipment designs for carbon adsorption are the fixed-bed and the pulsed-bed arrangements. Fixed-bed systems can take the form of either single or multiple columns which can operate in series, parallel, or both. In most situations, a multiple-column adsorber is used because of the operating flexibility it provides. Fixed single-column systems are only used when the additional cost of another carbon bed can not be justified (Cheremisinoff and Cheremisinoff, 1993). Fixed-bed systems can either have downflow columns, upflow-bed or expanded-bed systems. Continuous, downflow columns are most common. The downflow column is a gravity adsorber that operates as a filter and not a pressure vessel.

The interim system at FS-28 consists of two 10-ft diameter adsorber vessels filled with Calgon F-300 GAC. Each vessel contains 20,000 pounds of virgin bituminous carbon. The system has a two-stage, lead-lag, downflow arrangement, as shown in Figure 5-1. When the effluent from the first column reaches the breakthrough concentration, the leading bed column is removed and the second bed becomes the lead column. This arrangement assures high-quality effluent and complete contaminant removal.

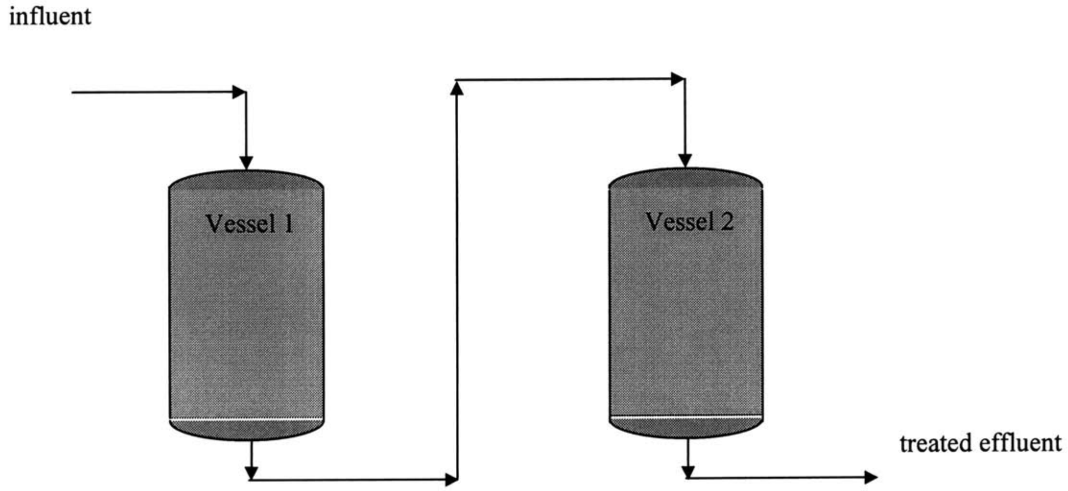

Figure 5-1: Configuration of a typical continuous, downflow column contactor

5.4.3.2 Influent and Effluent Concentrations/Characteristics

Influent concentrations are determined by the concentrations extracted by the pumping wells and will depend on the distance from the source site, the amount of contaminants reaching the aquifer, contaminant solubility and density, and the transformations that the contaminant undergoes. These factors will affect the size of the treatment system and the length of time required for cleanup. The amount of contamination reaching the aquifer will depend on the amount sorbed to the organic carbon present in the subsurface.

The pH at which the adsorption process occurs has been shown to have a strong influence on the extent of adsorption. However, this pH dependence is far more important for ionizable organic chemicals than for EDB (Faust and Aly, 1987). A review of Freundlich constants shows that some compounds, such as benzoic acid, show a strong dependence on pH, while others, such as EDB does not show a strong dependence.

The temperature will affect both the rate of adsorption (kinetics) and the extent to which adsorption occurs (equilibrium). Generally adsorption rates increase with increased temperature; however, since adsorption is an exothermic process, the degree of adsorption will decrease at lower temperatures. The temperature of extracted groundwater is generally constant, ranging from 50 °F to 60 °F and will therefore not influence the adsorption process significantly unless the water is not directly routed to the treatment system and has time to equilibrate with external temperatures.

At FS-28, influent levels of EDB were initially 4.7 μg/L and have subsequently leveled off at approximately 0.8 μg/L. The pH in the influent ranged from 6.19 to 8.08; the temperature of the extracted groundwater was at about 53 °F (Jacobs, 1998).

5.4.3.3 Flowrate

Unlike for industrial wastewater treatment plants, flowrates are a design variable in the design of carbon adsorption systems for the treatment of contaminated groundwater. The flowrate required will depend on the time needed for the cleanup, weighing the effect of flow on the cost of the system. The flowrate should be designed so that the contaminant plume is contained, considering the volumetric flowrate of contaminated groundwater, the number of wells to be installed, and the final use of the treated water.

The system at FS-28 has a maximum design flowrate of 750 gpm, but has been operating at an average flowrate of about 670 gpm.

5.4.3.4 Contact Time

One of the most critical design parameters for any adsorption system is contact time (also termed empty bed contact time [EBCT]). The EBCT is the time required for the flow per vessel to displace the same amount of volume as taken by the GAC bed and depends on the rate-limiting steps described in Section 5.4.2. Observation of the carbon usage rate versus EBCT shows that after an initial rapid decrease in carbon usage rate with increasing EBCT, no significant decrease in usage rate is obtained by further increasing the EBCT (Tillman, 1996). Therefore, an EBCT should be chosen in the region where the carbon usage rate has leveled off to its minimum value. Increasing the depth of carbon for a fixed flowrate or decreasing the flowrate for a fixed depth of carbon serve as methods to increase contact time.

Generally, most EBCT tests (in the laboratory) are conducted with contact times up to 1 hour as EBCTs greater than 1 hour are not considered practical in the field. However, some larger molecules may not reach equilibrium in less than 1 or 2 days and, as a result, isotherms for large molecules determined with 1 hour or less of contact time can only be used as a rough estimate of adsorbability (Najm *et al.*, 1991). As a consequence, field adsorption capacities for such compounds are lower than at equilibrium and need to be adjusted. The effects of short contact times experienced in actual operations or the accurate prediction of activated carbon usage rates can be gauged from a scaled column study. In general, a factor ranging from 0.25 to 0.5 is used in equation (9) (presented in the following section) to account for the adjustment of laboratory conditions to field conditions (Tchobanoglous and Burton, 1991).

Based on studies conducted by Calgon Carbon Corporation, EBCTs of 7.5 minutes (translating to 500 gpm per adsorber vessel) are adequate to achieve treatment objectives (Calgon Carbon Corporation, 1998) for most groundwater systems with low levels of contaminants. The contact time can thus be determined from the flowrate and the volume of carbon per vessel as follows:

$$EBCT = \frac{Bed\ Volume}{Flowrate} = \frac{20{,}000\ lbs}{670\ gpm} \bullet \frac{7.48\ gallon}{ft^3} \bullet \frac{1\ ft^3}{29\ lbs} = 6.5\ minutes \tag{5}$$

At FS-28, an EBCT of 6.5 minutes was designed for each vessel based on an operating flowrate of 800 gpm. (Jacobs, 1998).

5.4.3.5 Loading Rates

In practice, engineers often like to work with flowrates expressed in terms of hydraulic loading in gpm/ft^2. The surface loading rate is based on the cross-sectional area of the column and will vary depending on the EBCT and the vessel diameter. Surface loading rates in GAC systems can be as great as 10 gpm/ft^2. Higher surface loading rates typically result in slightly higher carbon usage rates as the adsorption zone (the area in the column where adsorption is taking place) may be extended, causing contaminant breakthrough to occur sooner (Stenzel, 1989). The downflow packed bed columns are designed so that the granular medium retards any channeling or short-circuiting assuring contact with the carbon (Calgon Carbon Corporation, 1998).

At FS-28, with a flowrate of approximately 670 gpm and a vessel diameter of 10 ft, the surface hydraulic loading can be calculated as:

$$Surface\ hydraulic\ loading\ rate = \frac{Flowrate}{Cross-sec\,tional\ Surface\ Area} = \frac{670\,gpm}{25\pi ft^2}$$

$$= 8.5\ gpm/ft^2 \tag{6}$$

In contrast, there is also a volumetric hydraulic loading which is the inverse of the EBCT:

$$Volumetric\ hydraulic\ loading\ rate = \frac{Flowrate}{Bed\ Volume} = \frac{1}{EBCT} = 0.13\ \frac{1}{min} \tag{7}$$

5.4.3.6 Calculations of Carbon Usage Rates Using Laboratory Isotherms

Both Calgon Carbon Corporation and the USEPA Drinking Water Research Water Division evaluated the removal of trace concentrations of EDB from water by activated carbon adsorption (Calgon Carbon Corporation, 1998). The adsorption isotherm developed by Calgon Carbon Corporation (shown in Figure 5-2 below) was based on influent concentrations on the order of 557 μg/L and was conducted using an isotherm mix time of 24 hours. The following calculations illustrate the estimation of theoretical carbon usage rates based on adsorption isotherms performed in the laboratory. It is important to note that the following equations are based on the assumption that the carbon/water mixture was stirred long enough for adsorption equilibrium to be achieved. This subject will be addressed in more detail later in this section.

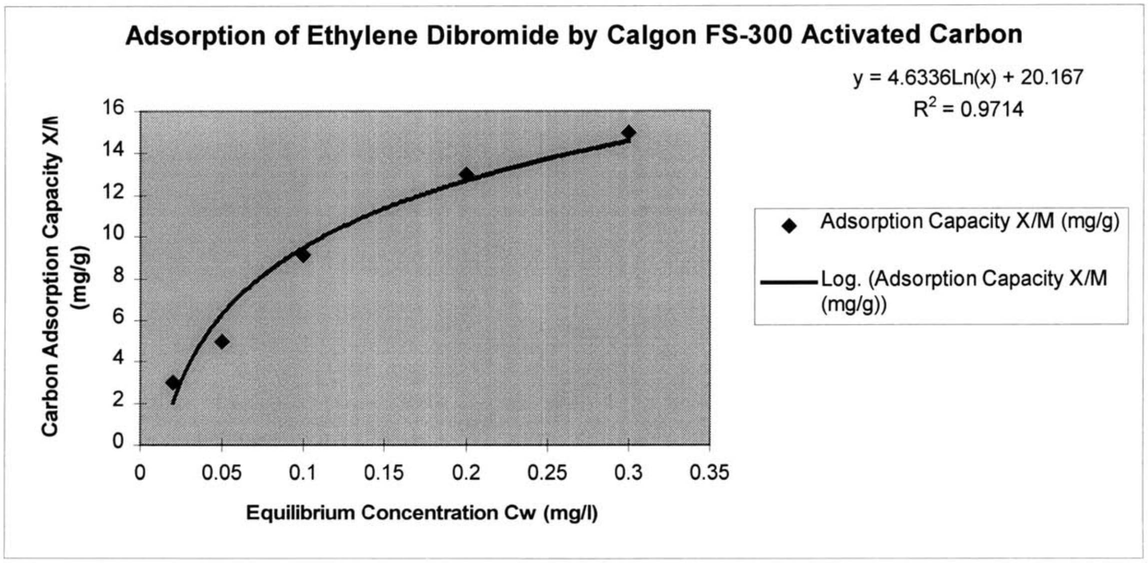

Figure 5-2: Adsorption Isotherm developed by Calgon Carbon Corporation
(Recreated and modified from Calgon Carbon Corporation)

To determine the Freundlich isotherm coefficients, the data was re-plotted on a log-log scale:

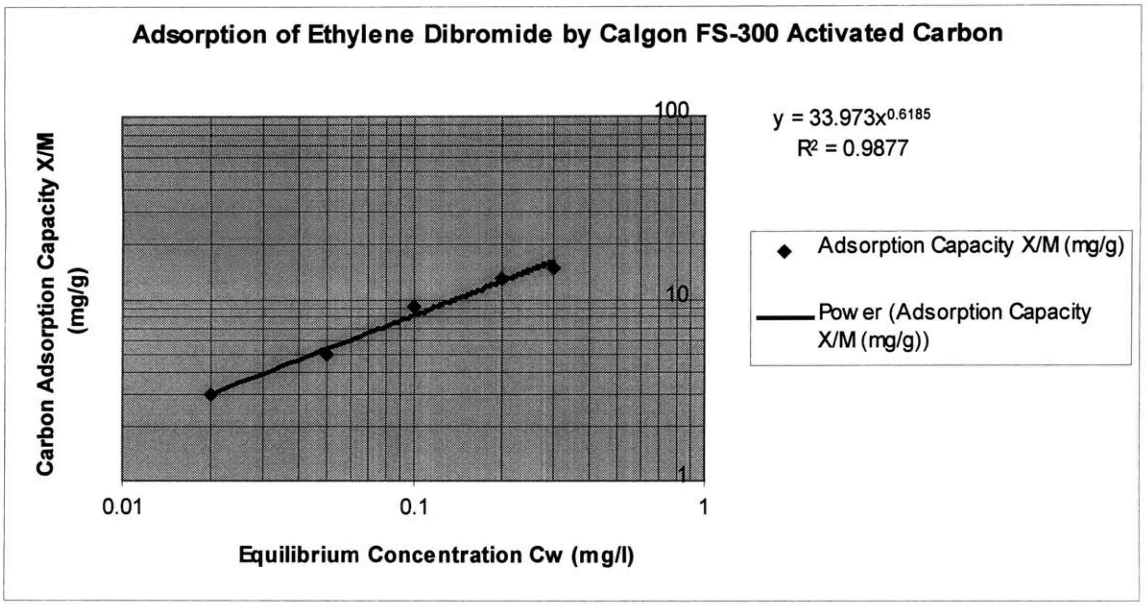

Figure 5-3: Determination of Freundlich Constants from Calgon Carbon Corporation Data

Based on the adsorption isotherm shown in Figure 5-3, the adsorption isotherm coefficients were determined from the graph. K was found to be 34 L/g and n was found to be 0.62 (dimensionless). Using these values, the Freundlich model can be expressed as:

$$\frac{X}{M} = 34 \bullet (C_W{}^{0.62})$$

Consequently, a theoretical usage rate *[lbs carbon/1000 gal treated water]* can be calculated from:

$$\text{Theoretical Usage Rate} = 1{,}000\ gal \bullet 3.785\ \frac{L}{gal} \bullet \frac{M}{X}\ \frac{[g\ carbon]}{[mg\ contaminant]} \bullet C_W \frac{[mg\ contaminant]}{[L]} \bullet \frac{1}{453.6}\ \frac{lbs}{g} \qquad (8)$$

At an influent concentration of 4.7 μg/L (the maximum influent concentration), the activated carbon capacity is 1.23 mg of EDB/g of carbon, translating into a theoretical usage rate of 0.032 lbs carbon/1000 gal of treated water. At an influent concentration of 0.8 μg/L (the concentration the system has leveled off to), the activated carbon capacity is 0.41 mg of EDB/g of carbon, translating into a theoretical usage rate of 0.016 lbs carbon/1000 gal of treated water. However, since field scale carbon adsorption is less efficient than the adsorption capacity determined in laboratory studies, the full-scale adsorption capacity is a percentage of the theoretical adsorption capacity. Typically, in practice, the capacity in the field has been shown to be 25 – 50% of the theoretical capacity (Tchobanoglous and Burton, 1991). Values of both 25% and 50% were used to determine field scale usage rates (summarized in Table 5-1):

$$\textit{Field-scale Usage Rate} = \textit{Adjustment Factor} \bullet \textit{Theoretical Usage Rate} \tag{9}$$

These usage rates are based on the assumption that the effluent concentrations are at 0 mg/L. Even though effluent concentrations increase in time until breakthrough occurs, this is a sufficiently close approximation as effluent requirements are very low (< 0.02 μg/L) at FS-28. For effluent concentrations that exceed the detection threshold, field-scale usage rates can be calculated using the revised formula *(10)* below:

$$\textit{Usage Rate} = 1{,}000\,\textit{gal} \bullet 3.785\,\frac{L}{\textit{gal}} \bullet \frac{M}{X}\,\frac{[\textit{g carbon}]}{[\textit{mg contaminant}]} \bullet (C_W - C_e)\,\frac{[\textit{mg contaminant}]}{[L]} \bullet \frac{1}{453.6}\,\frac{\textit{lbs}}{g} \bullet \textit{Adjustment Factor} \tag{10}$$

Table 5-1 below illustrates the carbon usage rates for three scenarios: 1) an influent concentrations of 0.8 μg/L, 2) a maximum influent concentration of 4.7 μg/L using a flowrate of 670 gpm, and 3) an influent concentration of 6 μg/L using a flowrate of 800 gpm, the conditions Calgon Carbon Corporation based their calculations on prior to the installation of the treatment system. Adjustment factors of both 25% (the maximum) and 50% (the minimum) were used.

Table 5-1: Comparison of Carbon Usage Rates for EDB

Scenario	Influent Concentration C_w (mg/L)	Adsorption Capacity X/M^1 (g Carbon/mg EDB adsorbed)	Field Usage Rate[1] (lbs carbon/ 1000 gal treated)	Adsorption Capacity X/M^2 (g Carbon/mg EDB adsorbed)	Field Usage Rate[2] (lbs carbon/ 1000 gal treated)
1 (670)	0.0008	0.10	0.064	0.21	0.032
2 (670)	0.0047	0.31	0.127	0.62	0.064
3 (800)	0.006	0.36	0.139	0.72	0.069

Notes:

[1] An adjusted carbon capacity of 25% was used to account for field conditions, as illustrated in equation (10).

[2] An adjusted carbon capacity of 50% was used to account for field conditions, as illustrated in equation (10).

For an influent concentration of approximately 6 µg/L, Calgon Carbon Corporation estimated a carbon usage rate ranging from 0.034 lbs carbon/1000 gal of treated water to 0.083 lbs carbon/1000 gal of treated water for complete removal of EDB in a column adsorber.

Based on the carbon usage rate, the flowrate, and the vessel capacity, a carbon exchange rate can be determined. The carbon exchange rate dictates how often the vessel containing the carbon has to be replaced. Again, carbon exchange rates were calculated for three scenarios: 1) at a maximum influent concentration of 0.8 µg/L, 2) at a maximum influent concentration of 4.7 µg/L using a flowrate of both 670 gpm and 750 gpm. Also, a carbon exchange rate was calculated using an influent concentration of 6 µg/L at a flowrate of 800 gpm. The carbon exchange rates are illustrated in Tables 5-2 and 5-3 below.

Table 5-2: Comparison of Carbon Exchange Rates for EDB Using an Adjustment Factor of 25%

Scenario	Maximum Influent Concentration (mg/L)	Flowrate (gpm)	Carbon Usage Rate (lbs carbon/1000 gal treated)	Carbon Exchange Rate (days)
1	0.0008	670	0.064	320
	0.0047	670	0.127	163
2	0.0008	750	0.064	286
	0.0047	750	0.127	146
3	0.006	800	0.139	125[1]

Notes: [1] Calgon Carbon Corporation predicted a carbon service life ranging from 210 days to 540 days.

Table 5-3: Comparison of Carbon Exchange Rates for EDB Using an Adjustment Factor of 50%

Scenario	Maximum Influent Concentration (mg/L)	Flowrate (gpm)	Carbon Usage Rate (lb carbon/1000 treated)	Carbon Exchange Rate (days)
1	0.0008	670	0.032	640
	0.0047	670	0.064	325
2	0.0008	750	0.032	572
	0.0047	750	0.064	291
3	0.006	800	0.069	250[1]

Notes:

[1] Calgon Carbon Corporation predicted a carbon service life ranging from 210 days to 540 days.

These calculated usage rates can be compared to an actual carbon usage rate at the time of breakthrough by the following relationship:

$$\text{Actual Carbon Usage Rate} = 1000 \bullet \frac{\textit{lbs carbon inside the column}}{\textit{gallons treated at breakthrough}}$$

$$= 1000 \bullet \frac{20000}{74487600} = 0.27 \textit{ lbs/1000 gal treated water}$$

As discussed earlier in this section, the above calculations for usage and exchange rates are based on the assumptions that:

1) the carbon/water mixture in the isotherm test was stirred long enough for equilibrium to be achieved (the basis for the isotherm),
2) the EBCT in the vessel is sufficient to achieve equilibrium conditions in the field, and
3) using a powdered version of the activated carbon does not considerably change Freundlich constants.

Because isotherm test performed at contact times of 24 hours are not necessarily sufficient to achieve equilibrium for larger molecules, these assumptions do not necessarily hold true. More importantly, at contact times of 8 minutes in the carbon vessel, equilibrium may not be achieved. Therefore, it is important to adjust the carbon capacity by an appropriate factor to account for these premises.

To obtain a more accurate estimate of the carbon capacity at low influent concentrations, the isotherm data can be re-plotted. Generally, one can assume that as the concentration of the contaminant becomes small, the isotherm is linear and thus n = 1. By only plotting the first three data points, the Calgon isotherm can be expressed as shown below in Figure 5-4. From the linear interpolation in Figure 5-4, one can assume that the distribution coefficient K_d can be approximated by 100 L/g. However, because the EBCT in the carbon vessel (8 minutes) was just a fraction of that one used in the laboratory (24 hours), the "effective" K_d also needs to be adjusted by a factor ranging from 25% to 50%. The "effective" K_d then ranges from 25 to 50. Carbon exchange rates for this value are shown in Table 5-4.

It should be noted that for a given K_d the product of in equation *(8)* reduces to a constant, irrespective of the influent concentration.

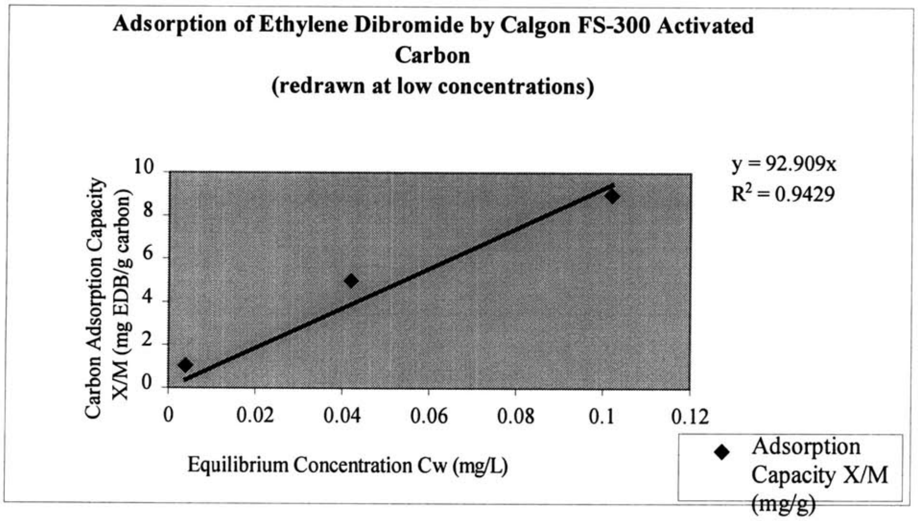

Figure 5-4: Adsorption Isotherm of EDB at Low Concentrations

Table 5-4: Comparison of Carbon Exchange Rates for EDB Using an Effective K_d of 25[1] and 50[2]

Scenario	Flowrate (gpm)	Carbon Usage Rate (lbs carbon/1000 treated)[1]	Carbon Exchange Rate (days)[1]	Carbon Usage Rate (lbs carbon/1000 treated)[2]	Carbon Exchange Rate (days)[2]
1	670	0.33	63	0.167	126
2	750	0.33	56	0.167	112
3	800	0.33	53	0.167	106

5.4.3.7 Summary

The carbon usage rates and the carbon exchange rates shown in Tables 5-1 through 5-4 are based on an extrapolation from the adsorption isotherm developed by Calgon Carbon Corporation. The carbon bedlife was calculated with two different approaches: 1) using the Freundlich model and the entire data set from the isotherm, and 2) adjusting the isotherm data to fit a linear relationship at low concentrations. With the first approach and using the same conditions Calgon Carbon Corporation used to determine the bed service life, the carbon exchange rate ranges from 125 days to 250 days, as compared to the 210-540 days Calgon Carbon Corporation had predicted. Using the second approach, the carbon exchange rates ranged from 53 to 126 days for the same conditions. These calculations are based on the assumption that equilibrium was achieved during the isotherm test and that an adjustment factor of 25% to 50% is sufficient to account for the change from laboratory to field conditions. Based on these observations, it appears that the carbon exchange rates predicted by Calgon Carbon Corporation may have been overestimated.

It is also important to realize that the laboratory isotherm was determined at controlled conditions. More importantly, the isotherm was determined at much higher influent concentrations than those present at FS-28; the lowest equilibrium concentration used in the isotherm was 4 μg/L. The isotherm should be determined within the concentration range corresponding to the levels likely to be encountered for the compound of interest since the extrapolation of isothermal data can lead to erroneous results (Faust and Aly, 1983). Calgon Carbon Corporation used a proprietary analytical technique based on laboratory isotherms to predict carbon usage rates. This model, however, becomes less reliable at lower concentrations and it is therefore very difficult to predict actual carbon usage rates at very low concentrations (Calgon Carbon Corporation, 1998).

Using the Freundlich model and the above calculations also assume that the vessel is operated to exhaustion, i.e., the entire carbon in the vessel is used until breakthrough occurs. Under operational conditions, however, adsorbed material accumulates at the top of the bed until the amount adsorbed is in equilibrium with the influent concentration. At this time, the adsorbent is loaded to capacity and that portion of the bed is exhausted. Below that zone is a second zone called the mass transfer zone (MTZ) where dynamic adsorption is occurring. Once that zone is formed, it moves down through the vessel until it reaches the bottom. As the mass transfer zone (MTZ) moves down the column, breakthrough of the contaminant occurs and an "S-shaped" curve illustrates the breakthrough profile, as illustrated in the figure below.

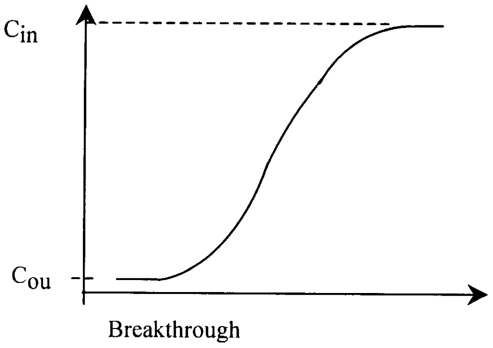

Figure 5-5: Typical S-shaped Breakthrough Curve
(Recreated and modified from Faust and Aly, 1983)

Breakthrough will, of course, not always occur in this idealized fashion. For single-solute systems when the influent concentration to the carbon column is assumed to be constant, smoothly S-shaped breakthrough curves are obtained. However, in natural systems, there are a wide range of organic contaminants and a wide variation in the concentration of any single contaminant is not unusual. Competitive adsorption, displacement of weakly adsorbed compounds, and concentration variations complicate and change the shape and position of the breakthrough curves. Therefore, adsorption studies for the application of activated carbon should be conducted using either a natural water or a synthetic medium of equivalent composition and concentration.

Another consideration is the time it takes for an isotherm to achieve equilibrium. A lot of the isotherms reported in the literature are being conducted with 2 hours at 22 °C. This, however, is not sufficient time to achieve equilibrium. Crittenden *et al.* reported adsorption capacities to be 2-3 times higher than those reported by Dobbs & Cohen for similar temperature, carbon, and adsorbates (1985), illustrating the divergence in data possible under different experimental conditions. As shown in the previous section, an adjustment might have to be made to correct for the short contact time in the field. Kinetic data would be needed to estimate the fraction of equilibrium obtained during an 8-minute EBCT in the field.

In the field, breakthrough occurred after 69 days of operation. It is therefore conceivable that the service life of the carbon beds was overestimated, assuming that the EBCT of 8 minutes is not sufficient to achieve adsorption equilibrium. It is not possible to determine this hypothesis without laboratory experiments and furthermore, other factors could also be responsible for the pre-mature breakthrough. The following sections undertake a more detailed analysis to explain the early breakthrough at FS-28.

5.4.4 Analysis of the Early Breakthrough at Fuel Spill 28

The following sub-sections investigate the possible causes for early breakthrough at FS-28, including:

- Overestimation of carbon bedlife,
- Backwashing
- Reversible adsorption/desorption,
- Pre-loading due to naturally occurring organic matter, and

- bacterial growth on the carbon column.

5.4.4.1 Overestimation of Carbon Bedlife

The following sections determine and compare carbon exchange rates by:

1) determining usage rates using single-solute isotherms and Freundlich isotherm constants from a literature search,

2) determining the effect of multi-component solutions on the usage rates using a model developed by DiGiano et *al.* (1978),

3) determining breakthrough times using

    a) equilibrium column model, and
    b) advection dispersion equation, and

4) determining the true adsorption capacity from the actual loading data at breakthrough.

5.4.4.1.1 Single-Component Adsorption Isotherm Calculations Using the Freundlich Model and Freundlich Constants from a Literature Search

Crittenden *et al.* (1985) conducted experiments to develop isotherms for both single- and multiple-component solutions and demonstrated that the Freundlich equation was sufficiently accurate in representing isotherm data that was collected in the laboratory. The degree of agreement of the data with the Freundlich equation was expressed in terms of an average percent error (APE) of 1.1% in q, the single-component solid phase concentration ($\frac{X}{M}$).

Because the carbon usage rates can vary widely with differing Freundlich constants, a literature search was conducted for Freundlich constants for EDB and the carbon usage and carbon exchange rates were summarized in the following Table 5-5:

Table 5-5: Comparison of Literature Freundlich Constants and Calculated Carbon Usage Rates at a Maximum Concentration of 4.7 µg/L and a Maximum Flowrate of 750 gpm

Concentration Ranges (µg/L)	K (L/g)	n	Source[8]	Notes	Adsorption Capacity, X/M (mg/g)[1]	Carbon Usage Rate (lbs/1000 gal)[1]	Bed Life (days)[1]
0.5-0.05[2]	69.3	0.5	1	Filtrasorb 400	1.34	0.029[3,4]	636
0.2-111	55.6	0.47	2	Filtrasorb 400	1.57	0.025[5]	740
0.06-7.2	33.05	0.62	3	PAC	0.42	0.093[6]	199
32-1750	49.71	0.48	4	Filtrasorb 400	1.32	0.029[7]	626
2-10,000	43.4	0.58	5	Hydrodarco GCW 12 x 40	0.67	0.058	319

Notes:

[1] An intermediate adjustment factor of 35% was used to account for the change from laboratory to field conditions.

[2] Freundlich constants were determined using an influent concentration of 0.5 µg/L and an equilibrium concentration of 0.05 µg/L.

[3] Freundlich constants were determined using Filtered Ohio water with a total organic carbon (TOC) content of 2 mg/L. A carbon usage rate of 0.053 lbs/1000 gal treated water and a bed life of 804 days was predicted in the literature, assuming a single, full-scale contactor with an EBCT of 15 minutes, hydraulic loading of 4 gpm/ft^2, using Filtrasorb 400 GAC. This calculation was performed using a pore-surface-diffusion flux ratio of 0.4 for relatively less strongly adsorbed volatiles.

[4] Using an adjustment factor of 40% to account for field conditions, a carbon usage rate of 0.059 lbs/1000 gal of treated water was calculated.

[5] Freundlich constants were determined using de-ionized water with a TOC content of < 0.1 mg/L.

[6] Freundlich constants were determined using water from Fairfield.

[7] Crittenden also noted that the adsorption capacities at 10-12 °C were approximately 2-4 times higher than those observed at 20-22 °C.

[8] Sources:

1	Weber and Pirbazari, 1981.
2	Texas Marketplace, 1998.
3	Montgomery Watson, 1998.
4	Crittenden *et al.*, 1985.
5	Norit Americas, Inc., 1998.

The carbon bedlives (exchange rates) calculated from the Freundlich constants found in the literature range from 199 days to 740 days using an intermediate adjustment factor of 35%. As discussed previously, these values are based on the assumption that equilibrium can be achieved in the field using an 8-minute EBCT. These estimates are notably higher than what was calculated previously. Some of the Freundlich constants were determined using a considerably higher influent concentration, which will distort the adsorption capacity at lower concentrations. Furthermore, some of the experiments used a lignite-based carbon which has a higher surface area than bituminous carbon. Generally, a powdered form of the carbon is used in laboratory isotherm tests which would also have a larger surface area than the granular form and therefore overestimate the carbon service lives. Only one estimate, namely the study conducted by Issam Najm (Montgomery Watson, 1998) was conducted at the concentration range that has been found at FS-28. The estimated carbon service life using the Freundlich constants that were determined using PAC and a contact time of 7 days was 199 days.

5.4.4.1.2 Multi-Component Adsorption Isotherm Calculations

As mentioned in Section 5.4.2.2, the adsorption capacity of any compound may be decreased by the presence of other contaminants in the influent. Preferential adsorption is important when considering selective removal of compounds. Generally, compounds with high melting point, high critical temperature, and low volatility are preferentially adsorbed and may displace other compounds that have already been adsorbed. If preferential adsorption occurs, the true capacity of the carbon is lower and therefore single-solute isotherms often are not of practical use.

After examining the analytical results for the influent data to the treatment system, it was noted that none of the contaminants that were found in the contaminant plume (i.e., carbon tetrachloride, chloroform, methylene chloride, PCE, toluene, or TCE) were actually detected in the influent samples. Low concentrations of ethylbenzene (0.56 μg/L) and total xylenes (2.9 μg/L) were detected in the influent after breakthrough occurred. It is possible that low levels of organics were present in the influent; however, competitive adsorption by these contaminants is not expected to significantly increase the usage rate. To confirm this assumption, usage rates were calculated using the model developed by DiGiano *et al.* (1978) described in Section 5.4.2.2. Appendix A presents usage rates for EDB if ethylbenzene had been present in the influent at a maximum concentration of 0.56 μg/L.

Table 5-6: Calculation of Carbon Usage Rates Using a Multi-Component Isotherm Model (Equation [4]) – Worst-Case Scenario[1]

Contaminant	Influent Concentration C_w (µg/L)	K (L/g)	n	Adsorption Capacity X/M[2] *(mg/g)*	Carbon Usage Rate (lbs /1000 gal)	Bed Life (days)
EDB	4.7	33.86	0.62	0.04	0.98	19
Ethylbenzene	0.56	147[4]	0.29[4]	3.02	0.00006[3]	-

Notes:

[1] Note the literature presents a wide range of Freundlich constants for ethylbenzene. Appendix A presents the calculations using different Freundlich constants; only the worst-case scenario is presented here.

[2] Adsorption Capacity was calculated using a flowrate of 750 gpm and an adjustment factor of 35% (see equation [8a]).

[3] It is assumed that ethylbenzene is being removed to the detection limit shown in this column.

[4] Source: Najm, 1991.

Generally, in a multi-component solution, the least sorbable contaminant will break through first, corresponding to a low adsorption capacity at equilibrium with the influent concentration. The overall carbon usage rate is determined by that compound with the highest usage rate, which in this case is EDB. As shown above in Table 5-6 (and contrary to the original assumption), the carbon usage rate could be significantly higher with ethylbenzene present in the influent. Using a usage rate of 0.98 lbs/1000 gal, a service life of 19 days would be predicted for the worst-case scenario.

Appendix A illustrates the usage rates for varying Freundlich constants for ethylbenzene. The Freundlich constants found in the literature for ethylbenzene vary widely and consequently the usage rates and exchange rates will vary as well (Appendix A). For equilibrium concentrations in the low-µg/L range, K ranges from 147 L/g to 175 L/g, and more importantly, n ranges from 0.29 to 0.53. It should be noted, however, that the value of 0.53 for n was determined using a 3-day contact time in the isotherm bottle, which does not represent field conditions. Therefore, a carbon exchange rate of 161 days (found for K equal to 175 L/g and n equal to 0.53) is most likely not representative for this scenario.

So, in summary, it is possible that even though no other contaminants were detected in the influent prior to breakthrough, usage rates may have been increased by the presence of very low levels of organic contaminants (other than EDB) in the influent. The 19-day carbon exchange rate was determined using the most conservative Freundlich constants (i.e., yielding the highest usage rates); this exchange rate also assumes that EDB is present consistently at a concentration of 0.56 μg/L. It is more likely, however, that other contaminants may have been present sporadically, increasing the carbon usage rate.

5.4.4.1.3 Comparison of Breakthrough Times

As defined previously, the length of time required for the appearance of some percentage of the initial concentration to reach the effluent is termed the breakthrough time. Several models are available in the literature to predict the performance of GAC. The following approach was taken to obtain a theoretical breakthrough time at FS-28:

1) the Equilibrium Column Model, and
2) the advection dispersion equation.

Using the Equilibrium Column Model (ECM)

The EC model is a simple model and is based on two assumptions explained below (Ram *et al.*, 1990):

1) Adsorption is instantaneous, i.e., there is no mass transfer zone. Based on this assumption, the breakthrough curve consists of a step rather than the S-shaped curve shown in Figure 5-5. Furthermore, the breakthrough time is independent of the breakthrough concentration.
2) This model also assumes that at the time of breakthrough, all of the carbon is saturated or in other words, its solid-phase concentration is in equilibrium with the contaminant liquid-phase concentration. If the actual breakthrough curve is symmetrical in shape, then the ECM breakthrough time should correspond to the time it takes for the effluent concentration to reach 50% of the influent concentration.

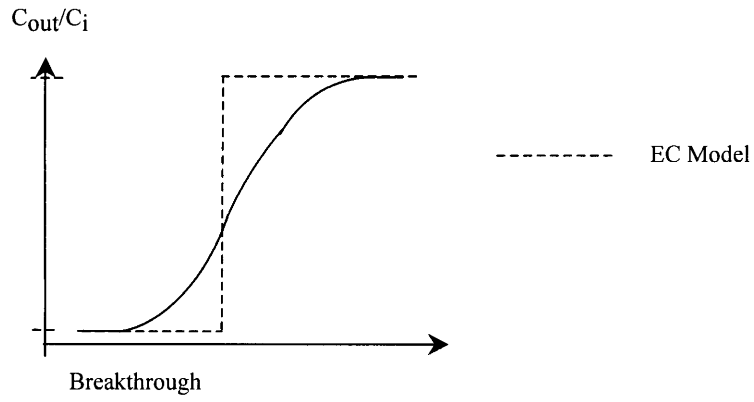

Figure 5-6: Illustration of EC Model

Mathematically, this model can be expressed as (Ram *et al.,* 1990):

$$t_B = \frac{(V_B \cdot \rho_B) \cdot \frac{X}{M}}{Q \cdot Cw} \tag{11}$$

where t_B = *breakthrough time [days]*

V_B = *volume of GAC in Column* $[m^3]$

ρ_B = *density of GAC in carbon bed* $[g/m^3]$

Q = *water flowrate [L/day]*

C_w = *influent concentration [mg/L]*

From Section 5.4.3.6, a distribution coefficient K_d of 100L/g can be assumed. Using a 35% adjustment factor, a breakthrough time of 125 days can be calculated.

Because kinetics are ignored in this calculation, the breakthrough time obtained from the ECM model only provides a very rough estimate for the GAC service life. It generally underestimates the breakthrough time because it neglects the mass transfer zone. Accordingly, it is common practice to divide the ECM breakthrough time by a factor of 2 when laboratory isotherm data is used (Narbaitz *et al.,* 1994).

Using the One-dimensional Dispersion Advection Equation

The one-dimensional dispersion advection equation can be expressed as (Hemond and Fechner, 1994):

$$Dx \bullet \frac{\partial^2}{R\partial x^2} \bullet C - v_x \bullet \frac{\partial C}{R\partial x} = \frac{\partial C}{\partial t} \qquad (12)$$

where D_x = *dispersion coefficient [ft²/sec]*

vx = *one-dimensional velocity [ft/sec]*

$\frac{\partial^2}{\partial x^2}$ = *change in concentration by Fickian transport*

$\frac{\partial C}{\partial x}$ = *chemical concentration gradient in the fluid*

$\frac{\partial C}{\partial t}$ = *rate of change of contaminant*

R = *Retardation factor*

In the case of a continuous input, the spreading of the chemical front can be described by:

$$C(x,t) = (C_w/2) \bullet erfc[\frac{Rx - vt}{2\sqrt{RDxt})}] \qquad (13)$$

where C_w = *initial concentration of the chemical [μg/L]*

$erfc$ = *complementary error function*

In this case, we can assume that :

C_0 = *4.7 μg/L*

$C(x,t)$ = *0.02 μg/L*

v = *0.046 ft/sec (surface hydraulic loading divided by porosity, assuming porosity equals 0.41)*

D_x = $\alpha \bullet v$

where α = *median grain size of the carbon particle*

Bituminous granular activated carbon has a grain size of about 1mm; a generous value of 1 cm was chosen for α. So then

$$D_x = 0.032\,ft \bullet 0.046\,ft/sec = 0.0015\,ft^2/sec$$

$$x = 9\text{ feet (effective length of the carbon column)}$$

From Section 5.4.3.6, one can assume that the distribution coefficient Kd = 100 L/g. Using an adjustment factor of 35% for Kd, the retardation factor R can be calculated as:

$$R = 1 + Kd \bullet \frac{\rho_b}{n} \tag{14}$$

Using a bulk density of 0.50 g/ml and a porosity of 0.41,

$$R = 1 + 35\,L/g \bullet \frac{0.50\,g}{ml} \bullet \frac{1000\,ml}{L} \bullet \frac{1}{0.41} = 42{,}684$$

Going back to equation *(12)*, [___] needs to be determined when erfc[___] = 0.0085. From the listed tables in Hemond and Fechner (1994), this is true mathematically when [___] = 1.89. Based on this calculation, a breakthrough time of approximately 97 days was computed for the effluent to reach 50% of the influent concentration (this would correspond to the estimate from the EC Model, but taking dispersion into account) and a breakthrough time of 77 days was computed for the effluent concentration to reach a concentration of 0.02 μg/L. This estimate is based on a retardation factor which was computed from the isotherm data at low concentrations.

Using this model, it is important to examine the spread (i.e., the deviation about the mean) of the concentration distribution within the carbon canister. A concentration distribution with a large standard deviation will be more spread out and breakthrough may occur earlier than in a flow field with a small standard deviation. Since the concentration distribution of a tracer can be modeled with a Gaussian distribution, the variance for a one-dimensional column can be expressed as follows:

$$\sigma = \left(\sqrt{\frac{2D_x t}{R}}\right) \qquad \text{where } \sigma = \text{standard deviation} \qquad (15)$$

Plugging in the numbers obtained from above results in a value for σ of 1.2 ft. This since value is larger than 10% of the length of the carbon column, dispersion plays a role in determining the breakthrough time.

5.4.4.1.4 Determination of Actual Adsorption Capacity

The averaged column loading data can be used to determine the actual adsorption capacity of the carbon vessel at breakthrough. Using this approach, the contaminant solid phase concentration can be calculated based on the assumption that the mass of contaminant removed by the water column has adsorbed to the carbon. This model does not provide a breakthrough time, but allows for comparison of adsorption capacities determined in the laboratory versus those experienced in the field. The loading will be significantly smaller than that predicted by the laboratory isotherm since the carbon vessel in the field typically does not get fully exhausted. Mathematically, this can be expressed as (Narbaitz *et al.,* 1994):

$$MCONT = \sum_{i=1}^{N} (C_{w_i} - C_{e_i}) \cdot Qi \cdot \Delta ti \qquad (16)$$

where $MCONT$ = *mass of contaminant removed by the carbon column [mg]*

Qi = *average flowrate during period i [L/d]*

Δti = *duration of period i [d]*

C_{wi} = *average contaminant influent concentration during period i [mg/L]*

C_{ei} = *average contaminant effluent concentration during period i [mg/L]*

The adsorption capacity can then be determined by:

$$\frac{X}{M} = \frac{MCONT}{V_B \cdot \rho_B} \qquad (17)$$

where $V_B \cdot \rho_B$ = *mass of GAC in the column (9,072,000 g)*

This approach yielded a removed contaminant mass of 386 g and an actual averaged adsorption capacity of 0.042 mg/g (see Appendix B). This adsorption capacity would translate into a carbon usage rate of 0.24 lbs/1000 gal for an averaged influent concentration of 1.4 μg/L and an averaged flowrate of 750 gpm. This compares to a theoretical carbon usage rate of 0.064 lb/1000 gal calculated from the laboratory isotherm for an influent concentration of 0.8 μg/L.

While it is important to compare breakthrough times and carbon usage rates, the actual breakthrough curve has to also be considered in this analysis. The actual influent loading curve can be determined from actual influent data and is shown in Figure 5-7 below (Jacobs, 1998):

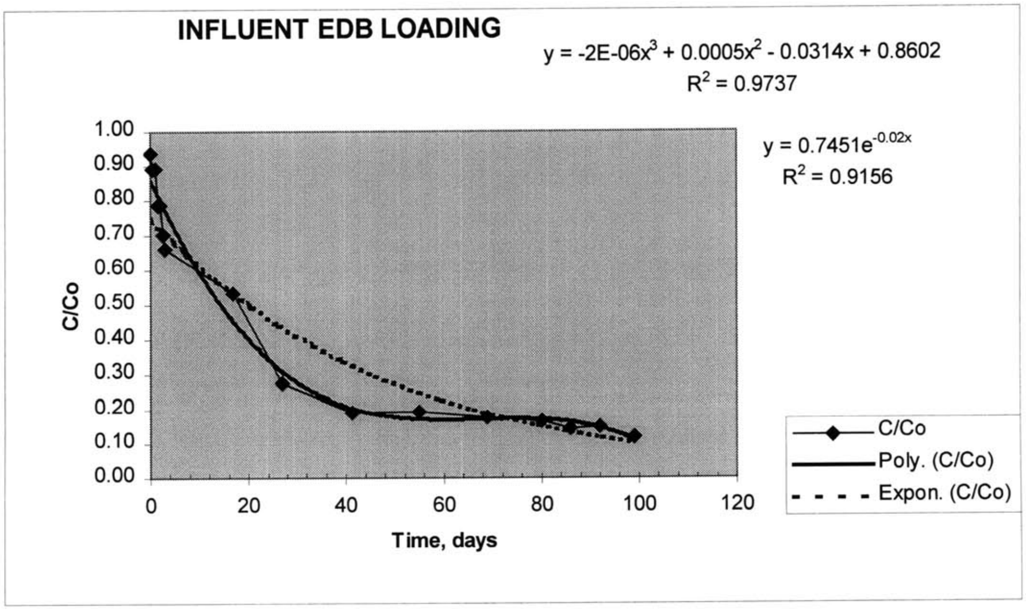

Figure 5-7: Influent EDB Loading

It is important to examine the actual breakthrough curve. If considerable time elapses before the breakpoint appears, and the breakthrough curve is sharply defined and steep, the adsorption zone is short relative to the over-all bed depth. If on the other hand breakthrough occurs almost immediately, a relatively deep adsorption zone is indicated (Calgon Carbon Corporation, 1998).

As shown in Figure 5-8, the breakthrough curve is considerably steep, then levels back out to a constant. This shape would indicate that other factors such as sudden desorption might have occurred.

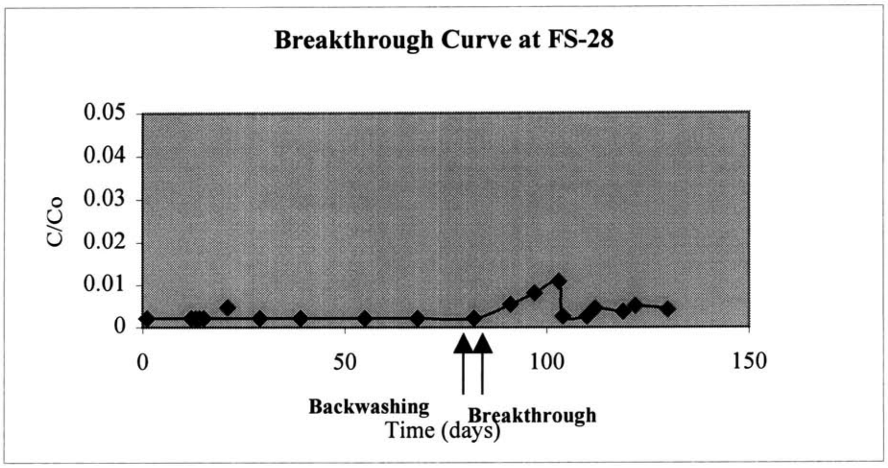

Figure 5-8: Breakthrough Curve at FS-28

5.4.4.2 Reversible Adsorption/Desorption

Adsorption to the carbon surface relies on electrostatic Van der Waals forces, which are relatively weak bonds, between the contaminant and the carbon. Because adsorption is a reversible process, desorption of contaminants may occur. Available literature cites the following causes for desorption of contaminants (Snoeyink *et al.*, 1987; Thacker *et al.*, 1983):

- competition from more strongly adsorbing species,
- reduced influent concentration, causing material to be desorbed as a new equilibrium is established,
- destratification of the GAC, causing carbon originally exposed to higher contaminant concentrations to establish a new equilibrium under low contaminant concentrations, and
- changes in water quality (e.g., pH).

Research conducted by Thacker *et al.* (1983) evaluated reversible adsorption caused either by a reduction in the influent concentration or by competition from stronger adsorbing species. A high rate of desorption following a reduction in the influent concentration would indicate higher effluent concentrations initially after desorption has begun. The findings showed that a change made in an adsorption system to improve mass transfer (by increasing surface diffusivity or film transfer coefficients) and adsorption efficiency (such as changing to a smaller size of carbon) could also result in greater desorption (Thacker *et al.*, 1983). On this basis, increasing the bed length or decreasing the hydraulic loading would also increase the rate of desorption.

During a study conducted by Narbaitz *et al.* (1994), pre-mature breakthrough of EDB in point-of-entry (POE) filters in Florida was attributed to excessive water use and to desorption induced by sharp variations in the EDB influent concentrations. Several studies have reported desorption of chloroform due to competitive adsorption at the column, resulting in an effluent concentration exceeding the influent concentration for the same timeframe (Faust and Aly, 1987).

Cited information in the literature suggests that halogenated aliphatics such as EDB desorb readily as they are adsorbed more weakly than other contaminants. Zenon Environmental Inc. (1984) conducted a desorption study in which a column was loaded with low levels of EDB, dibromochloropropane (DBCP), and 1,2,3-trichloropropane. During the time the columns were run in desorption mode, EDB was the only chemical to desorb, with the desorbing concentrations being approximately half of those fed during the loading phase.

A sharp drop in the influent concentration from 4.7 μg/L to 0.8 μg/L occurred at FS-28 within 40 days of operation. However, its effect on desorbing EDB from the bottom of the carbon column is debatable. Equilibrium concentrations at the bottom of the carbon column should not be affected by decreasing influent concentrations entering the top of the carbon column. Therefore, the breakthrough at FS-28 can not be attributed to desorption as a result of a decrease in the influent concentration.

5.4.4.3 Backwashing

It is plausible that the carbon fines in the column were redistributed during the backwashing event on December 9, 1997. Generally, backwashing has several effects on a GAC filter: it loosens and breaks down the suspended solids attached to the GAC granules and removes them from the filter. Backwashing also produces stratification of carbon particles according to their size (McGuire and Suffet, 1980). If redistibution occurred during backwashing, it is conceivable that carbon fines from the top of the carbon vessel traveled down to the bottom of the vessel. The exhausted carbon at the bottom would prevent further adsorption and possibly desorb previously adsorbed EDB to establish a new equilibrium.

A similar occurrence was reported by Andrew Hyde (McGuire and Suffet, 1980) who observed a difference in carbon performance for single- versus multiple-bed systems. He attributed the premature exhaustion of the single-bed system with respect to chloroform to mixing of the media during backwashing.

5.4.4.4 Pre-loading from Total Organic Carbon

The performance of GAC can also be affected by the presence of naturally occurring background organic material (NOM). According to studies conducted by Narbaitz *et al.* (1986, 1994), Murin *et al.* (1979), and Suffet *et al.* (1989), NOM in the influent is particularly important as it can reduce the carbon's adsorption capacity by 50% or greater. This reduction in carbon adsorption capacity can be attributed to the difference in adsorption characteristics of volatile organic compounds (VOCs) and dissolved NOM (NDOM). While VOCs have relatively fast adsorption kinetics and many are strongly adsorbed, NOM is very heterogeneic and generally diffuses slowly (Ram *et al.*, 1990). Predicting the adsorption of NDOM is extremely difficult because of the heterogeneity of TOC. Apparently, a substantial fraction of carbon particle pores are smaller than the humic material which would explain the slow adsorption kinetics associated with NDOM. Furthermore, a number of researchers have found that even though diffusion is slow for the organic matter, adsorption is usually irreversible, causing a carbon's capacity for a target compound to be reduced (Ram *et al.*, 1990).

Speth has shown a reduced isotherm capacity for TCE on carbon which was pre-loaded with natural water containing a TOC content of 0.7 mg/L (Ram *et al.*, 1990). Studies conducted by Speth and other researchers (Zimmer *et al.*, 1987 and 1988) also demonstrated that the adsorption kinetics (and therefore the carbon adsorption capacity) decreased with time of pre-loading.

A reduced carbon adsorption capacity due to pre-loading from TOC in the influent may be partially responsible for the pre-mature breakthrough at FS-28. Total organic carbon was not detected consistently in the influent to the treatment system at FS-28. The samples were only analyzed for TOC in October, 1997 (which showed no detections of TOC) and then again in January (which showed a TOC concentration of 0.5 mg/L). In June 1997, a groundwater sample collected form extraction well 69EW0001 showed a TOC concentration of 0.3 mg/L. Even though the samples did not show a detection of dissolved organic carbon, it is possible that DOC was present below the detection limit of 0.52 mg/L. Because the NDOM is weakly adsorbing, it can travel down the carbon column and slowly adsorb onto the activated carbon ahead of the adsorbing zone of EDB. Thus EDB is adsorbed in the top portions of the vessel media while the TOC is adsorbed in the lower portion of the vessel media, what is commonly termed "pre-loading" the carbon column. As the mass transfer zone passes through the media, the amount of EDB adsorption is decreased since there are less adsorption sites available. The carbon column near the bottom would therefore have a lower capacity than near the top of the column, suggesting a higher rate of carbon exhaustion deeper into the media (Ram *et al.*, 1990).

5.4.4.5 Bacterial Growth on the Activated Carbon Column

One of the most intricate issues related to the use of GAC is the presence of bacterial growth and its interaction with adsorption. As illustrated in Appendix C, groundwater contains a complex mixture of naturally occurring substances that are often lumped together as biological oxygen demand (BOD) or TOC. These organic substances may contain a wide range of bacteria which have been known to attach themselves to the macropores of the carbon, forming a biofilm that impedes the sorption process. As a result, adsorption takes place only after the contaminant has diffused across the film. For contaminants that are both adsorbable and biodegradable, these two processes may be complementary and beneficial. This biological phenomenon has been used as a treatment step to GAC where it is commonly termed biological activated carbon (BAC). For contaminants that can not be readily biodegraded, adsorption is reduced due to the slowed diffusion across the biofilm.

A number of hydrodynamic complications related to bacterial growth on the carbon column have been cited in the literature, including bed expansion as well as liquid and solids mixing (Tien, 1980). Bacterial films are thought to increase the effective size of the carbon granules. This in turn affects the porosity of the carbon column resulting in continuous expansion of the column and also in a stratification of the carbon particles. Carbon granules with a larger biofilm (typically encountered near the inlet of the column) will tend to settle more slowly and will therefore remain at the top of the column; those particles with the least biofilm will be placed at the bottom of the column. As a consequence, bed stratification is possible (Tien, 1980).

Other factors associated with bacterial growth on activated carbon columns include clogging, odors, and gases. Adsorption of the contaminant consists of diffusion into the porous network where physical adsorption takes place. Because EDB is a large molecule and because it is retained in the micropores of the carbon, access to the micropores may be hindered if biofilm is present, thereby restricting adsorption.

It is possible that the pre-mature breakthrough at FS-28 was caused by bacterial growth. Based on the results of an aerobic plate count, 100 cells were present in the influent and 500 cells were present in the effluent. The exact type of bacteria could not be identified from the analysis, but a number of bacteria, including *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans,* can attach themselves to the surface of the carbon column. These chemo-lithotrophs are iron-oxidizing bacteria that can oxidize ferrous iron to ferric ion under aerobic and acidic conditions. When ferrous iron is converted to ferric iron, it becomes insoluble and precipitates out of the water as a rust-colored deposit. The deposit is often in the form of a slimy gelatinous material which surrounds the bacterial cells (Brock and Madigan, 1991). The following stochoimetric equation represents this phenomenon:

$$O_2 + 4\,Fe^{2+} + 10\,H_2O \longleftrightarrow 4\,Fe(OH)_3 + 8\,H^+ \qquad (18)$$

The bacteria grow in stringy clumps and are found in most-iron bearing surface waters; they have been found to proliferate in waters containing iron as low as 0.1 mg/L. In order to function, these aerobic bacteria need at least 0.3 mg/L of dissolved oxygen in the water. Sulfate reducing bacteria (SRBs) often live in vicinity of iron bacteria, so both types may be present (Brock and Madigan, 1991). Iron bacteria and sulfur bacteria are often difficult to distinguish as they portray similar symptoms. The most obvious sign of sulfur bacteria is the distinctive hydrogen sulfide gas odor.

Based on the analytical results from extracted groundwater at FS-28, elevated levels of total iron are present in groundwater and are being removed by the GAC treatment system. Total iron levels removed during the backwashing event ranged from 32,400 µg/L initially to 3,460 µg/L at the end of the backwashing event (Jacobs, 1998). The iron was primarily removed at the top of the carbon bed. Additionally, during operation of the treatment system and prior to breakthrough, dissolved oxygen levels dropped by about 0.42 mg/L to 1.92 mg/L between the influent and effluent port of the first vessel.

A simple mass balance can be performed to evaluate the amount of oxygen that would be used up by iron-oxidizing bacteria. For this estimate, however, it is necessary to estimate the amount of dissolved ferrous iron in the groundwater. The influent samples to the treatment system were sampled for total iron, but not for dissolved iron. Based on analytical results from a monitoring well in the area, the maximum concentration of dissolved iron present at FS-28 is 1,100 µg/L. The form of iron present in groundwater will depend on the pH and the dissolved oxygen. Most natural waters, including the groundwater at FS-28, have pH values ranging from 2 to 12. Assuming that the dissolved iron is present as ferrous iron (which would be the pre-dominant species in the absence of an electron acceptor), the following back-of–the-envelope calculation can be performed:

$$1{,}100\ \mu g/L\ F_e\ x\ \frac{1\ mole\ F_e}{55.85\ g\ F_e} x \frac{1\ mole\ O_2}{4\ moles\ F_e} x \frac{32\ g\ O_2}{1\ mole\ O_2} = 0.16\ mg/L\ O_2$$

From that estimation, there is sufficient oxygen present in the carbon vessel to oxidize the maximum dissolved iron concentration present at FS-28. In summary, it is possible and very likely that biological growth in the carbon vessel caused the pre-mature breakthrough at FS-28. This explanation would also account for the presence of hydrogen sulfide odor at the carbon vessel.

6. Suggested Improvements and/or Alternatives to Carbon Adsorption

As mentioned previously, remedial technologies for EDB-contaminated groundwater have not been researched as thoroughly as the remedial options for some of the other contaminants more commonly associated with military sites. Moreover, pump-and-treat technology with GAC is considered BAT for remediating groundwater contaminated with EDB. It is therefore likely that pump-and-treat technology along with GAC will be chosen as the final remedial alternative at FS-28. However, considering the high operational costs of using granular activated carbon and the problems the GAC system at FS-28 is currently facing, it is important to consider alternatives to granular activated carbon adsorption. The following sections address suggested improvements and/or alternatives to the current system.

6.1 Alternatives to Carbon Adsorption

This section reviews alternative technologies that were identified as potentially applicable for the removal of EDB from groundwater.

6.1.1 Air Stripping

Air Stripping is commonly used with pump-and-treat systems to remediate contaminated groundwater and is basically a mass transfer technique. The feasibility of air stripping for removal of contaminants is determined by the mass transfer rate and Henry's Law Constant. The mass transfer rate increases with increasing temperature, increasing Henry's Law Constant, increasing turbulence, and decreasing solubility (USEPA, 1991). Due to the moderate solubility of EDB in water and its low Henry's Law Constant, conventional air stripping is not considered as efficient as GAC. Based on a study conducted by Environmental Science and Engineering, Inc. (Beaudet, 1983), removal rates of 99% can be achieved with air stripping. Considering the low influent concentrations at FS-28 (0.8 μg/L), the conventional air stripping process would require higher air-water ratios or greater packing depth to achieve effluent concentrations of 0.02

μg/L. Since air stripping is merely a mass transfer technique, off-gas treatment would still be required.

6.1.2 Reductive Dehalogenation

Ethylene dibromide has been shown in the laboratory to be readily degraded by reductive dehalogenation using zero-valent iron. Results from these laboratory studies have been highly promising, showing rates of degradation that are several orders of magnitude higher than those observed under natural conditions. The details of the exact processes and mechanisms are unknown, but it appears the process consists of abiotic reductive dehalogenation, in which the metal enhances reducing conditions and acts as a reactant by providing electrons for the reductive dehalogenation of the organic compounds. Reductive dechlorination is described in more detail in the Project Report (Indelicato, 1998).

To date, all of the plumes treated with reactive walls containing zero-valent iron have been at depths less than 15 m (50 feet). Many contaminant plumes, however, including FS-28, are deeper, prohibiting cost-effective installation of reactive walls at this time. Several methods are currently being researched to emplace granular iron at greater depths, including slurry walls, deep soil mixing, as well as hydrofracturing and injection. Above-ground treatment of EDB-contaminated water (see Section 6 of Project Report for the application of this method to chlorinated solvents) is not appropriate at FS-28 due to the high flowrate required to contain the hotspot concentrations.

Using zero-valent iron to remediate EDB-contaminated groundwater is promising as it is a cost-effective, simple, and long-term solution. Compared to pump-and-treat technology, it does not require energy and more importantly, there are no costs to extract, treat, and dispose of groundwater as this technology does not simply transfer the contaminants from one medium to another, but destroys the contaminants.

6.1.3 Advanced Oxidation Processes

Other technologies potentially applicable include advanced oxidation processes (AOPs), biological treatment processes, and membrane filtration processes. Advanced oxidation processes have shown to be useful for the transformation of a wide variety of pollutants found in water. AOPs generate the highly reactive hydroxyl radical, OH•, especially useful for treatment of low concentrations of organic pollutants in contaminated groundwater because they have the potential to completely oxidize the organic compounds. Little information is available in the literature on the application of AOPs to remove EDB from groundwater. Based on a treatability study conducted by Calgon Carbon Corporation (1998), EDB can be degraded using AOPs; however, the reaction rates are generally slow and are not considered feasible.

6.1.4 Biological Treatment Processes

Currently, reliance on natural attenuation processes is becoming increasingly popular. In laboratory studies, microbial degradation has been shown to be an important removal mechanism of EDB in the aquifer; however, despite the prediction of these laboratory studies, subsurface organisms are not degrading EDB to extinction in reasonable time-spans. It is therefore doubtful that biodegradation alone can be used to remediate the groundwater at FS-28. Several researchers have explored the use of biologically active carbon (BAC) for the removal of contaminants from water. With BAC, a microbial mass attaches itself to the carbon surface in a GAC bed. The biological community is exposed to nutrients and the carbon food source, which is dissolved in the aqueous phase (Brown *et* al., 1997). No studies have been found to report the use of BAC to degrade EDB in groundwater.

6.1.5 Reverse Osmosis

A variety of membrane separation processes are available for the removal of organic contaminants from water, including reverse osmosis (RO), nanofiltration, microfiltration, and ultrafiltration. The latter two processes are generally used for removing relatively large solutes such as proteins, drugs, or colloids and nanofiltration is a process conceived to soften water by removing divalent cations (Brown *et* al., 1997). Reverse osmosis has the greatest potential for removing EDB because it is designed to remove small solutes. One study tested the effectiveness of RO for the removal of pesticides and chlorinated hydrocarbons from water (Baier *et* al., 1986). In this study, the RO membrane was able to reduce 1,2-dichloropropane concentrations from 85 μg/L to 7 μg/L. Membrane filtration processes may be cost-prohibitive, especially at the low concentrations present at FS-28.

6.1.6 Adsorptive Resins

As described in the previous section 5, adsorption processes are widely used in the removal of organic contaminants. Polymeric resins might provide an alternative adsorption medium to GAC. Polymeric resins are water insoluble and consist of cross-linked beads with a high specific surface area, similar to GAC. While these resins are similar to ion exchange resins, they have a greater specific surface area and either a weakly ionizable exchange group, or no ionizable group at all (Kunin, 1977). These resins have trade names such as Amberlite, Ambersorb, XUS, and Reillex and are made of polystyrene, sulfonated polystyrene, polyvinylpyridine, and polymethylacrylate.

In a field study funded by the USEPA, Ambersorb XE-340 was compared to GAC and packed-tower aeration for the removal of cis-1,2-dichloroethene, 1,1,2-trichloroethene, and 1,1,2,2-tetrachloroethene and was found to have three times the capacity at twice the flowrate (Parker, G. *et* al., 1991). While Ambersorb adsorbents have demonstrated significant performance advantages over GAC for chlorinated hydrocarbons, no results could be found in the literature regarding their application to EDB

6.2 Improving Operating Procedures

Additionally, the following improvements can be made to improve the life of the carbon beds:

- Disinfection,

- Rotating vessels,
- Filtering influent, and
- Using another vessel as a safe-guard.

6.3 Using a Different Type of Carbon as an Adsorption Medium

A number of other types of carbons are available as an adsorptive medium, including lignite carbon. As shown in Section 4.4, Filtrasorb 400 carbon has a higher surface area and thus adsorbs more contaminant. An extended service life may significantly outweigh the additional costs involved with using lignite carbon or Filtrasorb 400.

7. Conclusions

Groundwater contamination by organic chemicals has become an increasingly prevalent problem at many military sites. As a result, many of these sites, including the MMR, have been declared Superfund sites. The pump-and-treat remediation approach is used at about three quarters of all Superfund sites where groundwater is contaminated and at most sites where cleanup is required by the Resource Conservation and Recovery Act (RCRA) and state laws (NRC, 1994). While a variety of techniques have evolved for the removal of the contaminants from the extracted water, GAC may be the most common and most approved technology.

Unfortunately, pre-mature exhaustion of the activated carbon poses a considerable problem at many of the sites where GAC is being used to treat the extracted water. The Honolulu Board of Water Supply uses GAC to treat EDB-contaminated groundwater on Oahu and has noted a greater usage of carbon than originally anticipated (USGS, 1998). Pre-mature exhaustion has also been noted at the FS-28 treatment system at the MMR where breakthrough occurred in the lead carbon canister following only 69 days of operation; the carbon bedlife was originally estimated to range from 210 to 540 days. The need for changeout (and reactivation) of the carbon beds after such a short period of operation will greatly add to operation and maintenance costs of the system.

The objective of this thesis was to evaluate the use of GAC to treat EDB-contaminated groundwater at the MMR. While this evaluation is specific to FS-28, the general approach may be applicable to other sites where pre-mature exhaustion of the carbon beds has been observed. Some possible explanations for the pre-mature breakthrough at FS-28 included:

- Overestimation of carbon bedlife,
- Backwashing
- Desorption,
- Pre-loading due to TOC, and

- Bacterial growth.

A number of approaches were used to determine whether the carbon bedlife was overestimated, including:

- Laboratory isotherms, and
- Simple analytical models.

7.1 Evaluation of Laboratory Isotherms

The most common means of evaluating adsorption on activated carbon is through the use of adsorption isotherms. Because isotherms are determined under laboratory conditions, the accuracy of performance predictions based on them needs to be examined. In the first part of this evaluation, the laboratory isotherm data determined by Calgon Carbon Corporation was used to estimate carbon bedlives. The data was fit to the Freundlich equation and a carbon adsorption capacity *[mg EDB/g carbon]* was determined. Because field-scale carbon adsorption is less efficient than the adsorption capacity determined in laboratory studies, adjustment factors of 25% and 50% were used to account for this change. Using the adjusted adsorption capacity, the carbon usage rate *[lbs carbon/1000 gal]* and carbon exchange rate *[frequency with which the carbon vessel has to be exchanged]* were computed.

Based on a maximum influent concentration of 4.7 μg/L and a flowrate of 670 gpm, carbon exchange rates (changeout intervals) were calculated from the Calgon Carbon Corporation Isotherm to range from 163 days to 325 days. Even though these numbers are well within the range Calgon Carbon Corporation had predicted, this approach should only be used as a very rough estimate as it is based on the following assumptions:

1) That the carbon/water mixture was stirred long enough for equilibrium to be established between the contaminant concentration in the water and the contaminant adsorbed to the carbon column. This assumption may not be valid as it has been shown that some larger molecules do not reach equilibrium within the time most isotherm tests are conducted at (typically 1 hour or 24 hours).

2) That an EBCT on the order of minutes is sufficient to achieve equilibrium conditions in the field. It is likely that equilibrium can not be achieved in the field and it is necessary to adjust the carbon capacity by an appropriate factor. The adjustment factors of 25% - 50% may be sufficient to account for this; however, kinetic data is necessary to obtain a more accurate estimate.

3) That the isotherms determined at high influent concentrations can be used to predict carbon usage and exchange rates at much lower influent concentrations; i.e., the isotherm is valid for all concentrations ranges. This assumption is not valid. In fact, ESE (Beaudet, 1986) has shown for some contaminants, such as EDB and methylene chloride, the replacement frequency increases with a decrease in influent concentrations. This observation may or may not be directly related to the validity of isotherm data at low concentrations.

To address this last observation and obtain a more accurate estimate of the carbon capacity at low influent concentrations, the isotherm data was re-plotted, assuming linearity for a small range of low influent concentrations. Using this approach, carbon exchange rates ranged from 63 days (25% adjustment factor) to 126 days (50% adjustment factor), which are likely more accurate estimates of the carbon life.

7.2 Sensitivity Analysis of Freundlich Constants

To illustrate the divergence in data possible under different laboratory conditions, a literature search for Freundlich constants was conducted. For a range of influent concentrations and a number of different carbon adsorbents, carbon exchange rates varied from 199 days to 740 days (assuming an intermediate adjustment factor of 35%, an influent concentration of 4.7 μg/L and a flowrate of 670 gpm). Because some of these constants were determined using considerably higher influent concentrations, the adsorption capacity was most likely overestimated by these constants. Furthermore, some of these experiments were conducted with a lignite-based carbon which has a higher surface area than bituminous carbon and should therefore also have a higher adsorption capacity. This divergence in data illustrates that it is extremely difficult to predict carbon bedlives based on laboratory isotherm data.

7.3 Effects of Competitive Adsorption

To account for the fact that natural systems typically contain a wide range of contaminants, competitive adsorption was examined using a simplified version of the IAS theory. Even though no other contaminants were detected in the influent to the treatment system in October 1997 when the system was started up, both ethylbenzene and total xylenes were detected after breakthrough had occurred in January 1998.

Carbon usage rates were computed for the scenario if ethylbenzene had been present in the influent at a maximum concentration of 0.56 μg/L. A wide range of Freundlich constants for ethylbenzene were found in the literature. Using extreme values from the literature, it was shown that carbon usage rates could be significantly increased in the presence of other contaminants such as ethylbenzene. However, due to the wide range of Freundlich constants and because of the uncertainty of the presence of other contaminants at FS-28, no definitive conclusions could be made regarding competitive adsorption at FS-28.

7.4 Determination of Breakthrough Times

The second approach used to determine carbon bedlives involved the use of several simple analytical models, including:

- The equilibrium column (EC) model, and
- The advection dispersion equation

7.4.1 Results from the Equilibrium Column Model

The EC model is a simple model which is based on the assumption that adsorption is instantaneous and that the breakthrough time is independent of the breakthrough concentrations. This model also assumes that at the time of breakthrough, the solid-phase concentration is in equilibrium with the influent concentration. This assumption does not hold for field conditions as the GAC may not achieve equilibrium in the carbon vessel. Approximately 125 days were calculated for the breakthrough time. The literature generally recommends using a factor of safety of 1.1-2, which would propose a service life of 63 to 114 days. Because kinetics are accounted for in this calculation by a 35% adjustment factor, the EC model only provides a very rough estimate for the GAC service life.

Because equilibrium models do not account for dispersion within the column, this can lead to a significant underestimation of the breakthrough time. To address this issue, the breakthrough time was also calculated using the advection dispersion equation.

7.4.2 Results from the Advection Dispersion Equation

The advection dispersion equation is a one-dimensional numerical model which computes the breakthrough time based on retardation of the contaminant to the carbon surface. This model incorporates dispersion and is therefore more complete than the EC model. A breakthrough time of approximately 97 days was computed for the effluent to reach 50% of the influent concentration (this would correspond to the estimate from the EC Model, but taking dispersion into account) and a time of 77 days was computed for the effluent concentration to reach a concentration of 0.02 μg/L. This estimate is based on a retardation factor which was computed from the isotherm data at low concentrations.

7.5 Determination of the Actual Adsorption Capacity

The averaged column loading data was used to determine the actual adsorption capacity of the carbon vessel at breakthrough. This model does not provide a breakthrough time, but allows for comparison of adsorption capacities determined in the laboratory versus those experienced in the field. Based on a removed contaminant mass of 386g, an actual averaged adsorption capacity of 0.042 mg/g was determined. This adsorption capacity would translate into a carbon usage rate of 0.24 lbs/1000 gal for an averaged influent concentration of 1.4 μg/L and an averaged flowrate of 750 gpm. This compares to a theoretical carbon usage rate of 0.064 lb/1000 gal calculated from the laboratory isotherm for an influent concentration of 0.8 μg/L.

It becomes clear from the models and calculations that the determination of carbon bedlives is not very accurate. Using laboratory isotherms raises questions about kinetics and it may be more appropriate to use a numerical model such as the advection dispersion equation that includes the effects of dispersion in order to estimate carbon service lives. It is likely that the carbon bedlife at FS-28 was overestimated; however, judging from the shape of the breakthrough curve, other factors, such as desorption, biological growth, and pre-loading due to TOC may be partially responsible for the pre-mature breakthrough.

7.6 Alternative Explanations

7.6.1 Desorption

Desorption of the contaminant from the carbon column as a result from a rapid decrease in the influent concentration has been cited in the literature as an explanation for pre-mature breakthrough. However, because this mechanism is not clear, this theory is not considered a viable explanation at FS-28.

7.6.2 Backwashing

Backwashing occurred prior to the breakthrough at FS-28 and it is possible that the carbon particles were re-distributed during the backwashing event. It is then conceivable that carbon particles previously located at the entrance of the column might have traveled to the other end. If this occurred, the exhausted carbon at the bottom would prevent further adsorption and could possibly desorb previously adsorbed EDB to establish a new equilibrium at the other end of the carbon vessel.

7.6.3 Pre-loading due to TOC

Pre-loading due to TOC is also a possible explanation -- a reduction in carbon adsorption capacity of 50% or greater due to naturally occurring background material has been observed in the literature. However, because insufficient data is available to evaluate whether TOC was continuously present in the influent to the treatment system, no definitive conclusions can be drawn for this hypothesis.

7.6.4 Bacterial Growth

Bacterial growth from iron-oxidizing bacteria is a likely phenomenon at FS-28. Monitoring wells in the area have shown elevated levels of iron in groundwater and the backwashing event showed that the carbon bed effectively removed total iron. Assuming that some of the iron is present as ferrous iron, it is feasible that iron-oxidizing bacteria may be present on the carbon column. These bacteria form an insoluble iron precipitate (biofilm) which would impede further adsorption. Because sulfide reducing bacteria often live in the vicinity of iron oxidizing bacteria, this hypothesis might explain the hydrogen sulfide odor observed at the carbon vessel.

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APPENDIX A

EDB LOADING RATES USING MULTI-COMPONENT ADSORPTION ISOTHERM CALCULATIONS WITH LITERATURE FREUNDLICH CONSTANTS FOR ETHYLBENZENE

1. K = 53; n= 0.79; Ranges of remaining aqueous concentrations: 2,100-22,500 ppb

C_i (mg/L)	C_e (mg/L)	K_i (L/g)	n_i	K'	n'	$K'^{(n'-1)/n'}$	$(K_i(C_i-C_e)^{n}{}_i)^{1/n'}$	$(K_i/K')*((C_i-C_e)^{n}{}_i))^{1/n'}$	$(X/M)_i$ (mg/g)	Usage Rate (lbs/1000 gal)	Exchange Rate$_I$ (days)
0.0047	0.00002	33.86	0.62	**43.43**	**0.71**	0.206	1.3	0.0062777	**1.216**	**0.032**	**576**
0.00056	0.0005	53	0.79				0.0	0.0000237	**0.005**	**0.10533**	
							Sum.	0.006			
							$(Sum)^{n'-1}$	**4.458**			

Source of ethylbenzene freundlich constant. LaGrega, 1994, Dobbs and Cohen, 1980

2. K =120; n= 0.29; Ranges of remaining aqueous concentration: 3,000-50,000 ppb

C_i (mg/L)	C_e (mg/L)	K_i (L/g)	n_i	K'	n'	$K'^{(n'-1)/n'}$	$(K_i(C_i-C_e)^{n}{}_i)^{1/n'}$	$(K_i/K')*((C_i-C_e)^{n}{}_i))^{1/n'}$	$(X/M)_i$ (mg/g)	Usage Rate (lbs/1000 gal)	Exchange Rate$_I$ (days)
0.0047	0.00002	33.86	0.62	**76.93**	**0.46**	0.006	1.5	0.0001102	**0.146**	**0.268**	**69**
0.00056	0.0005	120	0.29				74.0	0.0052982	**7.010**	**0.00007**	
							Sum:	0.005			
							$(Sum)^{n'-1}$	**17.198**			

Source of ethylbenzene freundlich constant Najm et al, 1991

3. K =175; n= 0.53; Ranges of remaining aqueous concentration: 5.6-565 ppb

C_i (mg/L)	C_e (mg/L)	K_i (L/g)	n_i	K'	n'	$K'^{(n'-1)/n'}$	$(K_i(C_i-C_e)^{n}{}_i)^{1/n'}$	$(K_i/K')*((C_i-C_e)^{n}{}_i))^{1/n'}$	$(X/M)_i$ (mg/g)	Usage Rate (lbs/1000 gal)	Exchange Rate$_I$ (days)
0.0047	0.00002	33.86	0.62	**104.43**	**0.58**	0.032	1.4	0.0004338	**0.970**	**0.040**	**460**
0.00056	0.0005	175	0.53				1.0	0.0003054	**0.683**	**0.00071**	
							Sum	0.001			
							$(Sum)^{n'-1}$	**21.418**			

Source of ethylbenzene freundlich constant Najm et al, 1991.

4. K =70.2; n= 0.4; Concentration Range: 2,000-21,000 ppb

C_i (mg/L)	C_e (mg/L)	K_i (L/g)	n_i	K'	n'	$K'^{(n'-1)/n'}$	$(K_i(C_i-C_e)^{n}{}_i)^{1/n'}$	$(K_i/K')*((C_i-C_e)^{n}{}_i))^{1/n'}$	$(X/M)_i$ (mg/g)	Usage Rate (lbs/1000 gal)	Exchange Rate$_I$ (days)
0.0047	0.00002	33.86	0.62	**52.03**	**0.51**	0.022	1.5	0.0006338	**0.801**	**0.049**	**380**
0.00056	0.0005	70.2	0.4				2.0	0.0008556	**1.081**	**0.00045**	
							Sum	0.001			
							$(Sum)^{n'-1}$	**24.279**			

Source of ethylbenzene freundlich constant: Texas Marketplace, 1998.

5. K =147; n= 0.29; Concentration Range: 4-2820 ppb

C_i	C_e	K_i	n_i	K'	n'	$K'^{(n'-1)/n'}$	$(K_i(C_i-C_e)^{n}{}_i)^{1/n'}$	$(K_i/K')*((C_i-C_e)^{n}{}_i))^{1/n'}$	$(X/M)_i$	Usage Rate	Exchange Rate[1]
(mg/L)	(mg/L)	(L/g)							(mg/g)	(lbs/1000 gal)	(days)
0.0047	0.00002	33.86	0.62	**90.43**	**0.46**	0.005	1.5	0.0000772	**0.115**	**0.340**	**54**
0.00056	0.0005	147	0.29				115.6	0.0058012	**8.621**	**0.00006**	
							Sum.	0.006			
							$(Sum)^{n'-1}$	**16.434**			

Source of ethylbenzene freundlich constant Austin, 1998

6. K =177; n= 0.53; Ranges of remaining aqueous concentration: 700-1,000 ppb

C_i	C_e	K_i	n_i	K'	n'	$K'^{(n'-1)/n'}$	$(K_i(C_i-C_e)^{n}{}_i)^{1/n'}$	$(K_i/K')*((C_i-C_e)^{n}{}_i))^{1/n'}$	$(X/M)_i$	Usage Rate	Exchange Rate[1]
(mg/L)	(mg/L)	(L/g)							(mg/g)	(lbs/1000 gal)	(days)
0.0047	0.00002	33.86	0.62	**104.93**	**0.58**	0.032	1.4	0.0004302	**0.968**	**0.040**	**459**
0.00056	0.0005	176	0.53				1.0	0.0003059	**0.689**	**0.00070**	
							Sum:	0.001			
							$(Sum)^{n'-1}$	**21.456**			

Source of ethylbenzene freundlich constant: Austin, 1998.

7. K =163; n= 0.415; Concentration Range: 26-565 ppb

C_i	C_e	K_i	n_i	K'	n'	$K'^{(n'-1)/n'}$	$(K_i(C_i-C_e)^{n}{}_i)^{1/n'}$	$(K_i/K')*((C_i-C_e)^{n}{}_i))^{1/n'}$	$(X/M)_i$	Usage Rate	Exchange Rate[1]
(mg/L)	(mg/L)	(L/g)							(mg/g)	(lbs/1000 gal)	(days)
0.0047	0.00002	33.86	0.62	**98.43**	**0.52**	0.014	1.5	0.0002057	**0.506**	**0.077**	**240**
0.00056	0.0005	163	0.415				7.5	0.0010614	**2.611**	**0.00019**	
							Sum	0.001			
							$(Sum)^{n'-1}$	**24.998**			

Source of ethylbenzene freundlich constant· Austin, 1998.

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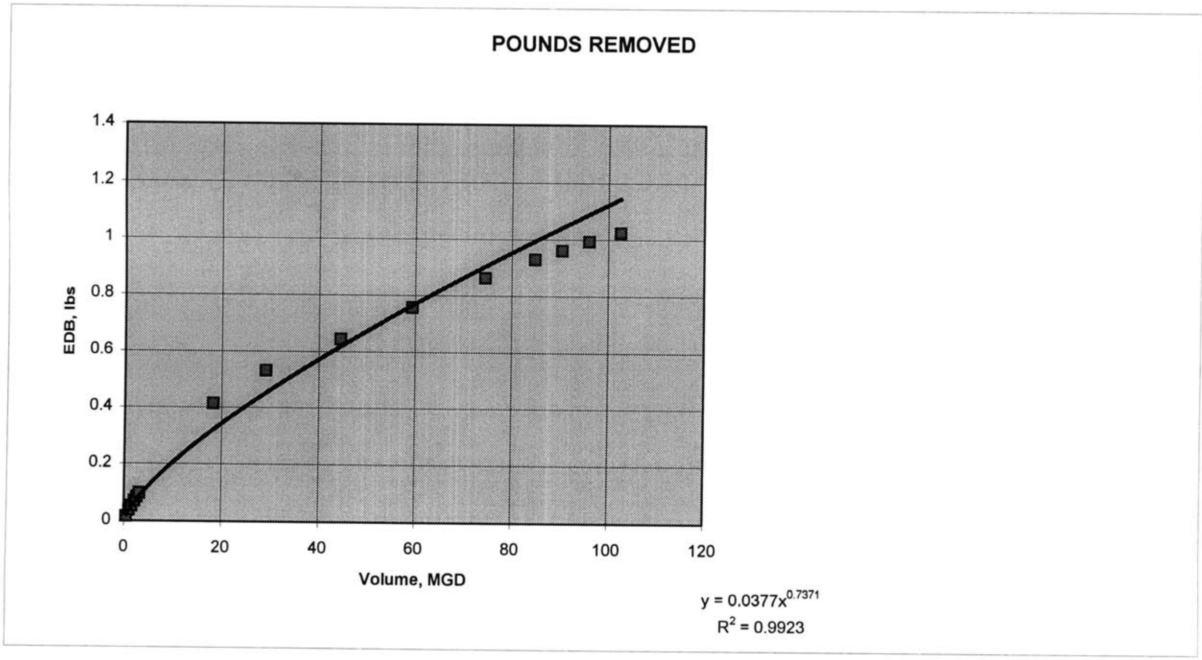
[1] Adsorption Capacities and Exchange Rates have not been adjusted for laboratory conditions (I.e., a factor of 0.35 has not yet been applied)

APPENDIX B

ADSORPTION CAPACITY CALCULATION USING FIELD DATA – EQUATIONS (16) AND (17) IN SECTION 5 OF THIS REPORT

Sample Date	Time	Cwi (mg/L)	Cei (mg/L)	Days	Flowrate (gpm)	Flowrate (L/day)	MCONT (mg)	Averaged Cwi (mg/L)	Avg.Flowrate (gpm)
14-Oct-97	10:00	0.0044	0.00002	0	750	4087800	0	0	0
15-Oct-97	10:10	0.0042	0.00002	1	750	4087800	17087.004	0.0042	750
16-Oct-97	10:10	0.0037	0.00002	1	750	4087800	15043.104	0.0037	750
17-Oct-97	8:45	0.0031	0.00002	1	750	4087800	12590.424	0.0031	750
31-Oct-97	8:10	0.0025	0.00002	14	750	4087800	141928.416	0.035	10500
10-Nov-97	8:50	0.0013	0.00002	10	750	4087800	52323.84	0.013	7500
24-Nov-97	15:10	0.00089	0.00002	14	750	4087800	49789.404	0.01246	10500
08-Dec-97	9:30	0.00091	0.00002	14	750	4087800	50933.988	0.01274	10500
22-Dec-97	9:30	0.00083	0.00003	14	750	4087800	45783.36	0.01162	10500
02-Jan-98	9:30	0.00078	0.000038	11	650	3542760	28916.00712	0.00858	7150
08-Jan-98	9:30	0.00068	0.000051	6	650	3542760	13370.37624	0.00408	3900
14-Jan-98	9:30	0.0007	0.000012	6	650	3542760	14624.51328	0.0042	3900
21-Jan-98	9:30	0.00056	0.00002	7	650	3542760	13391.6328	0.00392	4550
							385480	0.0014	750

Mass of EDB Removed: Data Obtained from Jacobs Engineering, 1998



APPENDIX C

GROUNDWATER CHEMISTRY AT FS-28 AS DETERMINED FROM INFLUENT AND EFFLUENT SAMPLES AT THE TREATMENT SYSTEM

Constituent	**Units**	**Influent Sample**		**Effluent Sample 1st Canister**	**Effluent 2nd Canister**		**Monitoring Well 69EW0001**
TDS	mg/L	**46**	-	-	**36**	-	**64**
TSS	mg/L	<2.54	-	-	<2.54	-	<3.6
Bromide	mg/L	**0.047**	**0.11**	**0.1**	<0.022	-	**0.09**
Chloride	mg/L	**7.71**	**10.2**	**10.2**	**7.15**	-	**8.4**
Nitrate	mg/L	**0.121**	**0.17**	**0.17**	**0.042**	-	**0.17**
Nitrite	mg/L	<0.021	<0.02	<0.02	**0.054**	-	<0.02
T. Orthophosphate	mg/L	<0.017	<0.26	<0.26	**0.108**	-	<0.26
Sulfate	mg/L	**5.04**	**6.6**	**6.7**	**4.15**	-	**5.1**
Alk. As CaCO3	mg/L	**16.7**	-	-	**31.3**	-	**36**
COD	mg/L	<4.67	-	-	<4.67	-	<20
BOD	mg/L	-	-	-	-	-	**0.2**
DOC	mg/L	<0.52	-	-	<0.52	-	-
TOC	mg/L	<0.52	**0.5**	-	<0.52	<0.2	**0.3**
Total Iron	µg/L	**196**	<19.7	-	<92.4	<88.1	**98.3**

- Data not available