

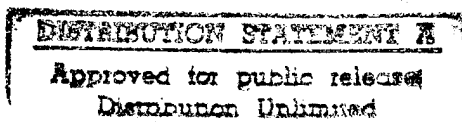
The Pennsylvania State University
The Graduate School
Department of Civil and Environmental Engineering

FATE AND TRANSPORT OF
TRICHLOROETHANE AND
TRICHLOROETHYLENE
CONTAMINATED GROUNDWATER,
BUILDING 719,
DOVER AIR FORCE BASE, DELAWARE

A Report in
Environmental Engineering
by

Kenneth J. Melchiorre

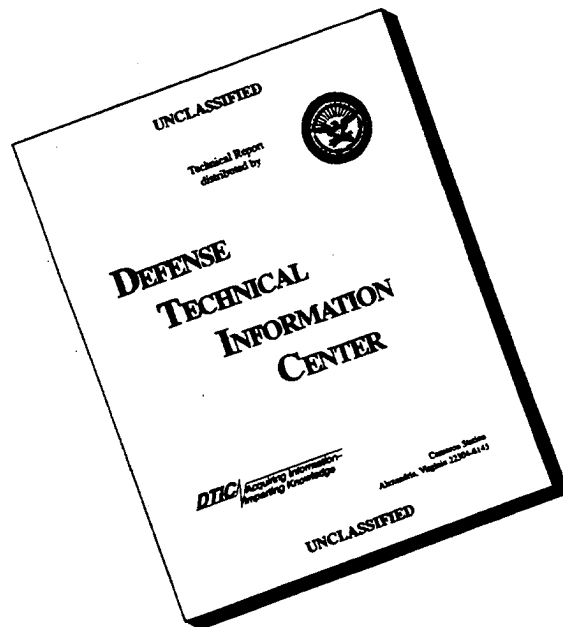
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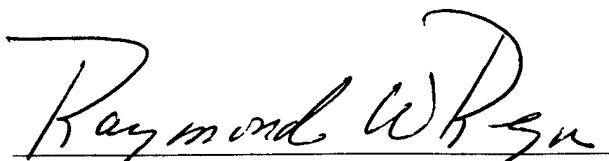
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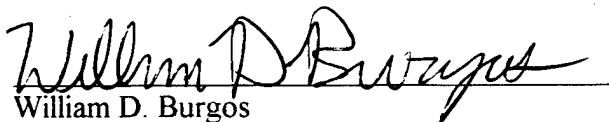
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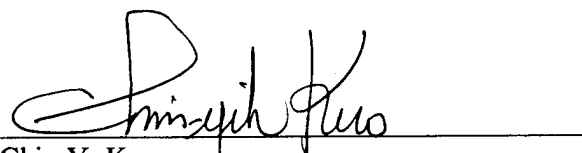
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Abstract

Title of Engineering Report: Fate and Transport of Trichloroethane and Trichloroethylene Contaminated Groundwater, Building 719, Dover Air Force Base, Delaware

Kenneth J. Melchiorre
M.E., August 1996
The Pennsylvania State University
Raymond Regan, Report Adviser

Trichloroethane and trichloroethylene are common chlorinated aliphatic industrial organic solvents used in degreasing operations. Both are typically found in groundwater environments as a result of leaking underground storage tanks, leachate from landfills, and contaminant migration from hazardous waste dump sites. Transformation by-products are also found in association with trichloroethane and trichloroethylene without any known source other than from reductive dechlorination. Dechlorinated by-products include 1,1-dichloroethane; *cis* and *trans* 1,2-dichloroethylene, 1,1-dichloroethylene, chloroethane, and vinyl chloride. Trichloroethane and trichloroethylene and their transformation by-products are suspected human health hazards. Vinyl chloride is a known human carcinogen, while trichloroethylene is considered a probable human carcinogen, and 1,1-dichloroethylene and 1,1-dichloroethane possible human carcinogens.

Trichloroethane, trichloroethylene, and their reductive by-products have been detected in the groundwater at Building 719, Dover Air Force Base, Delaware as a result of leaking underground storage tanks. Concentrations of *cis*-1,2-dichloroethylene are highest at maximum of 82 mg/L followed by trichloroethylene at 62 mg/L.

This report investigated the fate and transport of the Building 719 site contaminants and their ultimate impact on the Lower St. Jones River which is 7,200 feet south and in the direction of groundwater flow from Building 719. The lower St. Jones

River and the river's surrounding water shed are designated a National Estuarine Research Reserve.

A fourth order "Runge Kutta One Dimensional Finite Differences Model" was used to determine the fate and transport. Adsorption, dispersion, and degradation rates for the site contaminants were determined by empirical and kinetic methods as model input parameters based on existing site conditions. The results of the model indicated that the contaminants would reach the St. Jones River by the year 2029. Maximum concentrations will reach the river in approximately the year 2039 but at concentrations that would ultimately be diluted by the river flow below Delaware Water Quality Standards as well as Maximum Contaminant Levels (MCLs). *Cis*-1,2-dichloroethylene and vinyl chloride were determined to be the most persistent contaminants to reach the St. Jones River.

The plume's first point of contact with the greatest health risk is the Dover Air Force Base residential housing area which is approximately 2,000 feet south of the site. Based on model results, the plume will reach the housing area between the years 2000 and 2002 with maximum concentrations impacting the area by the year 2005. As a result, the report recommends ex-situ remediation efforts begin prior to the year 2000.

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CHAPTER 1

INTRODUCTION

1.1. Site Background

The Building 719 site is located to the south of the northwest/southeast runway at Dover Air Force Base (DAFB), Delaware (Figures 1.1 and 1.2). In 1993, the groundwater and soil below Building 719 were determined to be contaminated with trichloroethylene (TCE) and 1,1,1 - trichloroethane (TCA) (43). Daughter by-products of TCE and TCA have also been found to be localized at the site. The by-products include 1,1-dichloroethylene (1,1-DCE), *cis*-1,2-DCE (*cis*-DCE), *trans*-1,2-DCE (*trans*-DCE), 1,1-dichloroethane (1,1-DCA), vinyl chloride (VC), and chloroethane (CA). 1,2-DCA, not considered a by-product of either TCA or TCE, was also found. Maximum and average concentrations found at the site for each contaminant as a result of soil and water sampling in November 1995 as well as Safe Drinking Water Act Maximum Contaminant Levels (MCLs), and Delaware Water Quality Standards for Marine and Estuarine waters are listed in Table 1.1. A diagram of sample locations and sample results is provided in Appendix A. Figures 1.3 through 1.9 contain groundwater plume diagrams for each of the contaminants listed in Table 1.1 except *trans*-DCE and CA (Only trace amounts of *trans*-DCE and CA were found at the site.). The figures indicate that the groundwater contamination is concentrated under Building 719.

Since 1951, Building 719 has been used as a jet engine inspection/maintenance shop. TCE and TCA were originally used in cleaning operations but are no longer used in any operations at Building 719 (12). Although not specifically isolated, the contamination is believed to have originated from an underground storage tank (UST), several aboveground dip tanks, and/or the industrial cast iron drain pipes that service Building

Table 1.1. Building 719 Groundwater Contaminant Concentrations, MCLs, and Delaware Water Quality Standards for Marine and Estuarine Waters.

Contaminant	Groundwater Average Concentration (ug/L)	Groundwater Maximum Concentration (ug/L)	Delaware Water Quality Standards for Marine and Estuarine waters (44)	MCL (ug/L)
TCE	8,112	62,000	16 ug/L	5
TCA	413	2,300	28 mg/L	200
1,1 DCE	171	660	0.56 ug/L	7
cis - DCE	24,019	70,000	no standard	70
trans - DCE	BDL	BDL	19 mg/L	100
1,1 DCA	476	2,300	no standard	no standard
1,2 DCA	334	760	17 ug/L	5
VC	188	500	95 ug/L	2
CA	6	6	no standard	no standard

BDL: Below detection limits.

719. All of the tanks were removed in 1994 with only the underground piping system remaining (43). The actual contamination start time from the suspected sources is unknown.

1.2. Purpose and Scope.

The purpose of this report is to examine the groundwater fate and transport of TCA and TCE and the subsequent daughter products. The report will focus on groundwater transport of those chlorinated aliphatic hydrocarbons originating from the Building 719 site and the possible infringement/contamination of the St. Jones River which

is located approximately 7,200 feet to the south and in the direction of groundwater flow from the site (Figures 1.2 and 1.10). The report objectives are to:

- Summarize chemical backgrounds as well as the human health concerns associated with the contaminants covered in this report.
- Review site specific geology and hydrology.
- Determine the transformation process of TCA and TCE and the associated by-products at the site.
- Introduce the continuity equation and the fate and transport model to examine the impacts on the St. Jones River.
- Examine and determine the degradation and transport parameters/continuity equation coefficients that affect the fate and transport of the Building 719 contaminants.
- Apply the fate and transport model and state the results.
- Draw conclusions and make recommendations for further study, analysis, and remediation of the site.

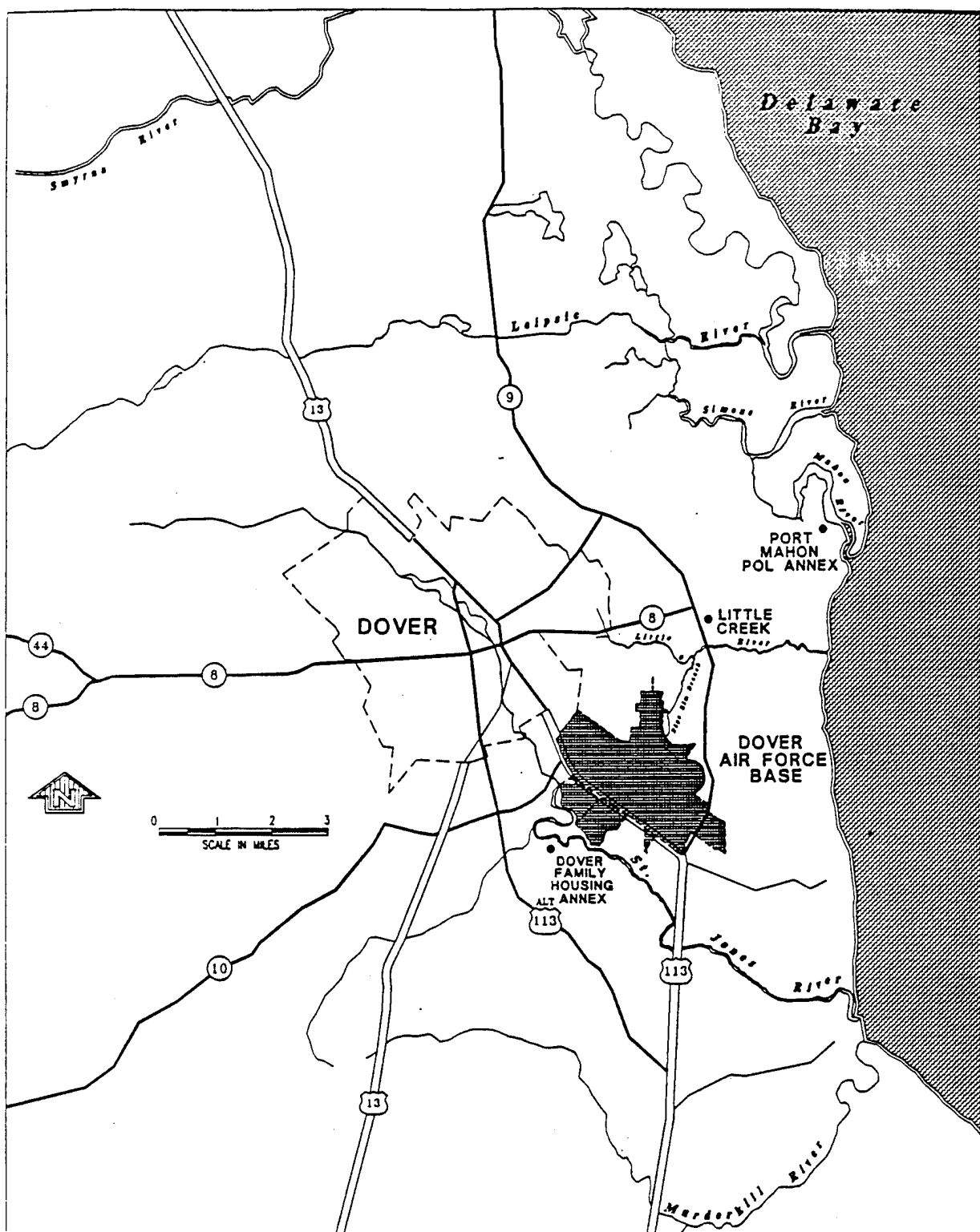


Figure 1.1. Area Location Map of Dover Air Force Base (11).

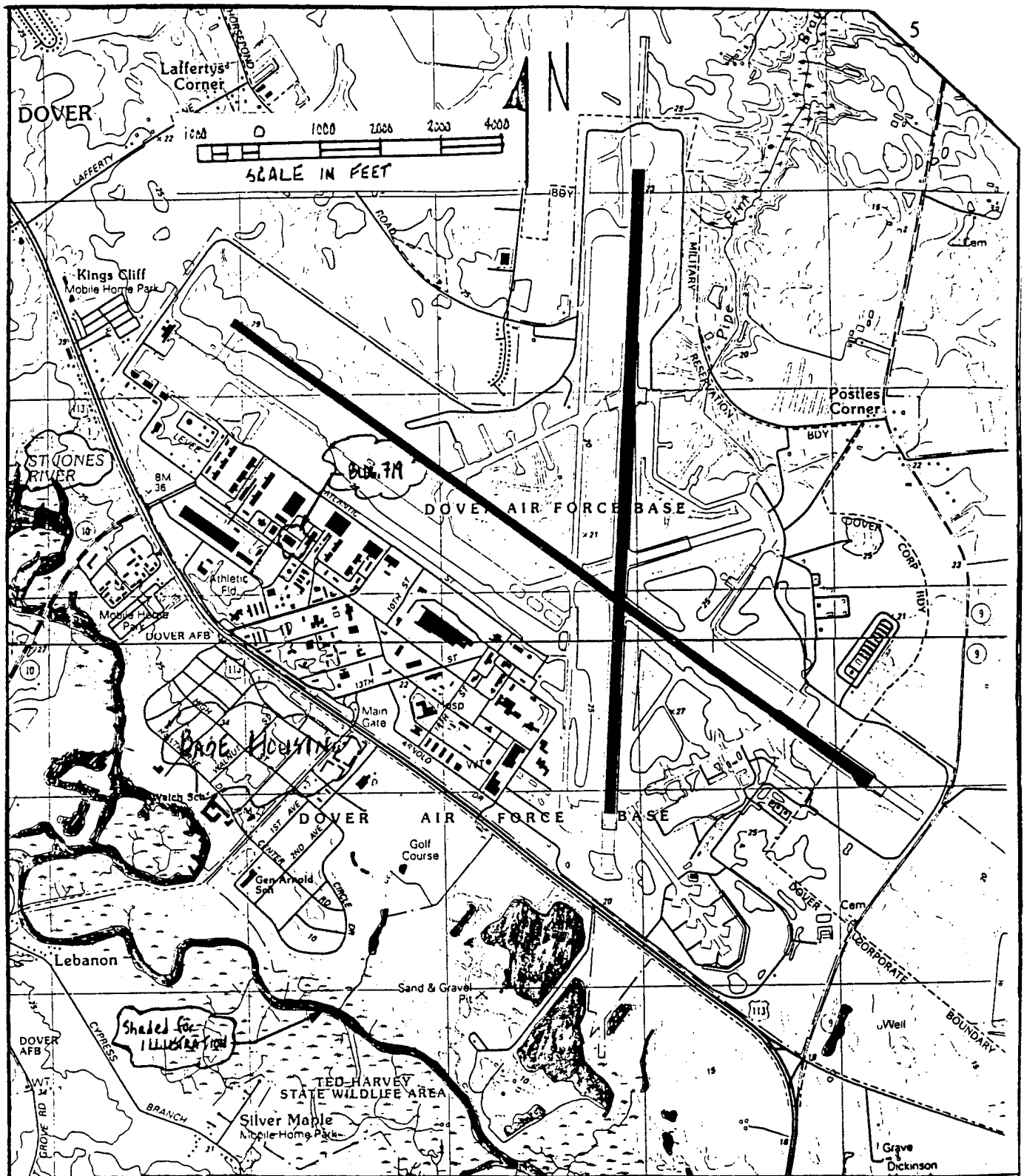


Figure 1.2. Site Location Map of Building 719 and the Building's Location with Respect to the St. Jones River.

Water:
TCE
µg / l

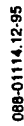


Figure 1.3. TCE Groundwater Plume (39).

Water:
111 TCA
µg/l



Figure 1.4. TCA Groundwater Plume (39).

TRW SAMPLING AT BUILDING 719 DAFB (Superimposed on Enviroscan Map with Dames & Moore Soil / Gas Sample Points)

Water:
1,2DCE_{cls}
µg / l

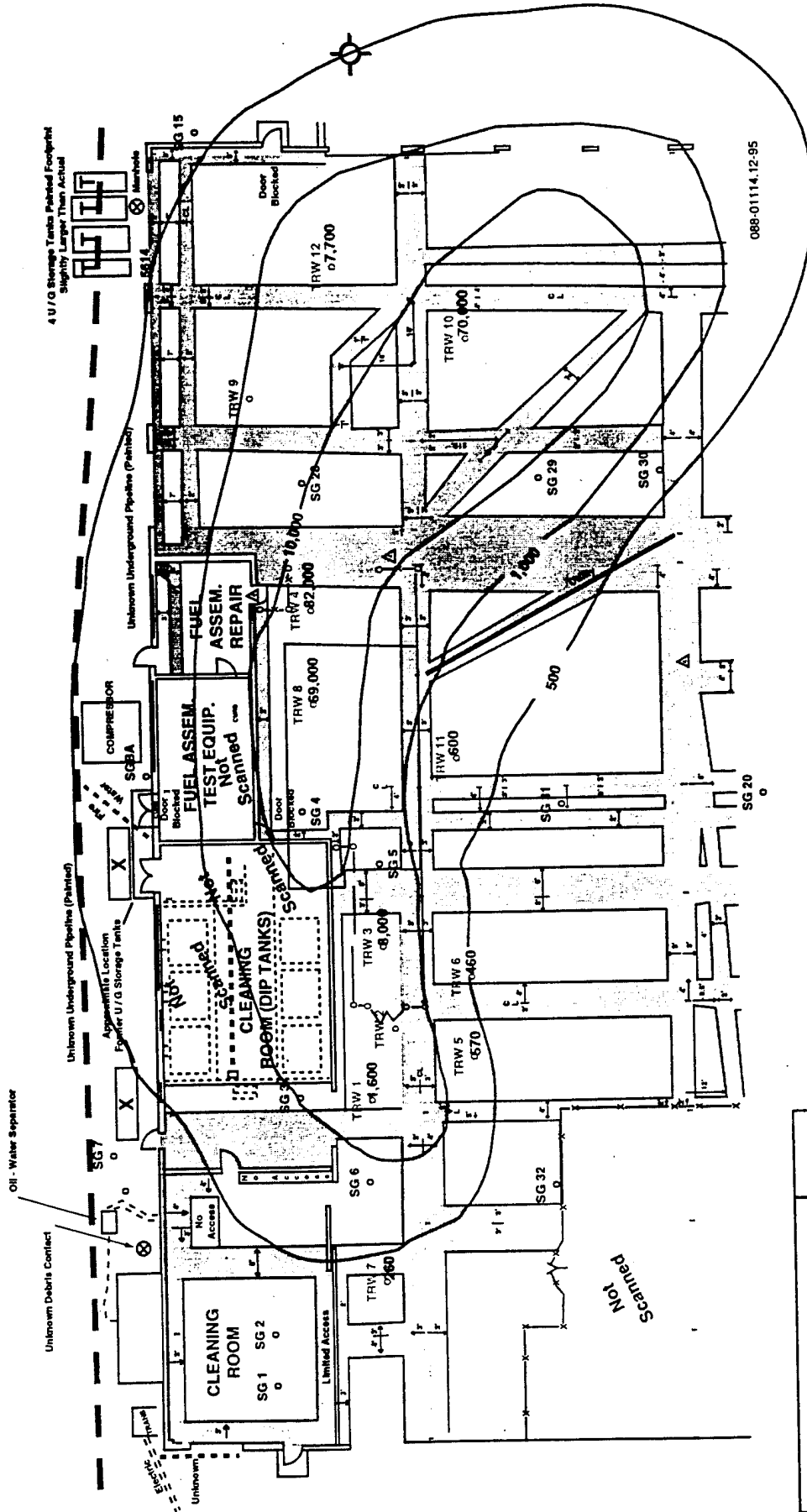
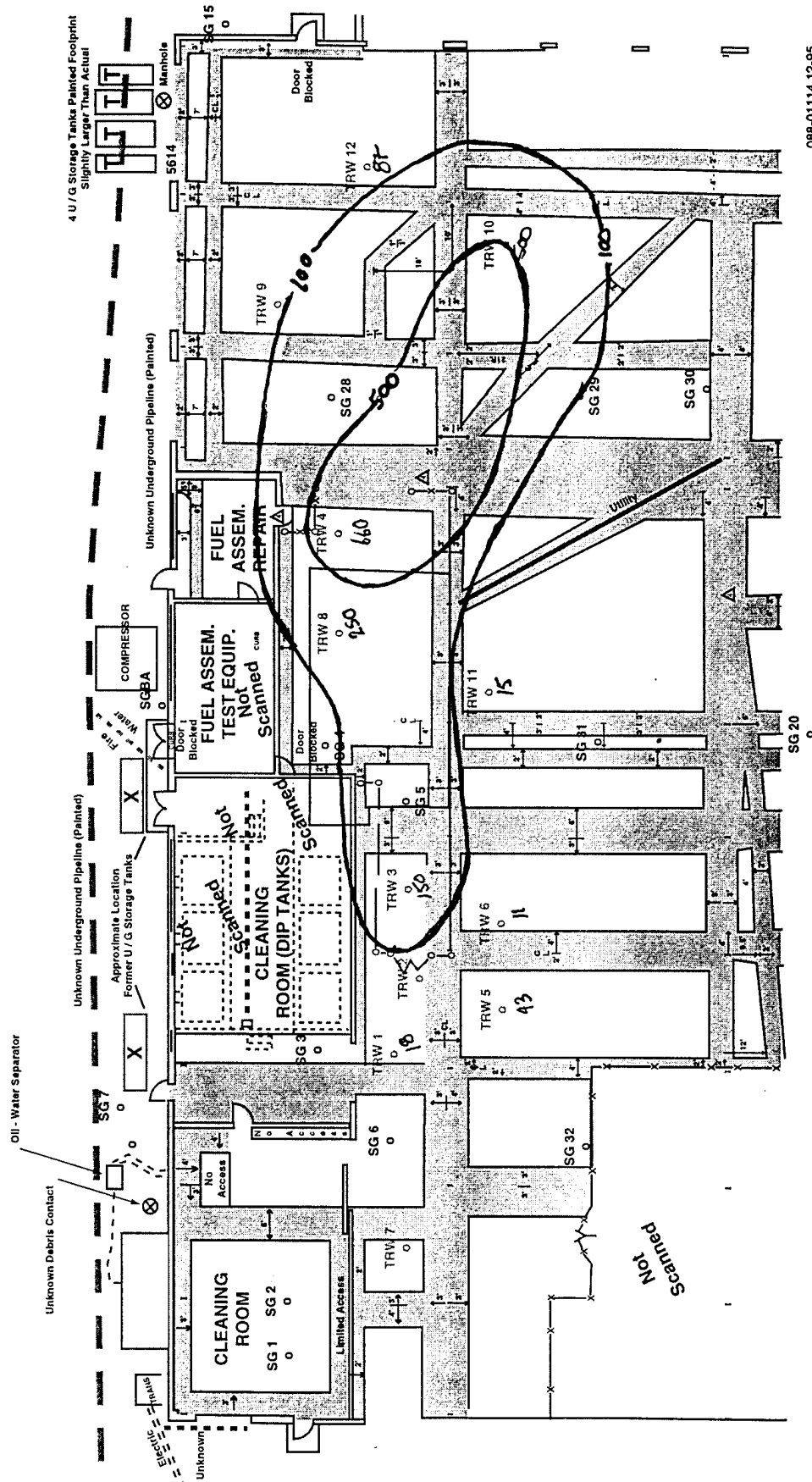


Figure 1.5. Cts -DCE Groundwater Plume (39).

LEGEND:	SCALE
TRW # - TRW Sample Point	1" = 10'
SG # - Dames & Moore Soil/Gas Sample Point	
- - - Underground Utilities	

Figure 1:

TRW SAMPLING AT BUILDING 719 DAFB (Superimposed on Enviroscan Map with Dames & Moore Soil / Gas Sample Points)



Water:
1,2 DCA
µg/l

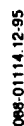
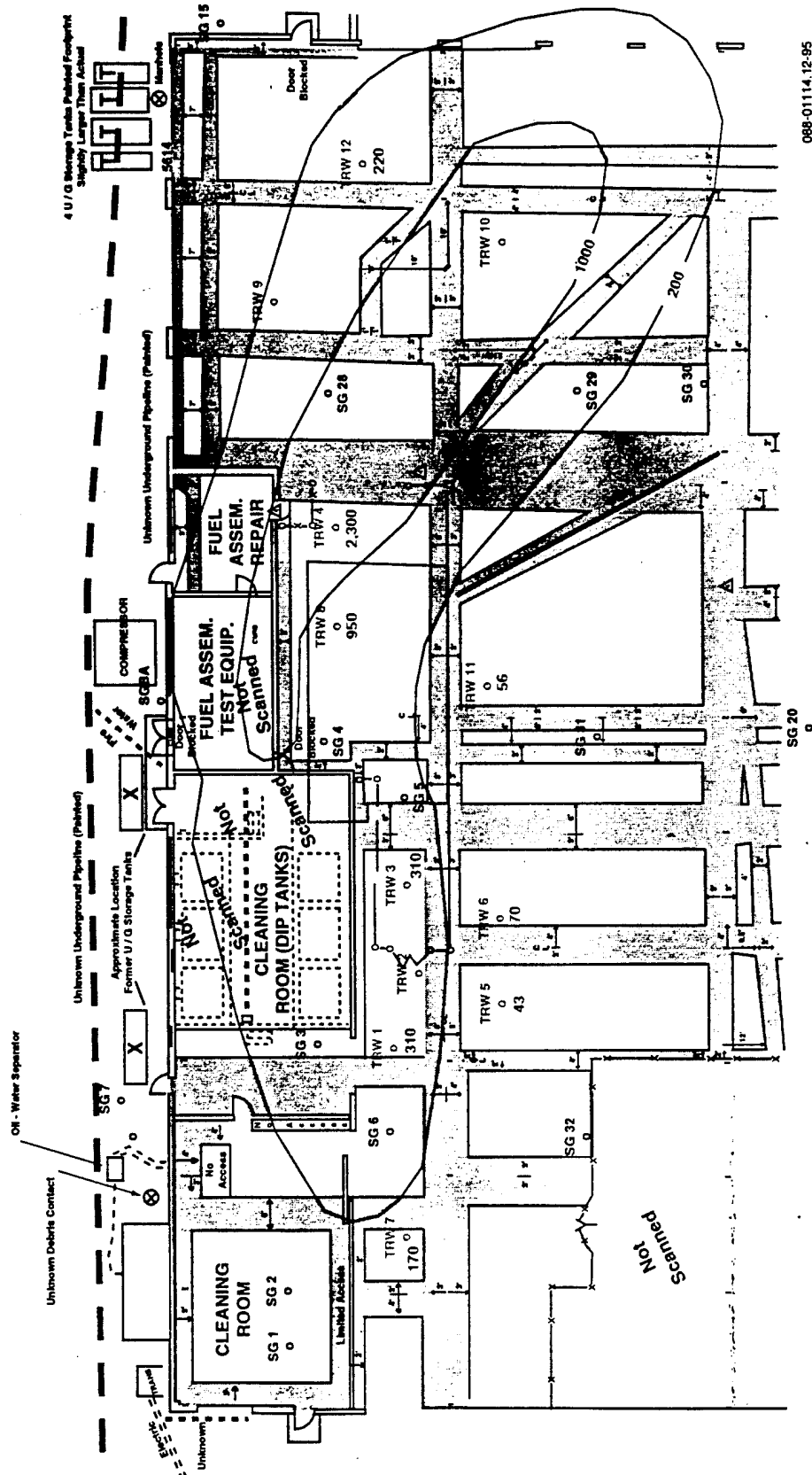


Figure 1.7. 1,2-DCA Groundwater Plume (39).

TRW SAMPLING AT BUILDING 719 DAFB (Superimposed on Enviroscan Map with Dames & Moore Soil / Gas Sample Points)

Water:
 1,1 DCA
 µg / l



088-01114.12-95

LEGEND:	
TRW # - TRW Sample Point	SCALE 1" = 10' ft.
SG # - Dames & Moore Soil/Gas Sample Point	
Unknown Underground Utilities	

Figure 1.8. 1,1-DCA Groundwater Plume (39).

Vinyl chloride
Water
µg / l

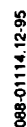


Figure 1.9. VC Groundwater Plume (39).

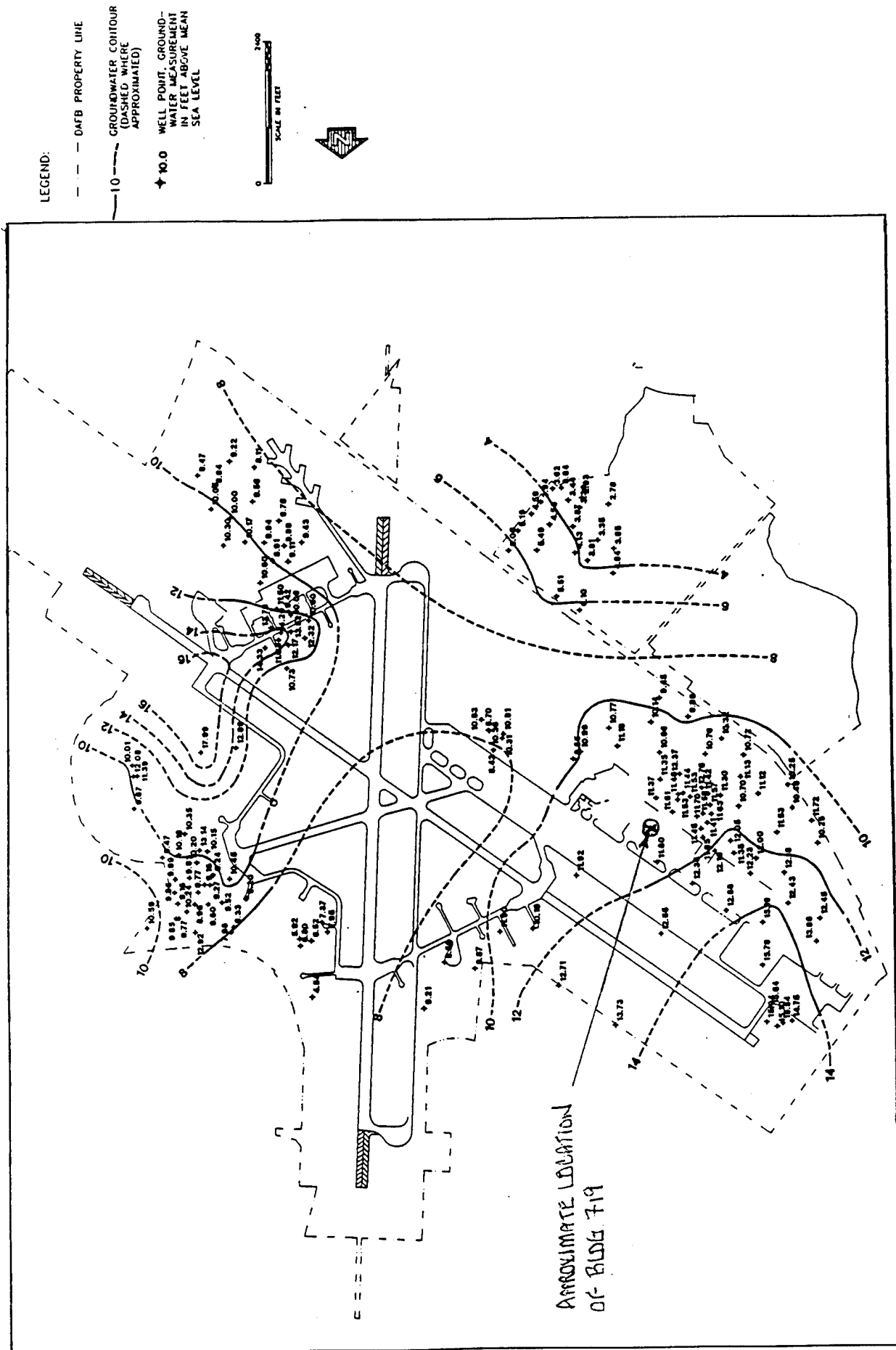


Figure 1.10. Groundwater Seasonal Shallow Columbia Aquifer Contour Map (October to December). NOTE: The general direction of groundwater flow does not change seasonal but the height above mean sea level does vary by approximately one foot between summer and winter months (11).

CHAPTER 2

CHEMICAL BACKGROUNDS AND HUMAN HEALTH CONCERNS

Halogenated aliphatic hydrocarbons are prevalent groundwater contaminants (64) that have been much studied and reported throughout the literature, including United States Environmental Protection Agency (USEPA) documents. The chlorinated alkanes and alkenes discussed in this report are of a major concern because of their potential harmful effects and sometimes carcinogenic nature. TCE; 1,1-DCE; trans-DCE; TCA; 1,1-DCA; 1,2-DCA; CA; and VC are classified as "priority pollutants," *cis*-DCE is not (21, 30, 57). All the compounds except 1,1-DCA and CA are regulated under the Safe Drinking Water Act.

This chapter provides a brief description on the harmful effects associated with TCA and TCE and their by-products. In addition, Table 2.1 is provided as a summary of the physical/chemical parameters for each chemical including the USEPA carcinogenic classifications.

2.1. Trichloroethylene.

TCE is a colorless, moderately hydrophobic ($\log K_{ow}$ between 2 and 3 (49)), volatile chlorinated aliphatic hydrocarbon (CAH) that is used by industry primarily as a metal degreasing agent as well as a dry cleaning, organic synthesis, refrigerant, and fumigant solvent (10,64). Kefoot and Barrows (1981) (as reported by reference (36)) reported that TCE had the highest ranking of all hazardous substances identified in groundwater at 546 Superfund sites. Acute inhalation studies with laboratory animals demonstrated central nervous system depression and some cardiac function inhibition. Various chronic exposure tests conducted on rats and mice showed no or minimal liver

damage. Mixed results have been obtained in mutagenicity testing of mice. TCE is listed by the USEPA as a probable human carcinogen (Group B2) (2).

Table 2.1. Physical/Chemical Parameters (3,21,30,33,55)

Contaminant	Molecular Weight	Specific Gravity*	Henry's Constant* (mol-L/mol-L)	log Kow **	Solubility (mg/L)*	Molecular Volume (cm(3)/mole)#	USEPA Carcinogenic Classification ***
TCE	131.38	1.46	0.309	2.42	1100	93.5	B2
TCA	133.4	1.33	0.561	2.48	2420	97.5	D
1,1 DCE	96.94	1.22	0.857	1.84	2250	76	C
cis 1,2 - DCE	96.94	1.28	0.162	1.52*	3500	76.0	D
trans 1,2 - DCE	96.94	1.26	0.361	1.10*	6300	76	D
1,1 DCA	98.96	1.18	0.179	1.79	5500	80.0	C
1,2 DCA	98.96	1.25	0.059	1.47	8690	80.0	B2
VC	62.50	0.91	0.902	1.38	2791**	58.5	A
CA	64.51	0.90	0.457	1.54	5700	62.5	No Classification

*20 ° C; ** 25 ° C , # (55, Table 9.3), *** Classifications/Groups are defined in Sections 2.1 through 2.8.

2.2. 1,1,1-Trichloroethane (2).

TCA is widely used as an industrial cleaner and degreaser and as a solvent of lipophilic substances. Humans who have inhaled high concentrations of TCA exhibit reversible central nervous system depression and minimal hepatic injury. Humans exposed at levels up to 450 ppm have demonstrated mild eye irritation and some transient psychophysiological function inhibition. Laboratory animals have shown weight loss with decreased survival when exposed to TCA. The USEPA has not classified TCA as a carcinogen (Group D) due to inadequate evidence.

2.3. 1,1-Dichloroethylene (2).

1,1-DCE is used primarily as an intermediate in synthesis of copolymers for food packaging films and coatings. 1,1-DCE is also used in the synthesis of TCA. No definitive human health studies on 1,1-DCE have been conducted. Acute effects noted in rats included hepatotoxicity (e.g., a decrease in liver enzyme levels) and nephrotoxicity (kidney toxicity). Chronic effects in laboratory animals also target the liver. Carcinogenicity tests have been uncertain. The USEPA has classified 1,1 DCE as a possible human carcinogen (Group C) because of limited evidence of carcinogenicity in animals and of humans.

2.4. 1,2- Dichloroethylene (*Cis and Trans*) (2,6).

Both *cis* and *trans*-DCE are used alone or in combination as solvents and chemical intermediates. Neither *cis* or *trans*-DCE have had wide industrial usage. Their principle source in groundwater appears to be from in-situ transformations from other chlorinated hydrocarbons. No human data on health effects exists nor have long-term carcinogenicity studies been conducted. Minimal impacts to laboratory animals has been observed. The USEPA has not classified *cis and trans*-DCE as a carcinogen (Group D) because of inadequate evidence.

2.5. 1,2-Dichloroethane (2).

1,2-DCA is used in the manufacture of VC and tetraethyl lead, as a lead scavenger in gasoline, an insecticidal fumigant, in tobacco flavoring, as a constituent of paint varnish and finish removers, as a metal degreaser, in soap and scouring compounds, in wetting agents, and in ore floatation. Human exposure to high vapor concentrations results in irritation of the eyes, nose, and throat, with continued exposure leading to central nervous

system depression and injury to the liver, kidneys, and adrenals. The USEPA has classified 1,2-DCA as a probable human carcinogen (Group B2) based on positive carcinogenicity in animal ingestion studies.

2.6. 1,1-Dichloroethane (6,62).

1,1-DCA is a colorless and oily liquid. 1,1-DCA is used as a solvent for plastics, oils, and fats; cleaning agent; degreaser; in rubber cementing; as a fumigant and insecticide spray in fabric spreading; and in fire extinguishers. 1,1-DCA is also a chemical intermediate of TCA. 1,1-DCA is not produced in the United States but is imported for use. Exposure to 1,1-DCA will result in central nervous system depression, injury to the liver, and eye and respiratory tract irritation. 1,1-DCA is considered moderately toxic and a possible human carcinogen (Group C).

2.7. Vinyl Chloride (2).

VC is commercially synthesized through halogenation of ethylene and is used in the production of polyvinyl chlorinated (PVC) pipe for the building and construction industry. Acute effects of VC in humans include central nervous system dysfunction, organic disorders of the brain, skin alterations, Raynaud's syndrome, and acoosteolysis. VC has proven to be a carcinogen to humans, as wells as mice, hamsters, and rats. Angiosarcomas of the liver was the most common form of cancer and has been diagnosed in VC workers. Brain tumors, hepatomas, nephroblastomas, and lung tumors have also been diagnosed as a result of VC exposure. The USEPA has classified VC as a human carcinogen (Group A).

2.8. Chloroethane (62).

CA is a chemical intermediate of 1,1- DCA, used as a refrigerant, solvent alkylating agent, and starting point in the manufacture of tetraethyl lead. CA in high concentrations causes central nervous system depression. Chronic effects from industrial exposure have not been reported. Liquid spilled on the skin may cause rapid cooling and possibly frostbite. CA is least toxic of all the chlorinated hydrocarbons.

CHAPTER 3

SITE SPECIFIC GEOLOGY AND HYDROLOGY

The Columbia, Frederica, Cheswold and Piney Point Aquifers have been developed as groundwater supply sources within the state of Delaware (Figure 3.1). The Cheswold and Piney Point Aquifers are the primary source of drinking water for the city of Dover and Dover AFB (11). The Frederica Aquifer is used as a drinking water source in areas south of Dover and the AFB (11,14). The Columbia Aquifer is used as a source of irrigation and domestic water supply throughout most of the state (11,14). Contaminated groundwater addressed in this report is associated with the Columbia Aquifer.

3.1. Columbia Aquifer (11).

The Columbia Aquifer under Dover AFB consists chiefly of discontinuous lenses of medium to coarse sand with gravelly sand, gravel, silt, and clay lenses. The aquifer varies in thickness from a few feet in the northern part of the state to over 180 feet in the southern part of the state. Recharge of the aquifer is mainly through precipitation at approximately one billion gallons/day.

The Columbia Formation in general was deposited under fluvial conditions and forms a broad sheet-like deposit of sand covering most of the state. The thickness of the formation varies from 30 to over 80 feet on DAFB. The confined bed below the Columbia Aquifer is the Calvert Formation which consists of gray to dark gray, firm, dense clay with thin laminations of silt and fine sand. The thickness of the formation ranges from 20 to 28 feet.

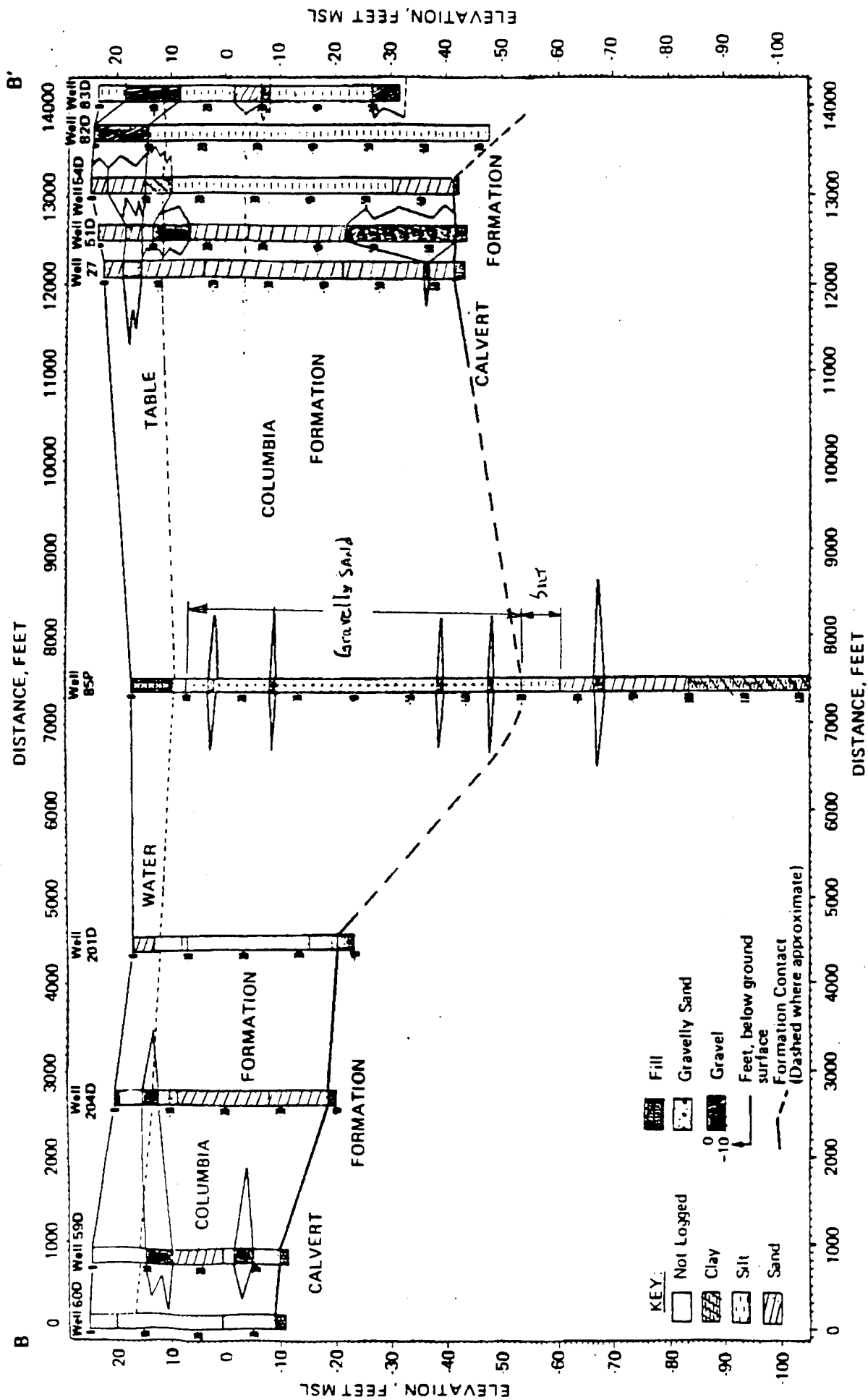


Figure 3.1. Cross Section of Aquifer System North of and Parallel to the Northwest/southeast Runway (11).

3.2. Columbia Aquifer Groundwater Characteristics (11).

The saturated thickness of the Columbia Aquifer ranges from approximately 15 to 20 feet in the western portion of the base to 70 feet in the eastern portion. The Building 719 site is located on the western part of the base. Figure 1.10 indicates the groundwater flows in several directions due to "groundwater divides." The flow of groundwater, however, from the Building 719 site is generally in a southerly direction and towards the St. Jones River. The groundwater velocity ranges between 0.18 to 0.5 feet/day.

3.3. St. Jones River.

The St. Jones River is approximately 7,200 feet south of the Building 719 site and the first surface water point of contact for the Building 719 contaminated groundwater. The St. Jones River basin drains approximately 86 square miles (mi²) of Central Kent County which encompasses the city of Dover and Dover AFB. The river extends over 28.6 miles from northwest to southeast and has a measured average discharge of 36.6 cubic feet/second (cfs) at a Dover gaging station over the last 28 years (14). The reported channel depth at the lower end of the St. Jones (The lower end is defined as the section of river that begins just south of the base golf course (Figure 1.1)) is 5 to 15 feet with river widths of 125 to 200 feet (61). The river is tidal from the mouth of the river through to the city of Dover and fluctuates at an amplitude of five feet.

The lower St. Jones River and the surrounding watershed is designated as a National Estuarine Research Reserve (42). An "environmental impact statement" for the designation reserve (61) reported a concern for potential groundwater contamination of volatile organic compounds originating from Dover AFB's shallow groundwater table. Besides the Building 719 site, Dover AFB has several other contaminated groundwater sites which has led to an extensive ongoing "installation restoration (IR)" program by the

base. Per reference (45) conversation, greater than 50 contaminated sites with varying concentrations of organic solvents and benzene, toluene, ethylbenzene, and xylene (BTEX) compounds have been detected in the same groundwater sector as the Building 719 site. Without any engineering evaluation at the time of the EIS, the EIS stated that any contamination from Dover AFB groundwater would probably be reduced to undetectable levels due to natural attenuation through the groundwater table or by dilution into the river. Modeling the Building 719 plume and the plume's movement towards the St. Jones River should help to confirm or refute the EIS conclusion.

CHAPTER 4

TRANSFORMATION PROCESSES

Halogenated aliphatic organic compounds can undergo both abiotic (non-microbial) and biotic (microbial) transformations. The transformation processes can be divided into two general classes. The first classification is “substitutions” and “dehydrohalogenation” transformations which do not require external electrons for the transformation to proceed. The second classification is “oxidation and reduction” reactions which do require an external electron source to proceed. Examples of each reaction are noted in Figure 4.1. Relative reactions rates are typically faster for “biotic” transformations versus “abiotic” (64). A further discussion on reaction rates as well as the method used to determine reaction rate constants to be used in the “finite differences” fate and transport model is provided in Chapter 6.

This chapter describes the general transformation reactions relevant to the groundwater environment and provides an analysis of the transformations that appear to be occurring at the site.

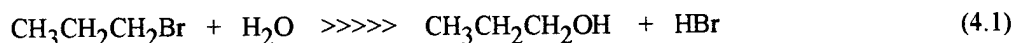
4.1. Substitution.

4.1.1 Hydrolysis.

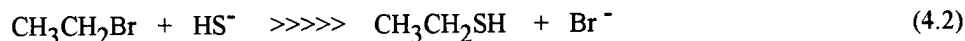
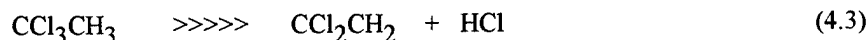
As indicated by equation (4.1) in Figure 4.1, hydrolysis reactions with water leads initially to the production of alcohols. If the products are also halogenated, then further hydrolysis can lead to acids or diols (64). Hydrolysis reactions are generally first order reactions that increase in rate with an increase in halogenation. Hydrolysis of ethene compounds in neutral and acidic conditions is negligible (24). Alkene hydrolysis does

Substitution (Abiotic (A)¹)

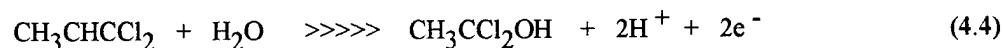
- Hydrolysis:



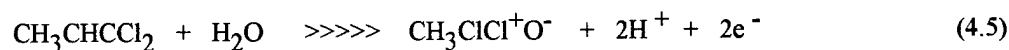
- Conjugation and Other Nucleophilic Reactions:

**Dehydrohalogenation (A²)****Oxidation (Biotic (B)³)**

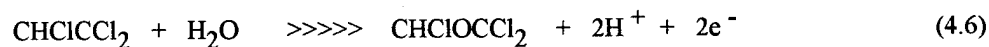
- α - Hydroxylation



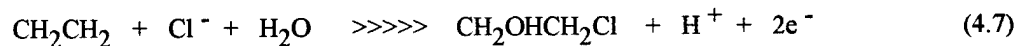
- Halosyl oxidation



- Epoxidation



- Biohalogenation

**Reduction (A/B)**

- Hydrogenolysis

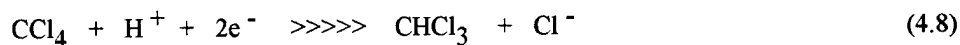


Figure 4.1. Examples of Abiotic and Biotic Reactions Associated with Halogenated Aliphatic Compounds in the Subsurface Environment (modified from Figure 1, reference (64)). ¹ Biotic reactions are only in the presence of microbial enzymes such as hydrolases or glutathione S-transferases (64). ² Biotic reactions occur in mammalian systems (64). ³ Abiotic reactions are not common in subsurface environments unless oxidizing agents are added for the purpose of oxidation (e.g. peroxides) (38).

occur at alkaline pH but is not considered pertinent because the average pH in the groundwater at Building 719 is 5.48 (Table 4.1). Hydrolysis does occur for alkane compounds, however, at neutral and acidic conditions and the rate of hydrolysis is pH independent (24). In a study by Jeffers et al. (24) and in the pH range of the Building 719 site, hydrolysis of 1,1-DCA, 1,2-DCA, and TCA occurred (TCE, 1,1-DCE, and *cis/trans*-DCE were also evaluated but did not hydrolyze under neutral or acidic conditions). Detection of ethylene glycol was found from 1,2-DCA hydrolysis while no chlorinated compounds were detected from either 1,1-DCA or TCA hydrolysis (TCA eventually hydrolyzes to acetic acid (64)).

Howard et al. (22) quoted Mabey and Mill (1978) that CA hydrolyzes to ethanol and Olsen and Davis reported hydrolysis of VC with a half life of < 120 months but did not provide pH conditions.

4.1.2. Conjugation and Other Nucleophilic Reactions.

Conjugation and other nucleophilic reactions are not consider an issue at the Building 179 site. The nucleophile concentrations listed in Table 4.1 (i.e. Cl^- , SO_4^{2-} , HS^- , etc.) are not high enough in concentration to compete with "groundwater" for substitution (55).

4.2. Dehydrohalogenation (Elimination Reactions)

In dehydrohalogenation reactions (equation (4.3)), an alkyl derivative will eliminate a halogen along with a proton from the adjacent carbon to form a double bonded alkene. Vogel et al. (64) report that monohalogenated aliphatics do not undergo dehydrohalogenation in water under normal environmental conditions and that polychlorinated alkanes undergo dehydrohalogenation only above pH 7. Again, since the

Table 4.1. Other Pertinent Water Analytical Site Data (39).

	pH	Temp Degrees C	Sulfate (mg/L)	Sulfide (mg/L)	Oxygen (mg/L)	Nitrate (mg/L)	Ca (mg/L)	Cl (mg/L)	CO(2) (mg/L)
Bore Hole									
1	NDA		NDA	NDA	NDA	NDA	9.52	NDA	NDA
2	5.56	19.5	9	BDL (2)	<0.2	<0.5	3.88	60	231
3	5.4	19.9	4	BDL (2)	0.4	<0.5	2.81	60	271
4	4.96	20.2	14	BDL (2)	<0.2	1	23.1	150	44
5	5.86	13.1	26	BDL (2)	8	3.7	1.16	28	22
6	5.32	15.8	47	BDL (2)	3.2	<0.5	1.32	32	105
7	5.58	13.2	34	BDL (2)	0.9	4.5	6.07	43	274
8	5.44	12.2	0.23	BDL (2)	7.4	1	21.8	170	29
9	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA
10	4.93	16.9	19	BDL (2)	1.1	<0.5	4.99	78	72
11	5.74	17.4	8	BDL (2)	5.6	<0.5	3.99	61	127
12	5.96	16.2	51	BDL (2)	4	3.6	7.32	12	50
AVERAGE	5.48	16	21.22	<2	3.1	1.6	9	69	123

NOTE: "<" counted in average concentration calculation.

NDA: No data available

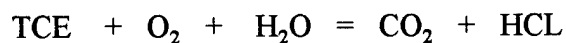
BDL: Below detection limits

Building 719 site pH is between 5 and 6, dehydrohalogenation is not considered a means of transformation.

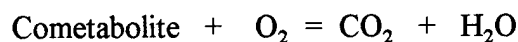
4.3. Oxidation.

Organic compounds normally contain reduced forms of carbon (i.e. glucose, acetic acid) that are energetically favorable for oxidation. Halogenated aliphatic compounds on the other hand are generally already in a "oxidized state" due to the presence of the halogen substituents. The more halogens present, the more the "oxidized state" of the compound, and thus, the more favorable is the compound to reductive processes rather than oxidative processes (64). Consequently, chlorinated aliphatic compounds are not easily degraded under oxidizing conditions but do degrade under anoxic conditions (5,7,18,23,29,31,38,40,41,56,64,65,69).

Successful degradation has been demonstrated, however, under aerobic conditions when microorganisms are induced with a primary substrate (e.g. methane, toluene, glucose (Table 4.2)) as a source of carbon and energy to sustain growth (16,17,32,37,47,52,67). The process is commonly referred to as "cometabolism." The simplified cometabolic reactions that occur simultaneously during the aerobic cometabolism of TCE are:



and



Cometabolites are considered primary substrates and the alkene (TCE) is the secondary non-growth substrate. Examples of primary and secondary substrates for both aerobic and anaerobic transformations are contained in Table 4.2.

Table 4.2. Examples of Aerobic/Anaerobic Cometabolic Primary and Secondary Substrates .

PRIMARY SUBSTRATES	COMETABOLITES: SECONDARY NON-GROWTH SUBSTRATES
Aerobic	Aerobic/Oxidation
alkanes, benzene, toluene, glucose, acetone, isopropanol, acetate, phenol, xylene, chlorobenzene, methane	TCE, dichloroethylene, dichloroethane, chloroform, VC
Anaerobic	Anaerobic/Reduction
glucose, acetone, isopropanol, acetate, phenol	TCA, TCE, tetrachloroethylene, DCE, DCA, DDT, lindane, polychlorinated biphenyls

Modified from reference (47).

Oxygen is known to have the highest reduction potential to support microbial oxidation of organic compounds. Should the oxygen supply be limited, other forms of oxidizing agents such as sulfate or nitrate can be used by microorganisms as an electron acceptor to stimulate growth. The nitrate concentrations in Table 4.1 appear too low to support microbial degradation. However, sulfate concentrations in Table 4.1 indicate that under anaerobic conditions sulfate may be an electron acceptor for microbial oxidation.

4.4. Reduction.

Unlike oxidation reactions that involve the removal of electrons from organic compound, reduction reactions involve the external transfer of electrons to the organic compound. In the subsurface environment, electrons can be provided through dissolution of reduced minerals and subsequent redox transformations of metal ions in solution by abiotic or biotic reactions (e.g. $\text{Fe}^{2+} + e^- \ggggg \text{Fe}^{3+}$), or through microbial oxidation of reduced organic compounds in an aquifer (38). The end result is a simultaneous gain

of a hydrogen and a loss of a chloride leaving group as indicated by equation (4.8).

Figures 4.2 and 4.3 describe the individual reductive processes and subsequent breakdown compounds for TCA and TCE. The pathways are the same regardless of whether the transition metals or microorganisms provide the reductant.

4.4.1. Microbial Assisted Reactions.

Generally, microbial reduction of polychlorinated ethanes and ethenes is a hydrogenolysis process (equation (4.8)) (64). The hydrogenolysis process and the subsequent reduction of TCA and TCE has been shown to occur under anaerobic/anoxic conditions. The only halogenated aliphatic compounds contained in the USTs and dip tanks at the Building 719 site were TCA and TCE which were used as degreasing agents (43). Consequently, the present concentrations of 1,1-DCE, *cis/trans*-DCE, 1,1-DCA, VC, and CA suggests that TCA and TCE degradation are a result of hydrogenolysis degradation as well as possible hydrolysis. The higher chloride concentrations (Table 4.1) at the same sample points as the high *cis*-DCE concentrations (Table A.1) are another indication that hydrogenolysis may be ongoing.

4.4.1.1. TCA Degradation. Under biotic conditions, TCA transforms to 1,1-DCA and subsequently to CA. CA is further degraded to ethanol by abiotic hydrolysis (Figure 4.2). Support of TCA to 1,1-DCA is provided by laboratory experiments conducted by Parsons et al. (38). Parsons et al. conducted biotransformation experiments of TCA in static microcosms and determined that 1,1-DCA results from the biotransformation of TCA in a pH environment between 5 and 7. Further reduction of 1,1-DCA to CA was shown by Strand and Shippert (1986) (as reported by reference (64)).

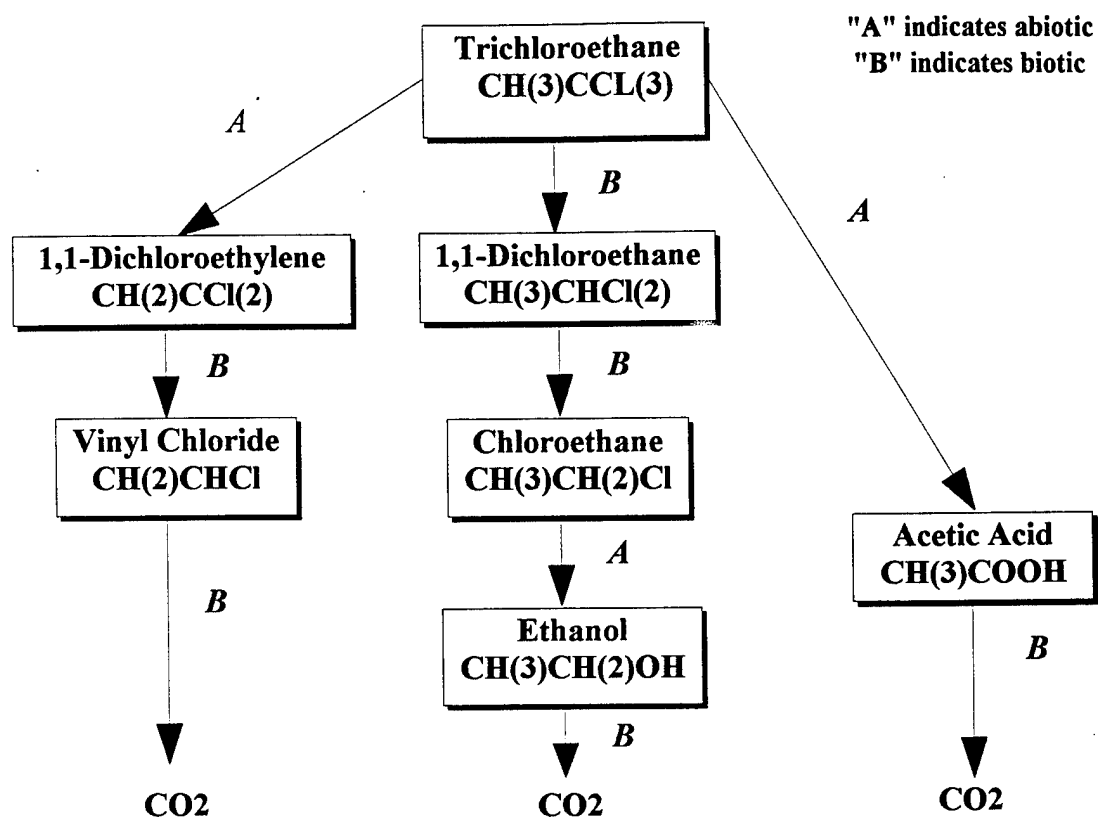


Figure 4.2. Pathways for the Transformation of TCA Under Anoxic Conditions (64).

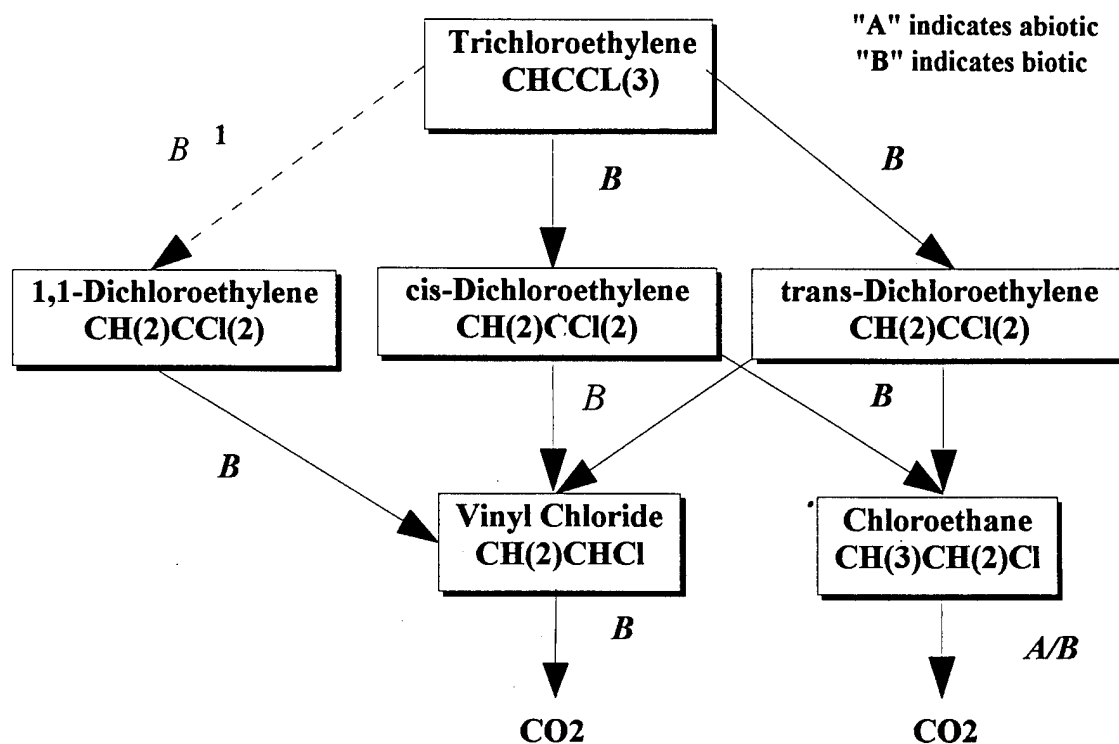


Figure 4.3. Pathways for the Transformation of TCE Under Anoxic Conditions (Generated from references (5), (29), (40), (41), (65), (69)). ¹ The pathway of TCE to 1,1-DCE has been reported by diagram in the literature (4,31,65). Kleopfer et al. (29) reported from a laboratory study that 1,1-DCE did not result from the biotransformation of TCE. Parsons et al. (41) suspected 1,1-DCE formation as a result of TCE biotransformation but did not confirm analytically.

TCA biotransformation to 1,1-DCA at the Building 719 site is evident based on the concentrations of 1,1-DCA present (Table A.1). Further degradation to CA may also be ongoing given the detection of CA in bore hole number 10 (TRW 10, Figure A.1).

Although the groundwater pH at the site is below ideal conditions for dehydrohalogenation (i.e. above pH 7) (Section 4.2), the presence of 1,1-DCE at the Building 719 site may still be a result of abiotic dehydrogenation (equation (4.2)) of TCA (66). Soil samples taken between the ground surface and the groundwater table from the same sample points used for water analysis showed basic pH conditions in several locations (e.g. above pH = 8 (39); high calcium concentrations were found in the same samples that contained increased pH (39,50)). The higher pH conditions in the soil suggest that dehydrogenation of TCA to 1,1-DCE may have occurred during the initial migration of TCA to the groundwater table.

4.4.1.2. TCE Degradation. The reductive microbial transformation of TCE is somewhat more complicated than TCA. The transformation is thought to proceed through three different pathways as indicated by Figure 4.3; degradation to 1,1-DCE, *cis*-DCE, and *trans*-DCE.

Parsons et al. (41) studied and compared the biotransformation by hydrogenolysis of tetrachloroethylene (PCE) and TCE in "groundwater samples" from two different Florida sites and "static microcosms." The microcosm results indicated that PCE was reduced to TCE while TCE was further reduced to *cis*-DCE and *trans*-DCE with eventual partial degradation of *cis*-DCE and *trans*-DCE to VC. The relative concentrations between the "microcosm results" and the concentrations found in the groundwater samples from two sites in Florida were consistent. The by-product *cis*-DCE from TCE reduction in the microcosms was between 25 to 35 times the concentration of *trans*-DCE. The results were similar to the relative concentrations found in one of the Florida aquifer

groundwater samples. The other groundwater sample had a *cis*-DCE concentration 200 times greater than *trans*-DCE from the same sample. The *cis* and *trans*-DCE concentrations at the Building 719 site are consistent with Parsons et al. findings. The *cis*-DCE concentration is between 30 to 275 times the detection limit of *trans*-DCE which was not detected in the groundwater nor the soil but was detected in a soil gas survey; detection in the soil gas phase indicates *trans*-DCE may be present in the groundwater but below detection limits.

Concentrations of VC are also present at the site in reduced concentrations which supports the hydrogenolysis theory. Reduced concentrations of VC would be expected considering the biotransformation process to VC is extremely slow (A half-life as high as 19 years (56)).

Biotic transformation of TCE to 1,1-DCE (Figure 4.3) is not believed to be the source of 1,1-DCE. Kleopfer et al. (29) studied the anaerobic degradation of TCE in soil and did not detect any 1,1-DCE but did detect 1,2-DCE from the degradation of TCE. Parsons et al. (41) suspected trace amounts of 1,1-DCE formation from TCE degradation studies but was unable to confirm by analysis.

A CA concentration of 6 $\mu\text{g/L}$ was detected in one bore hole, bore hole 10, at the plume front. Because of the high *cis*-DCE concentrations compared to *trans*-DCE and 1,1-DCA found at the site, the low level of CA detection suggests that CA may be a result of *trans*-DCE and/or 1,1-DCA biotransformation.

4.4.1.3. 1,2-DCA. The 1,2-DCA compound is transformed to carbon dioxide (CO_2) under anaerobic conditions (6); however, the source of 1,2-DCA at the Building 719 site is unknown. The 1,2-DCA contaminant is not considered a by-product/daughter product of either TCA or TCE under anoxic conditions (Figures 4.2 and 4.3). Speculation is since 1,2-DCA is used in the manufacturer of paint removers (2) and the concentrations

are relatively low at the site, the contaminant could be from paint removers that were occasionally used in Building 719 (11). Past disposal practices of paint removers may have been through the building industrial sewer system with subsequent leakage into the subsurface through a deteriorated drainage pipe (To date, the drainage system that supports Building 719 has not been tested as a possible source of contamination).

4.4.2. Transition Metal Reduction.

Reduction by transition metals involves the transfer of a single electron and the formation of an alkyl radical. The process occurs with a variety of metals including nickel, iron, chromium and cobalt (64). The transition metal reduction of halogenated aliphatic hydrocarbons is a hydrogenolysis reaction, equation (4.8) (Dihalo-elimination or coupling reactions are also possible (64, Figure 1)). Whether transition metal reduction is occurring at the Building 719 site is difficult to determine. The groundwater analysis for metals conducted at the site was for "total metals" and did not distinguish between valence states (data not provided in this report). Iron was the most abundant metal found at each of the sample locations; concentrations ranged between 0.86 to 39.2 mg/L (39). A site microbial characterization indicated the presence of iron reducers at the site which suggests ferrous iron (Fe^{2+}) may be available for transition metal reduction as a result of ferric iron (Fe^{3+}) reduction (46).

4.5. Oxygen and Carbon Dioxide Concentration Comments (Table 4.1).

4.5.1. Oxygen.

The groundwater samples from the Building 719 site were only taken at the groundwater surface. The dissolved oxygen concentrations at the surface indicate aerobic conditions on the outer edges of the contaminant plume, Figure 4.4, and anoxic

Water:
TCE
µg/l

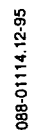


Figure 4.4. Oxygen Concentrations Illustrated on the TCE Plume.

conditions through the center of the plume. Given the presence of TCA and TCE anoxic breakdown products in the groundwater, the low dissolved oxygen concentrations through the center of the plume support the analogy that anoxic degradation is occurring within the saturated zone at the Building 719 site.

Because of the reduced concentrations of contaminants at the outer edges of the plume, a reduction in the dissolved oxygen deficit is expected. However, the concentrations found at the surface are not considered representative of actual concentrations throughout the saturated zone. Higher concentrations would be expected at the surface because of the air interface with the vadose zone. Additional sampling should be conducted throughout the groundwater and plume profile to determine the oxygen concentration as a function of depth and location within the plume.

The dissolved oxygen concentration found at TRW 8 (Figure 4.4) appears to be in error given the location and concentrations found throughout the remainder of the plume. The method used to determine dissolved oxygen concentration was the dissolved oxygen probe, USEPA method 360.1. The USEPA "Methods for Chemical Analysis of Water and Wastes (1974)" as well as "Standard Methods for the Examination of Water and Wastewater, 19th ed. (1995)" indicate that the probe is temperature sensitive. Speculation is that the probe may have been reading high due to improper calibration. The temperature at TRW 8 (Bore Hole 8, Table 4.1) is almost 4 ° C below the average sample temperature. A similar analogy may hold true for TRW 7 which had an 8 mg/L dissolved oxygen concentration at a about 3 ° C below the average.

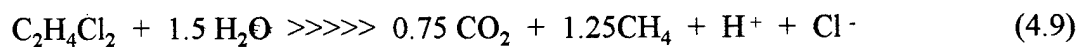
4.5.2. Carbon Dioxide.

The average CO₂ concentration is 123 mg/L per Table 4.1. Normal groundwater concentrations are in the range of 30 to 50 mg/L (53). The high CO₂ concentrations at

the groundwater surface may be associated with either aerobic cometabolism, general aerobic degradation of other organic compounds, or anaerobic degradation. The oxygen concentrations at the outer edge of the plume suggest possible support for microbial activity at the groundwater surface.

Production of CO_2 from anaerobic degradation has been documented by Vogel and McCarty (65) and Bouwer and McCarty (7). Vogel and McCarty studied the biotransformation of PCE to TCE, DCE, and VC under methanogenic conditions. Vogel and McCarty measured CO_2 production during their experiment and speculated that further degradation of VC resulted in the production of CO_2 and CH_4 through biooxidation.

Similar results were obtained by Bouwer and McCarty (6) during the degradation of 1,2-DCA. Again, Bouwer and McCarty speculated based on laboratory transformation results and stoichiometry per equation (4.9) that 1,2-DCA would produce CO_2 and CH_4 through biooxidation without the presence of molecular oxygen. They



$$\Delta G^\circ (w) = - 254 \text{ Joules/mole (at pH 7, 25 }^\circ\text{C)}$$

also suspected that some of the CO_2 may have been generated from the reduction of acetic acid used as a primary substrate in their microcosms. Hydrolysis of TCA to acetic acid at the Building 719 site may result in similar CO_2 production. Given the anoxic daughter products of TCA and TCE at the site and if the above anaerobic CO_2 production theories

are correct, the anaerobic biotransformation process of TCA and TCE may be the source of increased CO₂ concentrations at the site.

The increased CO₂ concentrations may also be responsible for pH depression which appears to be slightly low compared to other saturated zone sites with similar contaminants (31).

Table 4.3 summarizes the transformations processes discussed in this chapter and those processes that appear favorable given the halogenated aliphatic contaminants present and the environmental conditions at the Building 719 site (e.g. pH).

Table 4.3. Most Probable Transformation Processes Possible Within the Saturated Zone at Building 719.

Contaminant	Substitution (S)	Dehydrohalo- genation (D)	Oxidation (O)	Reduction (R)	Remarks
TCA	+	-- (+)	--	+	S: Hydrolysis D: (+) Section 4.4.1.1. O: **
TCE	--	--	--	+	O: **
1,1-DCA	+	--	--	+	S: Hydrolysis D: pH < 7 O: **
1,2-DCA	+	--	+	+	S: Hydrolysis D: pH < 7 O: Biooxidation other than by oxygen.
1,1-DCE	--	--	--	+	O: **
1,2-cis-DCE	--	--	--	+	O: **
1,2-trans-DCE	--	--	--	+	O: **
VC	--	--	+	+	S: Hydrolysis O: Biooxidation other than by oxygen (equation (4.9)).
CA	+	--	--	--	O: ** R: CA to ethanol is abiotic

"+" Favorable

"-" Not Favorable

O: ** Oxidation processes are considered minimal given the anoxic daughter products of TCA and TCE present at the site.

CHAPTER 5

CONTINUITY EQUATION AND THE
FATE AND TRANSPORT MODEL

Prediction of contaminant migration in the saturated zone requires quantitative representations of advection, dispersion, sorption and degradation that are specific or at least applicable to the site and contaminants present (24). Advection is the transport of a solute at groundwater velocities. Dispersion is the spreading of a concentration front as a result of spatial variation in aquifer permeability, fluid mixing, and molecular diffusion. Sorption (adsorption and absorption) is the retention of solute in the soil phase by means of partitioning between the aqueous phase and solids. Degradation is the removal of organic solute from solution when the solute is utilized by microorganisms as a substrate for energy and growth or is consumed as a reactant in a chemical reaction with the aquifer solids, water, waterborne solutes, or colloids (49). The continuity equation that describes contaminant migration in terms of advection, dispersion, sorption and degradation is described by equation (5.1) (69).

$$\frac{\partial c}{\partial t} = \frac{D'_x}{R_c} \left(\frac{\partial^2 c}{\partial x^2} \right) - \frac{\mu_x}{R_c} \left(\frac{\partial c}{\partial x} \right) - \frac{k_{deg}}{R_c} c \quad (5.1)$$

c = concentration (mass/volume)

t = time

D'_x = longitudinal dispersion coefficient (length²/time)

μ_x = advection coefficient (length/time)

x = distance

k_{deg} = first order degradation rate (time⁻¹)

R_c = retardation factor (sorption effects)

The equation that describes retardation is:

$$R_c = 1 + (\rho K_d / \Theta) \quad (5.2)$$

ρ = bulk soil density (mass/volume)

K_d = adsorption partition coefficient (volume/mass)

Θ = porosity of soil

At steady state conditions when all inputs, flows, exchanges, and reaction rates are temporally constant, then the continuity equation can be simplified by:

$$\frac{\partial c}{\partial t} = 0$$

However, since the sources of contamination at Building 719 are presumed to have been removed from the site (i.e. USTs and dip tanks), the groundwater plume under Building 719 does not have a continuous input of contaminants. Under actual field conditions, the concentrations at any given "x" within the plume (as defined by the November 1995 analytical data) are changing with time due to groundwater dilution, advection, dispersion, and degradation effects resulting in a non-steady state condition.

A one dimensional solution to the continuity equation (equation (5.1)) for non-steady state conditions is given by equation (5.3) where the function f is defined by the right side of equation (5.4).

$$V_i(dS_i/dt) = f(t, S_{i-1}, S_i, S_{i+1}) \quad (5.3)$$

$$V_i(dS_i/dt) = Q_{i-1,i}S_{i-1} - Q_{i,i+1}S_i + D'_{i+1}(S_{i+1} - S_i) \quad (5.4)$$

$$- D'_{i-1,i}(S_i - S_{i-1}) - k_i S_i V_i \pm W_i$$

$D'_{i,i+1}$ = bulk longitudinal dispersion segment i $((D_{i,i+1} \times A_{i,i+1}) / X_{i,i+1})$

$A_{i,i+1}$ = cross-sectional area between i and $i + 1$.

$X_{i,i+1}$ = average length of segments.

V_i = volume of segment $(X_{i,i+1} \times A_{i,i+1})$

k_i = degradation rate (day^{-1})

Note: To incorporate sorption effects, all the terms in equation except the loading term (W_i) are divided by the retardation term (equation (5.2)).

Equation (5.4) summarizes a one dimensional "finite differences" groundwater transport model. The model concept involves a finite difference approximation to each of the derivative terms in equation (5.1). By dividing the groundwater flow path (i.e. distance from the source to the St. Jones River) into a series of finite segments (Figure 5.1)

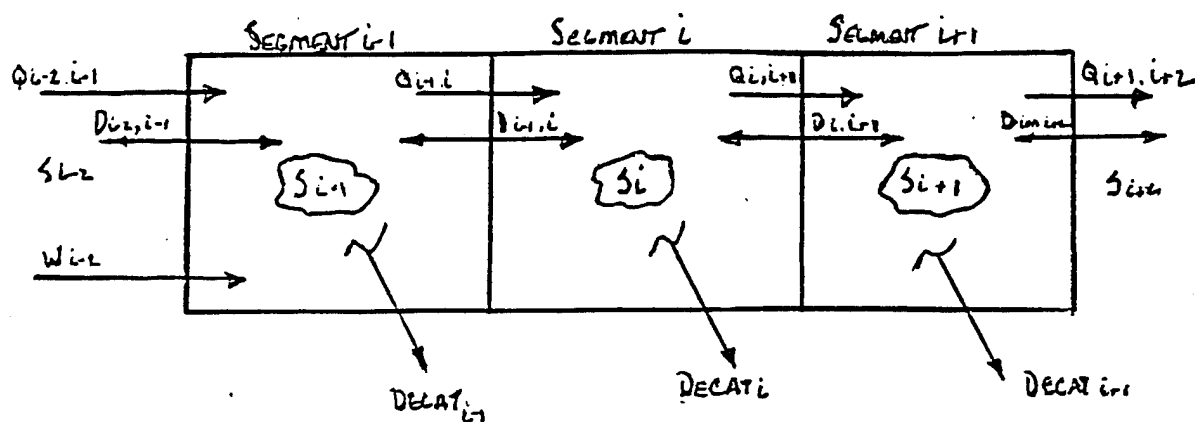


Figure 5.1: Series Segment i Noting Advective Flow, Dispersion, and Degradation.

and establishing a mass balance around each segment, a segment mass balance as described by equation (5.4) can be used to approximate equation (5.1) at non-steady state conditions (60).

Because the concentrations (S_i 's) are also a function of time, a numerical integration method is used to solve equation (5.4) with respect to time. The integration begins from an initial set of concentrations for all segments at time zero (e.g. November 1995 water analysis data (39)). Numerical integration is used to advance the solution one time step forward. After each step is completed, the new values S_i , S_{i+1} , S_{i+2} , etc. become the initial values of next step. The process is continued until the entire time span specified (i.e. 25 years, 50 years, etc.) has been completed. This numerical procedure can be accomplished using a fourth-order Runge-Kutta integration approximation, equation (5.5), for the time interval of integration given by "h" (60). Provided all the longitudinal dispersion coefficients, retardation factors, degradation rates, and flows are known for each segment, the concentration in each segment with respect to time can be determined.

$$(S_i)_{t+1} = (S_i)_t + 1/6(r_{0,i} + 2r_{1,i} + 2r_{2,i} + r_{3,i}) \quad (5.5)$$

$$r_{0,i} = (h/V)f(t, (S_{i-1})_t, (S_i)_t, (S_{i+1})_t)$$

$$r_{1,i} = (h/V)f(t+1/2h, (S_{i-1})_t + 1/2r_{0,i-1}, (S_i)_t + 1/2r_{0,i}, (S_{i+1})_t + 1/2r_{0,i+1})$$

$$r_{2,i} = (h/V)f(t+1/2h, (S_{i-1})_t + 1/2r_{1,i-1}, (S_i)_t + 1/2r_{1,i}, (S_{i+1})_t + 1/2r_{1,i+1})$$

$$r_{3,i} = (h/V)f(t+h, (S_{i-1})_t + 1/2r_{2,i-1}, (S_i)_t + 1/2r_{2,i}, (S_{i+1})_t + 1/2r_{2,i+1})$$

Equations (5.4) and (5.5) can be used to determine concentrations at various distances "x" along the groundwater flow path from the Building 719 site to the St. Jones River as well as concentration changes at various distances "x" with respect to time. Specifically, the solution will provide an estimation as to the concentration and the time rate of change with a specific time period ("h").

Dispersion coefficients, degradation rates, and retardation (sorption effects) factors to be used in the non-steady state model are contained in Chapter 6 as well as a discussion on how the parameters were determined. Application of equations (5.4) and (5.5) and the results of the fate and transport modeling is discussed in Chapter 7.

CHAPTER 6

FATE AND TRANSPORT PARAMETERS AND COEFFICIENTS

As discussed in Chapter 5, advection, dispersion, sorption, and degradation affect organic solute fate and transport in groundwater environments. The difficulty in applying the transport model described in Chapter 5, is determining the dispersion, convection, adsorption, and degradation effects and the subsequent coefficients. This Chapter focuses on determining the degradation rates as well as dispersion and retardation (adsorption) coefficients required to model the fate and transport of chlorinated aliphatic compounds from the Building 719 site.

6.1. Adsorption.

Adsorption is a major contributor to the fate and transport of organic chemicals (38). Adsorption can retard the movement of contaminants in the vadose and saturated zones and can also impact the ability of microorganisms to biodegrade organic compounds by creating an inaccessible food source (1,15). Many methods are used to determine adsorption. Common methods include:

- linear equation methods based on correlation between water solubility, octanol water coefficient (K_{ow}), and organic carbon content,
- methods based on adsorbent surface area,
- linear free energy methods based on molecular structure,
- laboratory batch and column experiments, and
- methods/experiments based on plume location.

The methods used in this report include linear equation methods and methods based on adsorbent surface area. Laboratory batch and column experiments were not conducted on the site soil nor were experiments related to plume locations.

6.1.1. Linear Adsorption.

Adsorption is normally described by an adsorption isotherm. An adsorption isotherm is used to relate the amount of a chemical species which is adsorbed and the chemical's (adsorbate's) bulk phase concentration at a given temperature (8). For low concentrations of organic compounds that are normally encountered in the subsurface environment, the adsorption isotherm generally follows a "linear isotherm (55)."

Karickhoff et al. (26) showed that for several organic compounds with concentrations less than 60-70 % of their solubility, the "linear isotherm" was appropriate. Equation (6.1) describes the linear isotherm relationship.

$$C_s = K_d \times C_e \quad (6.1)$$

C_s = concentration of sorbate on the sediment (mass of sorbate/mass of sorbent)

K_d = partition coefficient (volume of solute/mass of sorbent) used in equation (5.2)

C_e = equilibrium concentration of sorbate (mass/volume of solute)

The amount of adsorption that takes place is dependent on the types of sites (i.e. organic carbon, charged mineral sites, sorbate and sorbent functional groups, etc.) available for adsorption.

6.1.2. Organic Carbon Content.

Organic matter in soil tends to be relatively nonpolar in nature and offers an environment into which hydrophobic compounds may escape without competition with water (55). Research has shown that the organic carbon content of the soil as well as the sorbate hydrophobic nature have a major influence on the adsorption process in subsurface soils. Karickhoff et al. (26) showed that hydrophobic chemicals are readily adsorbed by organic carbon. Lambert et al. (1965) (as reported by reference (19)) studied the sorption of nonionic organic pesticides and suggested sorption could be attributed to an active fraction of the soil's organic matter. Karickhoff et al. (26) applied the organic carbon content of the soil media to the adsorption partition coefficient per equation (6.2).

$$K_{oc} = K_d / f_{oc} \quad (6.2)$$

K_{oc} = organic partition coefficient

K_d = adsorption partition coefficient

f_{oc} = fraction of organic carbon mass

6.1.3. Linear Equation Methods Used to Predict Adsorption.

Roy and Griffin (51) reported that Lambert (1968) proposed that the role of organic soil matter was similar to that of an organic solvent and that the partitioning of an organic solute between the soil material and water could be estimated by the chemicals tendency to partition between water and an immiscible organic solvent. Octanol-water partitioning has been used to describe Lambert's proposal and has been demonstrated to be linearly correlated to the organic carbon partition coefficient (K_{oc}) (26,51,55). Common linear equations used to describe K_{oc} as a function of the octanol-water

coefficient (K_{ow}) are listed in Table 6.1. Table 6.1 also contains a linear expression as a function of solubility (equation (6.5)). The solubility of the compound is also a strong indicator of adsorption. The greater the solubility of the compound, the stronger the affinity with the solution, and the smaller the extent of adsorption (68).

Table 6.1. Equations for Predicting K_{oc} (K_{om}).

Equation	Reference	Equation No.	Remarks
$\log K_{om} (l/kg) = 0.88 \log K_{ow} - 0.27$	(27), (55)	6.3	Based on TCA, TCE, PCB, 1,2-dichlorobiphenyl, methoxy chlor
$\log K_{oc} (l/kg) = 1.029 \log K_{ow} - 0.18$	(Referenced by 38)	6.4	44 pesticides
$\log K_{om} (mg/mg) = 4.040 - 0.557 \log$ (Solubility) $Solubility = (\mu moles/l)$	(9)	6.5	TCA, TCE, 1,2-DCA (at 20 degrees C)
$\log K_{oc} (l/kg) = 1.00 \log K_{ow} - 0.21$	(26)	6.6	$\log K_{ow}$'s between 2.12 and 6.34 (at 25 degrees C)

$$K_d = 1.724 \times f_{oc} \times K_{om} \text{ (approximately) (38)}$$

Although increased organic carbon content of the adsorbent has been shown to increase adsorption, mineral interfaces of the sorbent may contribute or in some cases dominate adsorption if the organic carbon content is too low (i.e. 0.1%) (28).

Non-hydrophobic interaction (i.e. mineral surface or function group) may contribute or dominate adsorption when one or both of the following occur (28):

- high sorbate polarity: highly polar or ionizable functional groups conducive to significant site-specific bonding with sorbent polar groups as charged sites on sorbent surfaces, and/or
- low organic carbon content in sorbent and in particular with high clay content.

The average organic content of the Building 719 site soil is 0.02 %. The recommended level of organic content at which adsorption of mineral surfaces should be investigated is 0.1% (28). McCarty et al. (35), however, developed a “critical organic carbon content (f_{oc}^*)” fraction relationship, equation (6.7), under which mineral surface effects should be considered. The “free-energy relationship” equation was derived from silica surface sorption tests conducted on benzene, chlorinated benzene isomers, TCE, and PCE. Table 6.2 summarizes the f_{oc}^* values for the Building 719 site compounds using a “specific surface area” of 0.88 meters²/gram (m²/g) (based on an average grain size diameter of 0.59 mm (39))(4). The f_{oc}^* values in Table 6.2 indicate that mineral surfaces should be considered for *cis* and *trans*-DCE, 1,2-DCA, VC, and CA.

$$f_{oc}^* = \frac{SA}{200(K_{ow})^{0.84}} \quad (6.7)$$

SA = specific surface area (m²/g)

K_{ow} = octanol-water coefficient

Table 6.2. Critical Organic Carbon Fractions for Building 719 Groundwater Contaminants.

Contaminant	K _{ow}	f _{oc} *
TCE	264	4.1E - 05
TCA	302	3.6E - 05
1,1 DCE	69	1.3E - 04
cis 1,2 - DCE	33	2.3E - 04*
trans 1,2 - DCE	13	5.1E - 04*
1,1 DCA	62	1.4E - 04
1,2 DCA	30	2.5E - 04*
VC	24	3.0E - 04*
CA	35	2.2E - 04*

* Values that are above the site's 2.0E - 04 organic carbon content fraction.

Based on the same chemicals used to develop the f_{oc}^* relationship, McCarty et al. (35) also derived equation (6.8) to determine the approximate sorption by silica surfaces when f_{oc}^* is greater than f_{oc} .

$$K_{i0} = \frac{SA (K_{ow})^{0.16}}{200} \quad (6.8)$$

K_{i0} = partition coefficient for solute with the inorganic phase (L/kg)

SA = specific surface area (m²/g)

K_{ow} = octanol-water coefficient

Provided that K_{oc} and the K_{i0} are the dominant means of adsorption and K_{oc} and the K_{i0} are additive, McCarty et al. proposed equation (6.9) as a two-phase adsorption model to predict the overall partition coefficient (K_d) when mineral surfaces are considered.

$$K_d = f_{io} (K_{io}) + f_{oc}(K_{oc}) \quad (6.9)$$

K_p , K_{io} , f_{oc} , and K_{oc} are as previously defined

f_{io} = the fraction of inorganic material = $(1 - f_{oc})$

Based on the low concentrations at the site (i.e. < 60 % solubility: Karickhoff (26)) and the sandy nature of the aquifer (i.e. "silica sand," equation (6.8)), the adsorption of the halogenated aliphatic organic compounds at the Building 719 site is assumed to be a function of equations (6.1) through (6.9) and K_d can be determined by their application. Once the K_d 's are known for each compound, the retardation factors, equation (5.2), can be determined.

6.1.4. Predicting Adsorption.

Table 6.3 contains calculated K_d values using equations (6.3) through (6.6) and (6.8) and (6.9) (K_{ow} values as well as solubilities are provided in Table 2.1). The K_d values obtained from equations (6.3) through (6.6) are fairly consistent with each other (i.e. order of magnitude basis). The K_d values obtained from equation (6.9) for the compounds that require consideration of mineral surface effects (Table 6.2) are based on a f_{io} of approximately "1" (i.e. $f_{oc} \cong 0$).

6.1.5. Retardation Factor.

The retardation factor is a function of the soil density, porosity, and adsorption/absorption partition coefficient K_d (equation (5.2)). The soil at the site is classified as very fine sand to very coarse sand with minimal clay particles. The average

Table 6.3. Predicted Partition Coefficients, K_d (l/kg).

Contaminant	log K_{ow}	log S ($\mu\text{mole/l}$)	Equation					Average ($\pm$ one std. dev.)
			6.3	6.4	6.5	6.6	6.9	
TCE	2.42	3.92	0.025	0.041	0.025	0.032		0.031 $\pm$ 0.0076
TCA	2.48	4.26	0.028	0.047	0.016	0.037		0.032 $\pm$ 0.013
1,1-DCE	1.84	4.37	0.0077	0.010	0.014	0.0085		0.010 $\pm$ 0.0016
cis-1,2-DCE	1.52	4.56					0.0077	
trans-1,2-DCE	1.10	4.81					0.0066	
1,1-DCA	1.79	4.74	0.0070	0.0092	0.0087	0.0076		0.0081 $\pm$ 0.0010
1,2-DCA	1.47	4.94					0.0076	
VC	1.38	4.65					0.0073	
CA	1.54	4.95					0.0078	

$$f_{oc} = 2.03E - 04$$

particle size is 0.59 mm (39) which is defined as "coarse sand" by the United States Department of Agricultural (6). The bulk density and porosity of the soil at the Building 719 site were not measured in the field but are assumed to be 2.05 g/cm³ (55) and 0.30 based on the soil grain size (6). Given the K_d values listed in Table 6.3, retardation factors for each of the contaminants at the site were calculated using equation (5.2) and are listed in Table 6.4. As recommended by Schwarzenbach et al. (55), temperature adjustments, as described in Section 6.1.6., were made to those K_d values determined as a function of f_{oc} and are also listed in Table 6.4.

Based on the values in Table 6.4, TCE and TCA appear to be the least mobile as expected due to their high K_{ow} compared to the other compounds (Table 6.2) (51). In general, adsorption does not appear to be a strong factor in restricting the movement of the organic contaminants through the aquifer. The low adsorption is somewhat expected given the low organic carbon content ($f_{oc} = 0.0002$) and the nature of the soil (i.e. sandy soil; average grain size = 0.59 mm). Further support for low soil adsorption potential is

Table 6.4. Retardation Factors (R_c) Calculated From Equation (5.2).

Contaminant	R_c (dimensionless)*	R_c (dimensionless)**
TCE	1.21	1.26
TCA	1.22	1.27
1,1-DCE	1.07	1.08
cis-1,2-DCE	1.05#	1.05
trans-1,2-DCE	1.05	1.05
1,1-DCA	1.06	1.07
1,2-DCA	1.05	1.05
VC	1.05	1.05
CA	1.05	1.05

* 25 °C; ** 16 °C.

Values for *cis/trans*-DCE, 1,2-DCA, VC, and CA are a function of K_{i0} and are assumed to be the same at both temperatures.

provided by November 1995 soil analysis in the vadose zone which indicated no chlorinated aliphatic contaminants above detection limits of 5 $\mu\text{g/kg}$ (39). A soil gas survey conducted at the same time from the same sample points, however, showed detectable amounts (Table 6.5) which suggests vapor phase detection is most likely a result of contaminant volatilization from the saturated zone rather than any contribution from the vadose zone. The lack of contaminant detection indicates little adsorption potential, otherwise concentrations from groundwater contaminant volatilization should have been adsorbed and detected in the vadose zone.

6.1.6. Temperature Effects.

The K_{ow} values used to calculate the K_d values were reported in the literature at 25 °C. Equation (6.10) was used to adjust K_{oc}/K_d 's to account for the average groundwater temperature of 16 °C at the site (Table 4.1). The ΔH°_s (enthalpy of

Table 6.5. Soil Gas Survey Data (39) (Levels are in ug/L.).

Bore Hole	TCE	TCA	Cis-DCE	Trans-DCE	1,2-DCA	1,1-DCA	1,1-DCE	VC	CA
1	252	107	448	21.4	ND	ND	188	ND	ND
2	292	147	547	ND	ND	104	212	ND	ND
3	362	104	573	ND	ND	ND	214	ND	ND
4	178	38.3	167	ND	ND	20.1	21.7	ND	ND
5	157	61.2	20.3	ND	ND	19.5	64	ND	ND
6	178	62.2	84.8	ND	ND	22.6	69.9	ND	ND
7	43.5	25.9	216	ND	ND	32.5	19.4	ND	ND
8	245	57.7	394	ND	ND	41.8	66.4	ND	ND
9	5.36	ND	226	ND	ND	ND	ND	ND	ND
10	131	ND	319	ND	ND	ND	ND	ND	ND
11	212	14.5	ND	ND	ND	ND	35.7	ND	ND
12	10.9	ND	ND	ND	ND	ND	ND	ND	ND

ND: non-detect

Samples taken 4 feet below ground surface.

solution) values were estimated from empirical methods provided by Schwarzenbach et al. (55). The estimated values are between 12 kJ/mole (high concentrations: Table A.1)) and 23 kJ/mole (low concentrations: Table A.1). At high concentrations the ratio of K_{oc} (298.2 K)/ K_{oc} (289 K) is 0.87 and at low concentrations is 0.75. The adjusted retardation factors (A ratio of 0.81 was used as an average) as a function of K_{oc} are also listed in Table 6.4. The temperature impact is insignificant given the already low retardation factors.

$$\frac{K_{oc}(T_1)}{K_{oc}(T_2)} \cong \exp(\Delta H_{es} / R(1/T_1 - 1/T_2)) \quad (6.10)$$

ΔH_{es} = enthalpy of solution (kJ/mole)

T = temperature in degrees Kelvin

R = 0.00831 kJ/mole

6.2. Advection and Dispersion

6.2.1. Advection.

In sandy aquifers, the dominant factor in the migration of dissolved contaminants is advection (34). Actual migration/transport can be three dimensional. The primary means of transport, however, is one dimensional along the X axis and in the direction of groundwater flow (down gradient) as a result of simple advection due to groundwater flow. Transport in the Y direction, across or perpendicular to the relative groundwater movement, is a function of both dispersion effects caused by advection through the pore space and molecular diffusion. Movement in the Z or vertical direction normal to the groundwater gradient is more complex and is a function of the contaminant density and volatility, permeability of the aquifer media, and amount of surface recharge. An immiscible chemical heavier than water (i.e. Dense Non-aqueous Phase Liquids (DNAPL)) will tend to move downward in the flow stream, settling to the bottom of the confining layer. Immiscible chemicals lighter than water (i.e. Light Non-aqueous Phase liquids (LNAPL)) tend to float to the top of the saturated zone. The settling or rising effects have little impact on the soluble portion of the immiscible contaminant which remains available for movement by advection.

The chlorinated aliphatic contaminants at the Building 719 site are classified as DNAPLs with the exception of VC and CA (Table 2.1) which are classified as LNAPLs. Whether any of the DNAPL contaminants have reached the aquifer bottom is uncertain since water sampling and analysis was only conducted at the groundwater surface.

If DNAPL contaminants have accumulated at the bottom of the aquifer, a flux from the free-product phase to the water phase will develop as a result of decreased concentration gradients from fate and transport and ultimately impact the migration and natural attenuation of the contaminants. Additional sampling and analysis should be conducted to define and verify the concentration profile as a function of depth within the saturated zone for further fate and transport evaluation.

6.2.2 Site Specific Advection.

The groundwater velocities reported by Dames and Moore (11) are between 0.18 to 0.5 ft./day. The exact advection at the site as well as the initial time at which the contaminants reached the groundwater table is unknown. If the tail end of the high TCA and TCE concentration plumes (bore hole 4/TRW 4) are assumed to be related to the time at which the tanks were removed (1994), the "apparent advection" is approximately 0.19 ft./day (70 ft./364 days). The 0.19 ft./day is on the low side of the values reported by Dames and Moore and may not be representative of the actual groundwater advection throughout the aquifer due to restrictions caused by underground utilities and various building foundations throughout the base. The actual advection may be higher and would be expected to increase as a result of percolation and a reduction in stormwater controls as the contaminants move further away from the site and the base.

Due to the difficulty in predicting the exact groundwater advection and since specific advection experiments have not been conducted between Building 719 and the St. Jones River, an above average advection of 0.42 ft/day will be used to incorporate a safety factor into the fate and transport model.

6.2.3. Dispersion.

Dispersion is when dissolved contaminants spread out as they move with the groundwater. The dispersion process results from molecular diffusion and mechanical mixing within the aquifer. Molecular diffusion is the kinetic activity of the dissolved contaminants that results in a net flux from a zone of high concentration to low concentration. The mechanical mixing effects result from variations in groundwater movement/velocity due to frictional forces with the soil, variations in pore size, and tortuous flow path of groundwater through the pore space. If dispersion effects are high enough, "dispersive spreading" may result in the arrival of detectable contaminant concentrations at a point "X" significantly ahead of the time expected by transport strictly due to advection. At low velocities, molecular diffusion will slow or reverse movement of the trailing edge, allowing limited transport up-gradient at low flow rates. Consequently, at high velocities, dispersion will dominate, at low velocities diffusion will dominate.

6.2.4. Prediction of Longitudinal Dispersion (D_x 's).

The main concern of contaminant transport is the infringement upon the St. Jones River. Consequently, "longitudinal dispersion" effects along the advective flow path (i.e. in the direction of groundwater flow) are the only dispersion effects to be considered for modeling purposes. Provided the "molecular diffusion coefficients (D_x)" are known, "longitudinal dispersion coefficients" can be determined directly from Figure 6.1. D_x is determined by application of equation (6.11) (55). The D_x 's calculated from equation (6.11) are tabulated in Table 6.6.

$$D_x = \frac{13.26 \times 10^{-5}}{u^{1.14} (V)^{0.589}} \quad (\text{cm}^2/\text{s}) \quad (6.11)$$

u = solution viscosity in centipoise ($10^{-2} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$)
at the temperature of interest.

V = Molecular volume (Table 2.1)

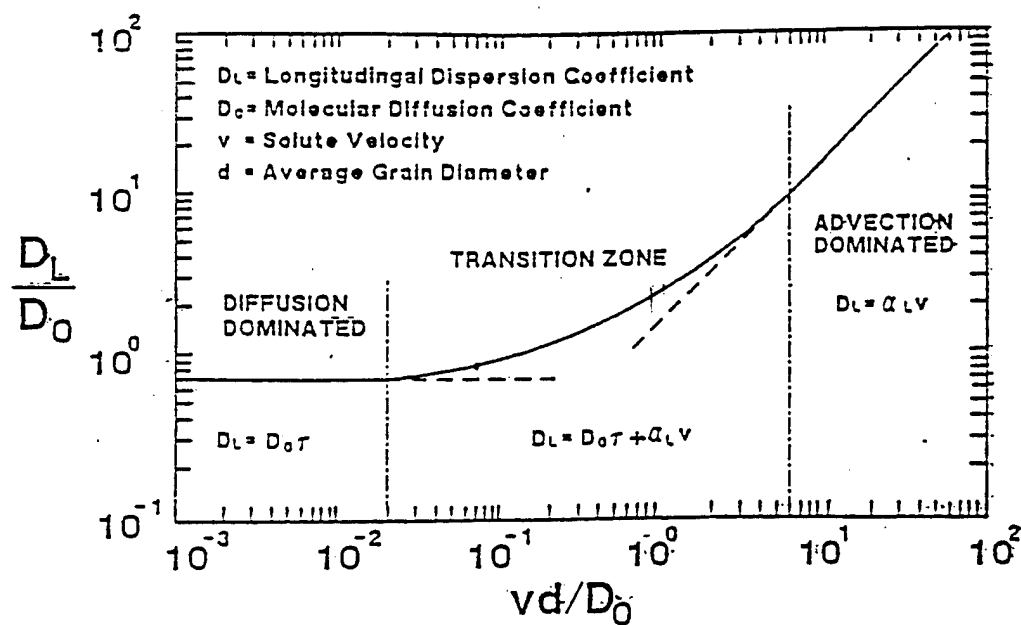


Figure 6.1. Longitudinal Dispersion Coefficient Graph (Perkins and Johnston (1963)).

Table 6.6. Diffusion and Dispersion Factors for the Building 719 Site Contaminants.

Contaminant	D _x (cm ² /s)* (Diffusion)	D _x ' (cm ² /s) (Dispersion)
TCE	8.13E - 06	2.1E - 05
TCA	7.93E - 06	2.1E - 05
1,1-DCE	9.18E - 06	2.0E - 05
cis-1,2-DCE	9.18E - 06	2.0E - 05
trans-1,2-DCE	9.18E - 06	2.0E - 05
1,1-DCA	8.91E - 06	2.0E - 05
1,2-DCA	8.91E - 06	2.0E - 05
VC	1.07E - 05	2.1E - 05
CA	1.03E - 05	2.1E - 05

* $\mu = 1.11 (10^{-2} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1})$ centipoise at 16 ° C

At a solute velocity of 0.42 ft./day and an average grain size diameter of 0.59 mm, the longitudinal dispersion coefficients (D'_x) were calculated at 16 ° C and are also listed in Table 6.6. The values determined from Figure 6.1 indicate longitudinal dispersion is in the transition zone between diffusion and advection domination. The D'_x values in Table 6.6 were used in the fate and transport model analysis, Chapter 7.

6.3. Volatilization.

A volatile chemical has the potential to volatilize at the soil-air and/or air-water interface in the vadose and saturated zones. The importance of volatilization as a transport mechanism in the subsurface depends on the depth of the aquifer, the contaminant and concentration, and the geology of the unsaturated zone. Within the groundwater phase, provided the fugacity of the air phase in the vadose zone is less than the groundwater phase, a net flux of the contaminant will occur from the water to the air

phase. As a result, contaminant migration through the groundwater will be reduced due to reduced concentrations from mass transfer to the air phase.

6.3.1. Volatilization Site Evaluation

In an evaluation of volatilization of organic chemicals residing below the soil surface, Jury et al. (25) derived a method to determine the soil-cover thickness required at infinite time to restrict volatilization from a contaminated layer to less than 0.7% of mass incorporated in the soil. The method described by Jury et al. assumes that volatilization in the vadose zone is a result of diffusion alone, the ground surface is unrestricted (i.e. no pavements or buildings), the contaminants are exposed to chemical/biological degradation, and water evaporation is minimal. Although Jury et al.'s method is based on volatilization within the vadose zone, actual upward diffusion of contaminants from groundwater volatilization will follow a similar transport path to the ground surface as would volatilization from the vadose zone. Consequently, the method described by Jury et al. methods was applied to the Building 719 site given the existing/assumed conditions (i.e. 16°C , $\rho = 2.05\text{ g/cm}^3$, $\Theta = 0.3$) to determine whether volatilization will help to mitigate (i.e. reduce) contaminant transport by the groundwater.

As indicated by Table 6.7, all the contaminants do appear susceptible to removal from the groundwater by volatilization through an unrestricted ground surface. Actual topographical conditions at the Building 719 site, however, as well as ground conditions over the groundwater path are not unrestricted. The various parking lots, roads, and buildings at the ground surface (at least on Dover AFB) will tend to reduce the required "soil-cover thickness" identified in Table 6.7. Since the Building 719 site only has an average of 10-feet of soil-cover thickness to the groundwater table, "ideal" percent volatilizations were determined at 10-feet of soil-cover thickness using the Jury et. al

method. The percent volatilizations at 10-feet of soil-cover thickness for the site contaminants are reported in Table 6.7. The results indicate that TCE and TCA are the most susceptible to volatilization and will volatilize more readily while cis-DCE and 1,2-DCA are the least susceptible.

Table 6.7. Soil-Cover Thickness (feet) Required to Restrict Volatilization to Less Than 0.7% of the Mass in the Soil Zone and the Percent Volatilization at 10 feet of Soil-Cover Thickness.

Contaminant	Sandy Soil (feet)	Percent Volatilization at 10-feet of Soil-Cover
TCE	109	63
TCA	84	55
1,1-DCE*	39	27
cis-1,2-DCE*	18	6
trans-1,2-DCE*	26	15
1,1-DCA	20	9
1,2-DCA	18	6
VC	35	24
CA	32	21

* Jury et. al (25) did not provide first order aerobic biodegradation rates in the vadose zone for 1,1-DCE, *cis*-DCE, and *trans*-DCE. The values are required to predict soil-cover thickness. Consequently, rates were estimated from Howard et al. (22).

6.3.2. Volatilization Rates.

Actual prediction of volatilization rates from the groundwater is difficult due to the non-homogeneous nature of the soil, the tortuous upward flow path, percolation recharge, and ground surface restrictions. The vast majority of rates reported in the literature are related to lake and river surface water environments. The potential for

groundwater degradation by volatilization (K_v) at the Building 719 site as indicated by Table 6.7 does exist. However, to simplify the fate and transport model and due to the uncertainty of volatilization rates, the fugacity in the vadose zone will be assumed to equal "one" and the K_v equal to "zero." In reality the fugacity is not equal to one nor is the fugacity equal to zero but somewhere between these two limits. A fugacity level of one is a conservative approach to modeling volatilization. Should any volatilization occur, the end result will be a reduction in contaminant concentrations for groundwater transport and will aid in reducing possible St. Jones River contamination.

6.4. Degradation.

The degradation processes believed to be associated with the TCA and TCE at the Building 719 site are hydrolysis and biodegradation. Hydrolysis and anaerobic biodegradation first order rate constants were obtained from the literature and are listed in Table 6.8.

6.4.1. Hydrolysis.

Hydrolysis transformation was discussed in Chapter 4. Most of the hydrolysis rates identified in Table 6.8 were obtained from a study conducted by Jeffers et al. (24). Jeffers et al.'s determined first order hydrolysis rate constants for several chlorinated ethane and ethene compounds. The rates were reported at 25 °C but have been corrected to 16 °C per the Arrhenius equation, equation (6.12) (64). Only TCA and CA appear to have hydrolysis rates that are significant relative to the biodegradation rates.

Table 6.8. Degradation Rates (K_{deg}) Cited From the Literature.

Contaminant	Hydrolysis (H)*	Anaerobic (A)	Remarks
TCA	0.00049/day (24)	0.000635/day to 0.00124/day (22); 0.00301/day (48)	
1,1-DCA	0.0000086/day (24)	0.001125/day to 0.00541/day (22)	
1,2-DCA	0.0000073/day (24)	0.000963/day to 0.00173/day (22)	
CA	0.0049/day (38)	0.000990/day to 0.0693/day (38)	
TCE	0 (24)	0.000419/day (22) to 0.0071 (38)/0.00301 (56); 0.003/day (48) To VC: 0.000144/day To 1,2-t-DCE: 0.00003/day (56)	H: pH<7
1,1-DCE	0 (24)	0.00401/day to 0.00856/day (22); 0.00240 (5*)	H: pH<7
1,2-cis-DCE	0 (24)	0.000963/day (22) to 0.00619/day (5*);	H: pH<7
1,2-trans-DCE	0 (24)	0.000963/day to 0.00619/day (22); 0.00499/day (5*)	H: pH<7
VC	0.000044/day (24)	0.000963/day to 0.00619/day (22)	

* 16 °C

(5: 25°C); (22,38,48,56: No temperature reported);

Per reference (63), rise in temperature of 10 to 15 °C between temperatures of 5 °C and 35 °C results in a doubling of biodegradation rates.

$$\ln \frac{k(16^\circ\text{C})}{k(25^\circ\text{C})} = \frac{E_a}{R} \left(\frac{1}{T(16^\circ\text{C})} - \frac{1}{T(25^\circ\text{C})} \right) \quad (6.12)$$

E_a = Activation Energy (kJ/mole)

R = Universal Gas Constant (8.314 J/mole-K)

T = Degrees Kelvin

The E_a value for chlorinated aliphatic hydrocarbons is approximately 100 kJ/mole (64).

6.4.2. Biodegradation.

The biodegradation process appears to be one of anaerobic degradation as indicated by the presence of TCA and TCE daughter products that are normally associated with anaerobic degradation within groundwater aquifers (13,31,56) (As previously noted, the daughter products were not previously used in Building 719 operations).

The anaerobic degradation rates cover a broad range of values. Values reported by Silka and Wallen (56) were a result of studying biodegradation within a sand and gravel aquifer located in Tacoma, Washington. Values reported by Roberts et al. (48) are also from a silty sand and gravel aquifer. The other reported values in Table 6.8 are based on laboratory experiments or estimations based on a combination of "aqueous aerobic and anaerobic biodegradation half-lives (22)."

6.4.3. Fate and Transport Model Degradation Rates.

Table 6.9 contains the relative degradation percents for the transformation of TCA and TCE to subsequent daughter products. The TCA transformation values are based on

Table 6.9. Transformation Degradation Percents for TCA, TCE and Subsequent Daughter Products.

Conversion	Transformation Percent
TCA	
TCA to 1,1-DCA (46)	85
TCA to Acetic Acid (22)	15
TCA to 1,1-DCE	0
1,1-DCA to CA	100
CA to CO(2)	100
TCE	
TCE to 1,2-cis-DCE	98
TCE to 1,2-trans-DCE	2
TCE to 1,1-DCE	0
1,1-DCE to VC	100
1,2-cis-DCE to VC	100
1,2-trans-DCE to CA	100
VC to CO(2)	100
1,2-DCA	
	100

Refer to Figures 4.2 and 4.3 for the transformation path.

ratios of hydrolysis to biodegradation rates in Table 6.8. Further accumulation of 1,1-DCE from TCA (Figure 4.2) dehydrogenation is assumed to no longer occur due to the low groundwater pH. *Cis* and *trans*-DCE have been shown to biodegrade to both CA and VC (5). However, given the higher concentrations of VC compared to CA, *cis*-DCE as well as 1,1-DCE (Figure 4.2) are assumed to transform to VC and any *trans*-DCE that is formed from TCE hydrogenolysis will transform to CA. TCE transformation to 98 percent *cis* and 2 percent *trans*-DCE is based on minimal *trans*-DCE detection at the site (Tables 1.1, 6.5, and A.1).

The ability to determine the exact degradation rates for in situ degradation is extremely difficult because of the continuously changing subsurface environment and non-steady state conditions. However, based on the degradation rate values in Table 6.8, the percent transformation values noted in Table 6.9, and the "apparent advection" of 0.19 ft./day directly under Building 719, approximate degradation rates can be determined using a first order degradation equation, equation (6.13). Equations (6.14) through (6.16) were derived by combining equations (6.13) and (4.8) and represent the general first order time rate of change for degradation of TCE to CO₂.

$$C = C_i e^{-kt} \quad (6.13)$$

C = concentration at time (t) in ug/L

C_i = initial concentration at time ($t=0$) in ug/L

k = first order rate constant (day^{-1})

t = time (days)

$$TCE = TCE_i \times e^{-(k(tce) \times t)} \quad (6.14)$$

$$cis-DCE = cis-DCE_i \times e^{-(k(cis) \times t)}$$

$$cis-DCE = 0.98 \times 0.74 \times TCE_i \times (1 - e^{-(k(tce) \times t)}) \times e^{-(k(cis) \times t)} \quad (6.15)$$

$$VC = VC_i \times e^{-(k(vc) \times t)}$$

$$VC = 0.98 \times 0.65 \times 0.74 \times TCE_i \times (1 - e^{-(k(tce) \times t)}) \times (1 - e^{-(k(cis) \times t)}) \times e^{-(k(vc) \times t)} \quad (6.16)$$

$$\frac{\text{Molecular Weight (MW) } cis\text{-DCE}}{\text{MW TCE}} = 0.74$$

$$\frac{\text{MW VC}}{\text{MW } cis\text{-DCE}} = 0.65$$

$$X_i = \text{Initial concentration}$$

To determine approximate rate constants for the Building 719 site, the initial concentration of TCE in equations (6.14) through (6.16) must be determined. Equation (6.17) was used to determine the "initial average" concentration of TCE. The equation

$$\begin{aligned} \text{TCE (98\%)(0)} = & \text{TCE (T days)} + cis\text{-DCE (T days)/(0.74 x 0.98)} + \\ & \text{VC (T days)/(0.74 x 0.65 x 0.98)} + \text{VC decay (T days)/} \\ & (0.74 \times 0.65 \times 0.98) \end{aligned} \quad (6.17)$$

assumes an ideal enclosed completely mixed system and that the degradation of TCE is strictly a result of degradation through the anaerobic/anoxic degradation path (Figure 4.3). Under actual conditions, however, the initial concentration of TCE was likely a "time rate of change input function" from the source. Without knowing the time rate of change input, determining the actual initial concentration is extremely difficult unless sampling had been conducted at each of the sampling ports over time (The analytical data provided from the site was for a one time analysis.).

Four separate "T" days in equation (6.17) were determined by dividing the distance between the source of contamination and bore holes 4, 8, 10, and 12 (TRW 4, 8, 10, and 12 in Figure A.1) by the "apparent advection" of 0.19 ft./day under the building. The approximate times generated were 364, 315, 684, and 684 days respectively.

The only unknown in equation (6.17) is the "VC decay" term. Since the degradation of VC is the rate limiting step (similarly with CA degradation in the TCA transformation process) in the anaerobic transformation because of the single remaining chlorine (18), the most conservative degradation approach is to let VC decay equal zero. By setting VC decay equal to zero, the TCE initial can be determined.

With TCE initial determined from equation (6.17), equations (6.14) through (6.16) were solved by iteration. Degradation rates were varied until the bore hole concentrations from bore holes 4, 8, 10, and 12 listed in Table A.1 were obtained. A similar method was used to determine degradation rates for the transformation of TCA to CA. Like VC decay, CA decay was set equal to zero.

The degradation rates determined by the iteration process were averaged over the four bore holes and are provided in Table 6.10 (Rates for *trans*-DCE to VC and TCA to acetic acid were not determined by iteration due to insufficient analytical data but estimated based on values in Table 6.8). The TCE and TCA biodegradation values are consistent with the literature. *Cis*-DCE and 1,1-DCA values (0.00004/day and 0.00002/day respectively) are significantly lower than the literature values but lower than TCA and TCE rates as expected due to reduced chlorine substituents that require additional energy for removal. The values reported in the literature, however, are often based on laboratory experiments which include inoculating the microcosms with a primary anaerobic food source such as acetic acid. The inoculation results in increased degradation rates. A previous analysis of the microbial activity at the site indicates an

Table 6.10. Model Degradation Rates.

Conversion	"k" value (day-1)
TCA	
TCA to 1,1-DCA	0.00265
TCA to Acetic Acid	0.00049 (24)
TCA to 1,1-DCE	0
1,1-DCA to CA	0.00002
CA to CO(2)	0.0049 (38)
TCE	
TCE to 1,2-cis-DCE	0.0053
TCE to 1,2-trans-DCE	0.00003 (56)
TCE to 1,1-DCE	0
1,1-DCE to VC	0.00004
1,2-cis-DCE to VC	0.00004
1,2-trans-DCE to CA	0.00499 (5)
VC to CO(2)	0.00004
1,2-DCA to CO(2)	0.00002

insufficient carbon food supply may exist and may be the reason for the low values. A microbial characterization of the site's groundwater at the surface did show the presence of methanotrophs, iron reducers, and heterotroph anaerobic bacteria but in low densities (46).

The degradation rates in Table 6.10 were used in the fate and transport model. The value determined for *cis*-DCE was also used for VC degradation. Under actual conditions, the VC value would be expected to be less than *cis*-DCE due to the increased energy required for further hydrogenolysis. However, since a conservative estimate has been previously incorporated into the initial rate determinations (i.e. VC decay was set to

zero) and due to the already small degradation values, any error that might be incorporated is not considered to be significant.

The degradation rate for 1,2-DCA was assumed equivalent to 1,1-DCA and the rate for 1,1-DCE equivalent to *cis*-DCE for the fate and transport model.

CHAPTER 7

FATE AND TRANSPORT MODEL RESULTS

7.1. Model Results.

As indicated in Chapter 5, the fate and transport of the chlorinated aliphatic organic compounds at the Building 719 site can be modeled by the "Runge Kutta" numerical approximation (equation (5.5)) for non-steady state conditions. Table 7.1 contains all the relevant data required for the "Runge Kutta Finite Differences Model." The segment width chosen for the model was 60 feet (Figure 7.1). The 60 ft width was based on an approximate average concentrated width of the plume and an assumption that the width of the plume will remain fairly constant with time. Over a period of 30 years, the "Y" direction of migration is not expected to exceed 10 feet in either the east/west direction as illustrated Example 7.1.

Example 7.1

Travel distance as a result of diffusion through a saturated soil medium can be represented by equations (7.1) and (7.2) (54).

$$D_{\text{eff}} = \frac{D}{R_c} \quad (7.1)$$

$$Y = (2 \times D_{\text{eff}} \times t/T)^{1/2} \quad (7.2)$$

T = tortuosity factor (approximately 1.5)

t = time

D = diffusion coefficient (Table 6.6)

R_c = retardation factor (Table 6.4)

Table 7.1. Model Input Data.

Parameter	Coefficient	Comments
Longitudinal dispersion coefficient (liters/day)	Table 6.6	
Retardation factors	Table 6.4	Values varied from 1.05 to 1.27
Degradation Rates (day-1)	Table 6.10	
Advection (ft./day)	0.42	
Model Width (ft.)	60	Width selected based on existing plume locations.
Shallow Groundwater Depth (ft)	15	
Delta X (ft.)		Delta X set at 50 feet for the first two years to obtain a better concentration profile.
X (1):	50	
X (2):	200	
Flow (liters/day)	10,697	
Area (ft ² perpendicular to flow)	900	
Volume (liters)		Volumes varied as a result of Delta X.
Volume (1):	1.3E + 06	
Volume (2):	5.1E + 06	
Time (days)		Time varied between 91 days for first two years, 181 days for year two to year 10, and 364 days for the remainder.
Time (1):	91	
Time (2):	181	
Time (3):	364	

Over a period of 30 years the "Y" distance traveled for VC is:

$$D_{\text{eff}} = \frac{1.7\text{E} - 05}{1.01} = 1.7\text{E} - 05 \text{ cm}^2/\text{sec.}$$

$$Y = (2 \times 1.7\text{E} - 05 \times 30 \text{ year} \times 3.14\text{E} + 07 \text{ sec./1.5})^{1/2}$$

$$Y = 146 \text{ cm or 4.8 feet}$$

TRW SAMPLING AT BUILDING 719 DAFB

(Superimposed on Envirosan Map with
Dames & Moore Soil / Gas Sample Points)

Water:
1,2DCE_{cis}
µg / l

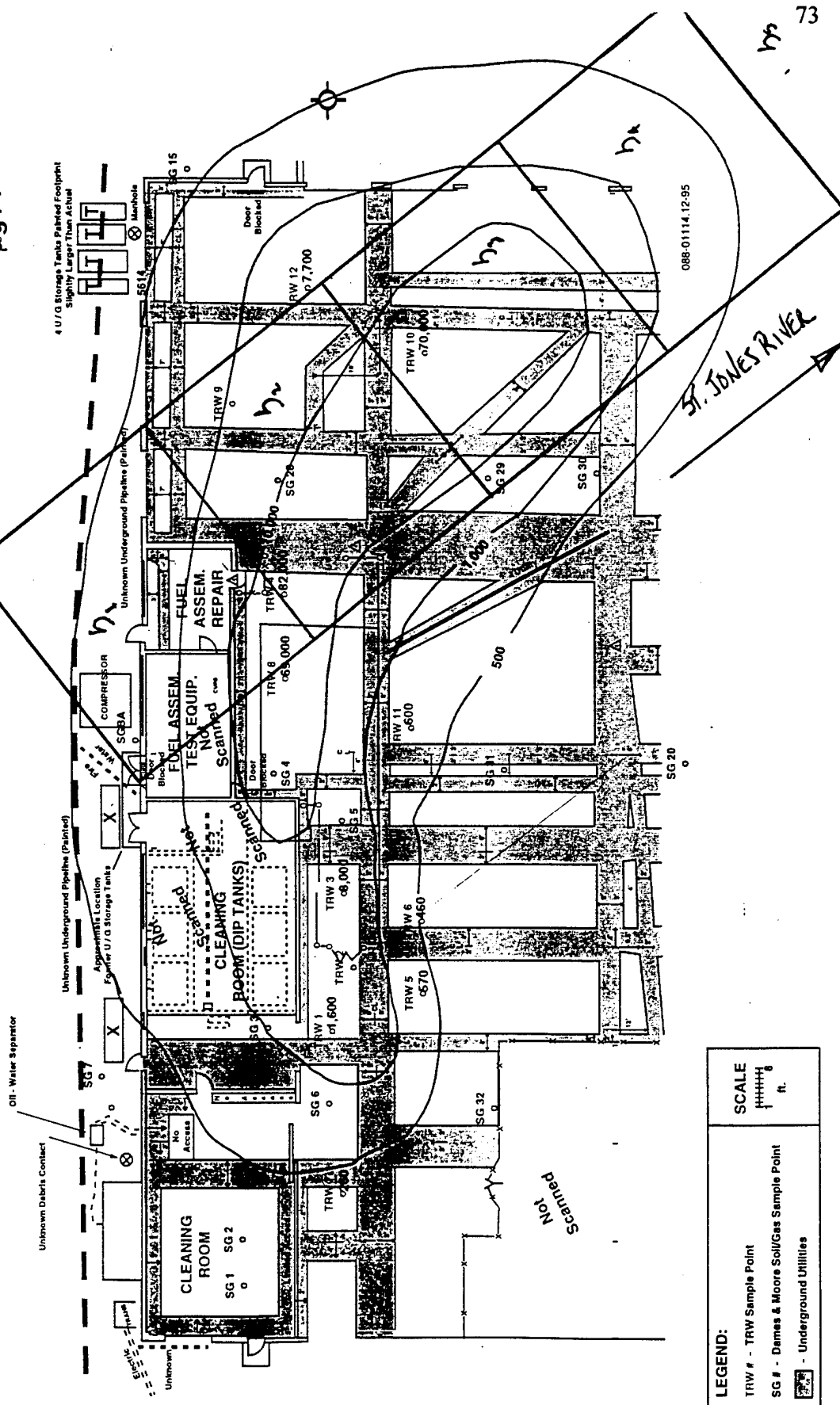


Figure 7.1: Illustration Over the Cis-DCE Plume of "Segment Boxes" Used in "Runga Kutta Finite Differences Model."

Given that diffusion effects in the saturated zone are minimal, the assumption is that the initial spill progression through the vadose zone initially caused the plume spreading before the bulk of TCA and TCE reached and contaminated the groundwater. Some spreading may also be a result of restrictions in the flow path previously discussed in section 6.2.2. Input concentrations (i.e. initial concentrations) for each of the contaminants were estimated by take-offs from Figures 1.3 through 1.9 and the segment overlay from Figure 7.1. Concentrations were taken from the center of segments S1, S2, S3, and S4 (Figure 7.1) and are provided in Table 7.2. A depth of 15 feet was chosen to represent the shallow groundwater depth.

Table 7.2. Initial Concentrations ($\mu\text{g/L}$) for "Runga Kutta Finite Differences Model."

Contaminant	Segment 1	Segment 2	Segment 3	Segment 4
TCE	750	70000	1000	400
TCA	50	2300	500	50
1,1 DCE	50	620	200	50
cis 1,2 - DCE	920	78000	40000	600
trans 1,2 - DCE	0	0	0	0
1,1 DCA	200	2300	1000	50
1,2 DCA	90	630	500	75
VC	50	200	500	50
CA	0	0	0	6

Figures 7.2 through 7.7 are graphical representations of the "Runga Kutta" model results for the chlorinated aliphatic compounds at the site (Appendix B contains concentration tables for various years between 1997 and 2039). Figures 7.2 and 7.3 indicate that TCE and TCA will attenuate fairly rapidly. Both contaminants are expected to be transformed by the year 2002. The remainder of the contaminants reach the river by

the year 2029 while maximum concentrations look to arrive by the year 2039.

Cis/trans-DCE and 1,1-DCE and VC (Figures 7.4 and 7.5 respectively) appear to be extremely persistent which is expected given their low degradation rates. The maximum concentration of *cis/trans*-DCE and 1,1-DCE (95% percent of "1,2-DCE and 1,1-DCE," Figure 7.4, is assumed to be of the *cis* form) that will reach the St. Jones River is approximately 3,300 $\mu\text{g/L}$. The maximum VC concentration that discharges to the river is 1,300 $\mu\text{g/L}$. Figures 7.6 and 7.7 indicate the maximum 1,1-DCA concentration to reach the St. Jones River is approximately 140 $\mu\text{g/L}$ and the maximum 1,2-DCA concentration is below 30 $\mu\text{g/L}$ just prior to reaching the river respectively.

If a line is used to connect the peak VC concentrations in Figure 7.5 together, the slope would be decreasing with time. The negative slope effect is a result of decreased *cis*-DCE hydrogenolysis to VC with time.

Concentration profiles for CA are not provided. Results of the fate and transport model showed CA concentrations remaining close to zero with time. The "zero concentration" effect is a result of the difference in degradation rates between the CA hydrolysis rate and the *trans*-DCE and 1,1-DCA hydrogenolysis rate. The rate of hydrolysis for CA (Table 6.8) is much greater than the hydrogenolysis rate. A similar effect may be ongoing at the site and the reason why CA was only detected once.

Although the model results indicate *cis/trans*-DCE, 1,1-DCE, and VC to be fairly persistent, actual degradation rates may increase with time due to "enzyme induction." As concentrations of TCE are reduced, the microbial community may adapt more readily to the *cis/trans*-DCE and 1,1-DCE contaminants and increase production of enzymes specific to *cis/trans*-DCE and 1,1-DCE degradation. The same may hold true for VC as *cis/trans*-DCE and 1,1-DCE concentrations are reduced.

The plume's first point of contact with the greatest health risk is the Dover Air Force Base residential housing area which is approximately 2,000 feet south of the site. Based on model results, the plume will reach the housing area between the years 2000 and 2002 with maximum concentrations impacting the area by about the year 2005.

7.2. Impact to the St. Jones River.

Given the flow rate of the river at 36 cfs and the flow rate of the groundwater table, $3.9E-6$ cfs, based on the parameters established in the model, the dilution conclusion/effect commented on in the St. Jones River Estuarine EIS (Chapter 2) seems accurate for this particular case. The amount of VC that would need to discharge to the river from the Building 719 site would be 16 mg/L to reach 0.002 mg/L (MCL) or 760 mg/L to reach Delaware Water Quality Standards (0.095 mg/L) in the river (570 mg/L in the case of *cis*-DCE to reach the MCL of 0.07 mg/L). The Building 719 site, however, is only one source of contamination at Dover AFB as previously noted in Chapter 3. The combined migration of several contaminated sites from Dover AFB could significantly impact the water quality of the St. Jones River should the combination of contaminants arrive at the same time.

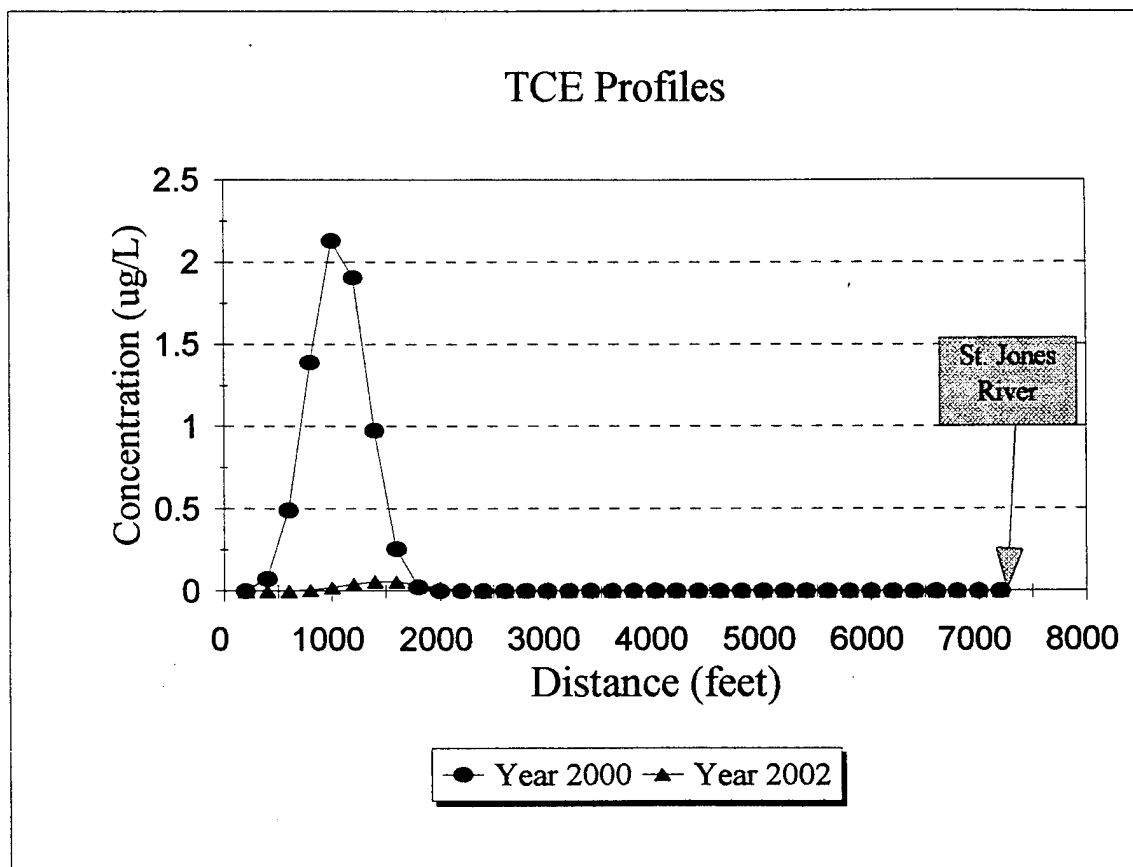


Figure 7.2. TCE Concentration Profiles.

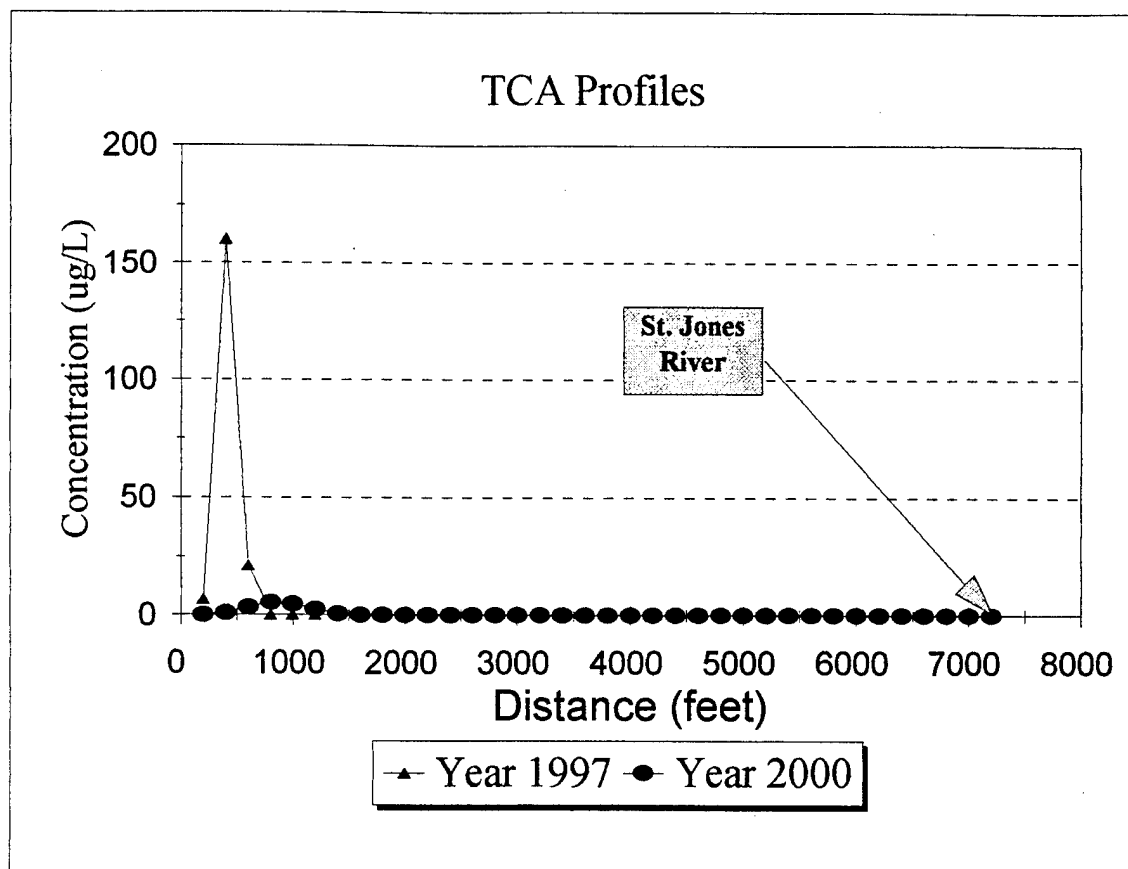


Figure 7.3. TCA Concentration Profiles.

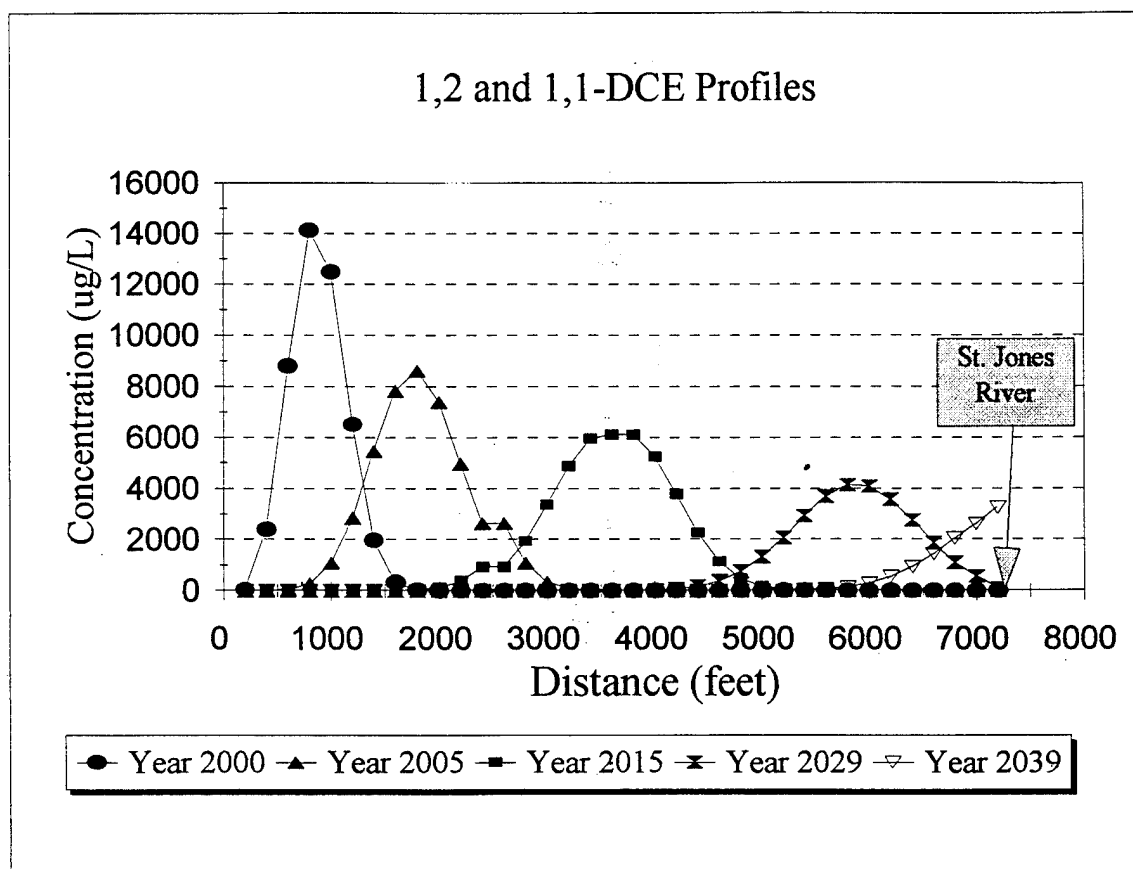


Figure 7.4. 1,2 and 1,1-DCE Concentration Profiles.

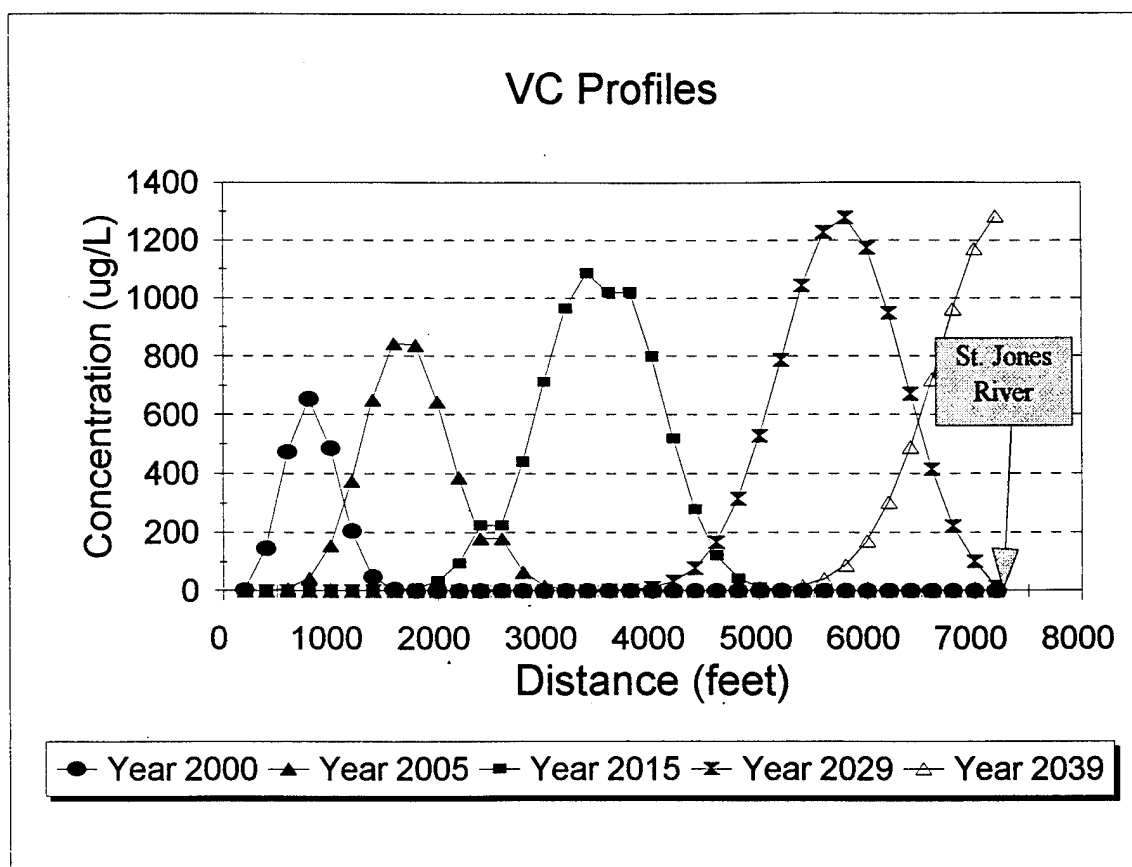


Figure 7.5. VC Concentration Profiles.

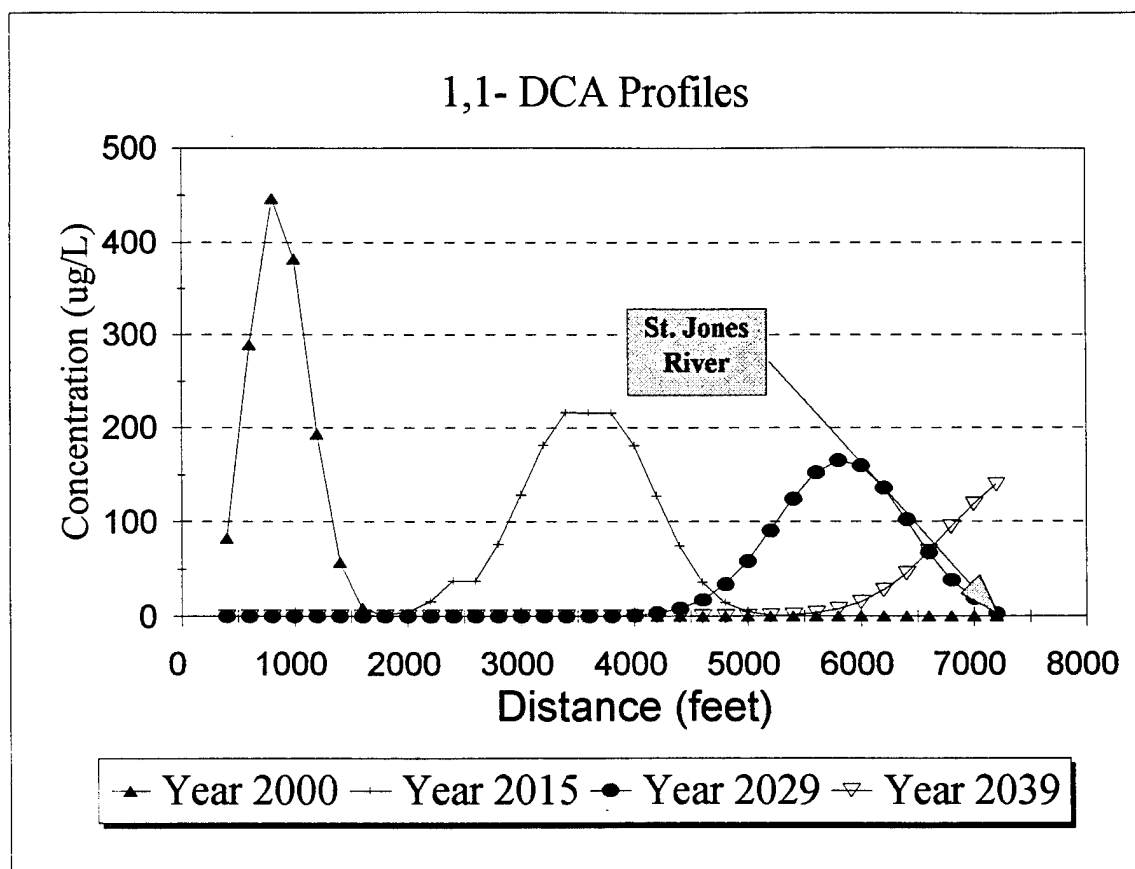


Figure 7.6. 1,1-DCA Concentration Profiles.

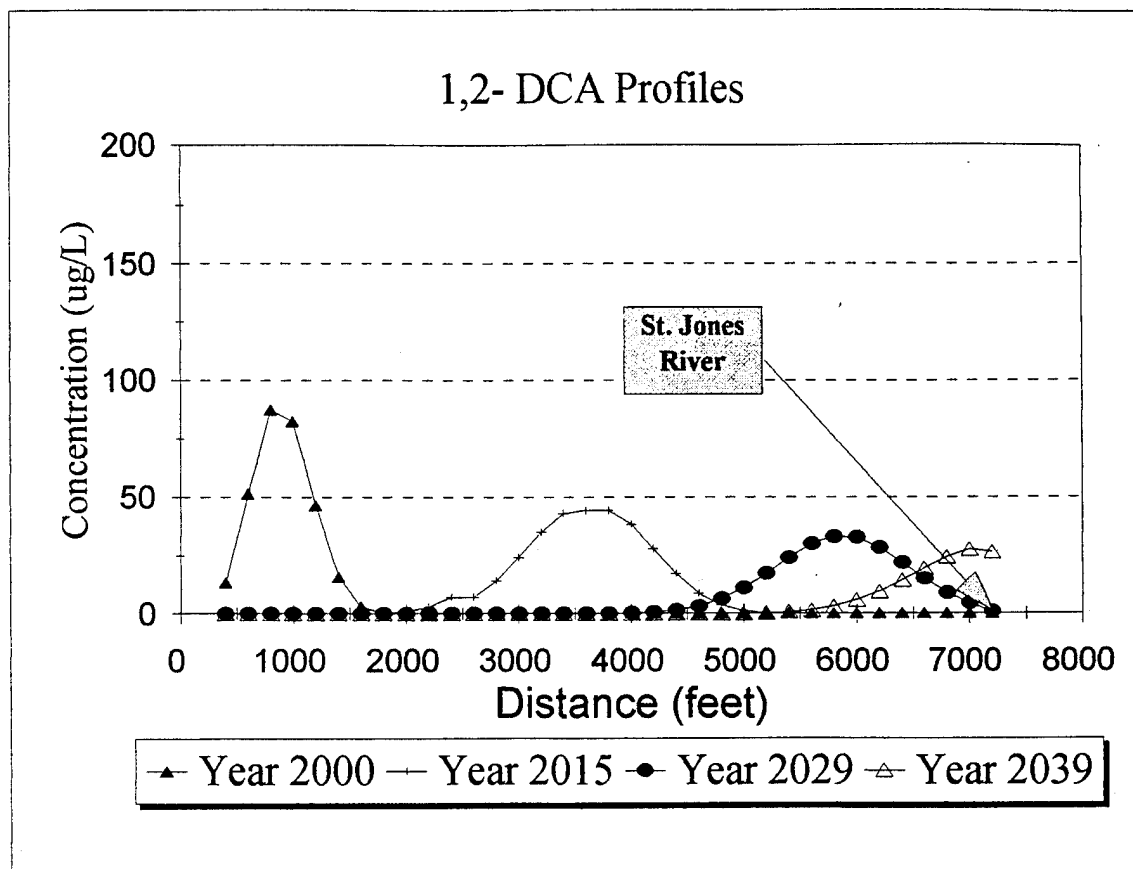


Figure 7.7. 1,2-DCA Concentration Profiles.

CHAPTER 8

SUMMARY AND RECOMMENDATIONS

8.1 Summary.

- TCA and TCE transformation by-products, *cis/trans*-DCE, 1,1-DCE, 1,1-DCA, VC, and CA, are a result of hydrogenolysis degradation which typically occurs in groundwater aquifer systems under anaerobic conditions.
- Low degradation rates are most likely the result of insufficient primary substrate for the microorganisms.
- Linear empirical relationships indicate that adsorption effects are low. The sandy grain soil, low organic carbon content and minimal clay content are the contributing factors. If remediation of the site is considered, lack of adsorption will assist remediation efforts since the contaminant will not be "locked" to the soil matrix.
- Volatilization was not considered in the fate and transport model. Any volatilization that does occur will help to mitigate the migration of the contaminants from the site. TCE and TCA appear to be most susceptible to volatilization.
- Model results indicate all the Building 719 site contaminants except TCA, TCE, and CA will reach the St. Jones River by the year 2029. Increased adsorption or a decrease in advection (i.e. < 0.42 ft./day), however, will

increase the time required to reach the river. Increased rates of biodegradation and/or volatilization will reduce the concentration impact to the river.

- *Cis*-DCE and VC are the most persistent contaminants due to the initial high TCE concentrations. Maximum concentrations will reach the river in the year 2039 but at levels that should not impact the river quality due to dilution effects. However, when considered in total with the various other contaminated sites throughout Dover AFB, the St. Jones River may be significantly impacted by the overall contaminant migration from the base.
- If DNAPL has accumulated on the bottom of the aquifer, the fate and transport of the Building 719 site contaminants will create a concentration gradient with a net flux from the DNAPL to the aqueous phase further complicating the fate and transport of chlorinated organics and increasing the risks on the St. Jones River.
- As indicated by Figures 7.2 through 7.7, between the years 2000 and 2002 the plume will have reached the groundwater table below the base residential housing area which is approximately 2,000 feet south of the Building 719 site (Figure 1.2). Maximum concentrations will impact the area by the year 2005. If no action is taken, by the year 2022, the plume will reach the wetlands 6,000 feet south of the site.
- A remediation effort prior to the year 2000, will lessen the health impacts and risks to the local environment as well as control plume migration. If no action

is taken, the plume will continue to migrate from the site, making remediation efforts other than natural attenuation difficult.

8.2. Recommendations.

- Although the Building 719 contaminants alone do not appear to be a detriment to the St. Jones River, the general presence of the contaminants within the Columbia Aquifer warrants notifying the local populace that use of the groundwater south of the Building 719 site for purposes such as drinking water as well as agricultural and industrial usage contains certain health risks.
- Additional monitoring should be conducted throughout the groundwater table to establish concentration profiles of contaminants, inorganics, and oxygen as well as determining whether any DNAPL has accumulated on the bottom of the aquifer. The additional monitoring will also provide the ability to verify and adjust modeling degradation rates as necessary.
- Hydraulic conductivity tests should be conducted in the shallow groundwater between Building 719 and the St. Jones River to obtain a better approximation as to actual groundwater advection.
- Laboratory batch and column tests should be conducted for comparison and possible adjustment of empirical adsorption partition coefficients.
- Given the various other groundwater contaminated sources throughout the base as well as risks to the local populace between the base and the St. Jones

River, the recommendation is for immediate remediation design and implementation. As a minimum, remedial action should begin prior to the year 2000 to reduce the risks to the base housing area. Remediation efforts/attempts beyond the year 2000 may require evacuating the housing area which could create a significant hardship on base operations and "quality of life."

- Remediation Recommendations:

- * **Long-Term:** Ex-situ treatment (i.e. pump and treat) is recommended as the primary remediation method because of the difficulty in controlling the subsurface environment as well as confining the contaminants to the site during in-situ treatment. Ex-situ treatments that should be considered and investigated include biological reactors, air stripping, granular activated carbon reactors, and steam stripping (59).
- * **Short-Term:** In-situ injection of methane through wells installed down gradient of plume and up gradient of the housing area now may help to increase natural attenuation through cometabolism and reduce migration while waiting for full scale ex-situ remediation design and implementation. Another short-term remediation method to consider is "zero-valent iron" abiotic reductive dechlorination. The zero-valent iron technology has been shown in the laboratory to significantly enhance degradation of halogenated aliphatic hydrocarbons by oxidation of zero-valent iron

$(2\text{Fe}^0 \rightarrow 2\text{Fe}^{2+} + 4\text{e}^-)$ as an electron source for reductive dechlorination (20). The method appears to be viable for either ex-situ or in-situ treatment.

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APPENDIX A
GROUNDWATER ANALYSIS RESULTS
AND SAMPLE LOCATIONS

Table A.1. Groundwater Contaminant Concentration Data by Bore Hole (TRW) (39).

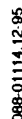
Bore Hole	TCE (ug/L)	TCA (ug/L)	Cis DCE (ug/L)	Trans DCE (ug/L)	1,2 DCA (ug/L)	1,1 DCA (ug/L)	1,1 DCE (ug/L)	VC (ug/L)	CA (ug/L)
1	780	91	1600	BDL (50)	86	310	18	100	BDL (50)
2	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA
3	1200	270	8000	BDL (50)	260	310	150	320	BDL (50)
4	7600	2300	82000	BDL (500)	BDL (500)	2300	660	BDL (500)	BDL (500)
5	930	26	570	BDL (5)	170	43	6	6	BDL (5)
6	620	11	460	BDL (5)	480	70	11	13	BDL (5)
7	130	7	260	BDL (5)	26	170	14	14	BDL (5)
8	5800	850	69000	BDL (250)	BDL (250)	950	BDL (250)	BDL (250)	BDL (250)
9	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA
10	62000	500	70000	BDL (500)	760	BDL (500)	BDL (500)	BDL (500)	BDL (500)
11	560	46	600	BDL (5)	47	15	15	5	6
12	1500	32	7700	BDL (2.5)	760	87	87	170	BDL (25)

NDA: No data available

BDL: Below detection limits

Detection Limits for 1,1-DCE, 1,2-DCA, 1,1-DCA, and VC were used to calculate average concentrations (Table 1.1)

Note: Groundwater table was approximately 10.5 feet below grade during testing.
 Samples were taken just below the groundwater table.



LEGEND:

	TRW Sample Point
	Scale
	Dam & Moore Soil/Gas Sample Point
	Underground Utilities

Figure A.1. Building 719 Groundwater Analytical Sample Locations Noted by TRW (Illustration is partial layout profile of Northeast Section of Building 719) (39).

APPENDIX B

CONTAMINANT MODEL CONCENTRATIONS
AS A FUNCTION OF TIME

Table B.1. TCA Concentrations ($\mu\text{g/L}$).

Distance (ft.)	YEAR					
	1997	2000	2002	2005	2010	2020
200	7	0	0	0	0	0
400	160	1	0	0	0	0
600	21	3	0	0	0	0
800	0	5	0	0	0	0
1000	0	5	1	0	0	0
1200	0	2	1	0	0	0
1400	0	1	1	0	0	0
1600	0	0	0	0	0	0
1800	0	0	0	0	0	0
2000	0	0	0	0	0	0
2200	0	0	0	0	0	0
2400	0	0	0	0	0	0
2600	0	0	0	0	0	0
2800	0	0	0	0	0	0
3000	0	0	0	0	0	0
3200	0	0	0	0	0	0
3400	0	0	0	0	0	0
3600	0	0	0	0	0	0
3800	0	0	0	0	0	0
4000	0	0	0	0	0	0
4200	0	0	0	0	0	0
4400	0	0	0	0	0	0
4600	0	0	0	0	0	0
4800	0	0	0	0	0	0
5000	0	0	0	0	0	0
5200	0	0	0	0	0	0
5400	0	0	0	0	0	0
5600	0	0	0	0	0	0
5800	0	0	0	0	0	0
6000	0	0	0	0	0	0
6200	0	0	0	0	0	0
6400	0	0	0	0	0	0
6600	0	0	0	0	0	0
6800	0	0	0	0	0	0
7000	0	0	0	0	0	0
7200	0	0	0	0	0	0

Table B.2. TCE Concentrations ($\mu\text{g/L}$).

Distance (ft.)	Year					
	1997	2000	2002	2005	2010	2020
200	9	0	0	0	0	0
400	910	0	0	0	0	0
600	198	0	0	0	0	0
800	0	1	0	0	0	0
1000	0	2	0	0	0	0
1200	0	2	0	0	0	0
1400	0	1	0	0	0	0
1600	0	0	0	0	0	0
1800	0	0	0	0	0	0
2000	0	0	0	0	0	0
2200	0	0	0	0	0	0
2400	0	0	0	0	0	0
2600	0	0	0	0	0	0
2800	0	0	0	0	0	0
3000	0	0	0	0	0	0
3200	0	0	0	0	0	0
3400	0	0	0	0	0	0
3600	0	0	0	0	0	0
3800	0	0	0	0	0	0
4000	0	0	0	0	0	0
4200	0	0	0	0	0	0
4400	0	0	0	0	0	0
4600	0	0	0	0	0	0
4800	0	0	0	0	0	0
5000	0	0	0	0	0	0
5200	0	0	0	0	0	0
5400	0	0	0	0	0	0
5600	0	0	0	0	0	0
5800	0	0	0	0	0	0
6000	0	0	0	0	0	0
6200	0	0	0	0	0	0
6400	0	0	0	0	0	0
6600	0	0	0	0	0	0
6800	0	0	0	0	0	0
7000	0	0	0	0	0	0
7200	0	0	0	0	0	0

Table B.3. *Cis* and *Trans* 1,2 and 1,1-DCE Concentrations (ug/L)
(95 % is of the *Cis*-DCE Constituent).

Distance (ft.)	Year						
	1997	2000	2002	2005	2015	2029	2039
200	801	45	7	0	0	0	0
400	38973	2395	363	3	0	0	0
600	7647	8816	2135	43	0	0	0
800	0	14130	5933	277	0	0	0
1000	0	12483	9949	1082	0	0	0
1200	0	6508	11107	2865	0	0	0
1400	0	1986	8639	5472	1	0	0
1600	0	325	4767	7836	8	0	0
1800	0	22	1861	8619	35	0	0
2000	0	0	503	7391	126	0	0
2200	0	0	89	4980	379	0	0
2400	0	0	9	2640	941	0	0
2600	0	0	9	2640	941	0	0
2800	0	0	0	1096	1945	0	0
3000	0	0	0	352	3366	0	0
3200	0	0	0	86	4887	1	0
3400	0	0	0	15	5959	2	0
3600	0	0	0	2	6107	8	0
3800	0	0	0	2	6107	8	0
4000	0	0	0	0	5254	24	0
4200	0	0	0	0	3785	68	0
4400	0	0	0	0	2274	169	0
4600	0	0	0	0	1132	375	0
4800	0	0	0	0	463	743	1
5000	0	0	0	0	154	1317	4
5200	0	0	0	0	41	2084	10
5400	0	0	0	0	8	2941	27
5600	0	0	0	0	1	3698	66
5800	0	0	0	0	0	4133	147
6000	0	0	0	0	0	4096	297
6200	0	0	0	0	0	3589	551
6400	0	0	0	0	0	2771	934
6600	0	0	0	0	0	1877	1445
6800	0	0	0	0	0	1109	2041
7000	0	0	0	0	0	569	2625
7200	0	0	0	0	0	95	3260

Table B.4. VC Concentrations ($\mu\text{g/L}$).

Distance (ft.)	YEAR						
	1997	2000	2002	2005	2015	2029	2039
200	29	4	1	0	0	0	0
400	679	148	33	1	0	0	0
600	72	474	179	8	0	0	0
800	0	654	451	44	0	0	0
1000	0	486	682	157	0	0	0
1200	0	206	679	376	0	0	0
1400	0	48	464	651	0	0	0
1600	0	5	221	845	2	0	0
1800	0	0	73	839	9	0	0
2000	0	0	16	646	33	0	0
2200	0	0	2	388	95	0	0
2400	0	0	0	181	225	0	0
2600	0	0	0	181	225	0	0
2800	0	0	0	65	440	0	0
3000	0	0	0	18	713	0	0
3200	0	0	0	4	964	0	0
3400	0	0	0	1	1086	1	0
3600	0	0	0	0	1021	4	0
3800	0	0	0	0	1021	4	0
4000	0	0	0	0	800	13	0
4200	0	0	0	0	520	34	0
4400	0	0	0	0	280	79	0
4600	0	0	0	0	123	168	0
4800	0	0	0	0	44	315	1
5000	0	0	0	0	13	528	3
5200	0	0	0	0	3	788	7
5400	0	0	0	0	0	1044	18
5600	0	0	0	0	0	1228	42
5800	0	0	0	0	0	1278	89
6000	0	0	0	0	0	1174	172
6200	0	0	0	0	0	949	304
6400	0	0	0	0	0	673	490
6600	0	0	0	0	0	416	720
6800	0	0	0	0	0	223	963
7000	0	0	0	0	0	103	1170
7200	0	0	0	0	0	13	1284

Table B.5. 1,2-DCA Concentrations (ug/L).

Distance (ft.)	YEAR					
	1997	2000	2002	2005	2015	2039
200	3	0	0	0	0	0
400	220	13	2	0	0	0
600	84	52	13	0	0	0
800	0	87	36	2	0	0
1000	0	83	62	7	0	0
1200	0	47	72	18	0	0
1400	0	16	59	35	0	0
1600	0	3	34	51	0	0
1800	0	0	14	58	0	0
2000	0	0	4	51	1	0
2200	0	0	1	35	3	0
2400	0	0	0	19	7	0
2600	0	0	0	19	7	0
2800	0	0	0	8	14	0
3000	0	0	0	3	24	0
3200	0	0	0	1	35	0
3400	0	0	0	0	43	0
3600	0	0	0	0	44	0
3800	0	0	0	0	44	0
4000	0	0	0	0	38	0
4200	0	0	0	0	28	1
4400	0	0	0	0	17	1
4600	0	0	0	0	9	3
4800	0	0	0	0	4	6
5000	0	0	0	0	1	11
5200	0	0	0	0	0	17
5400	0	0	0	0	0	24
5600	0	0	0	0	0	30
5800	0	0	0	0	0	33
6000	0	0	0	0	0	33
6200	0	0	0	0	0	29
6400	0	0	0	0	0	22
6600	0	0	0	0	0	15
6800	0	0	0	0	0	9
7000	0	0	0	0	0	5
7200	0	0	0	0	0	1

Table B.6. 1,1-DCA Concentrations (ug/L).

Distance (ft.)	YEAR					
	1997	2000	2002	2005	2015	2039
200	32	2	0	0	0	0
400	1085	83	13	0	0	0
600	220	290	75	2	0	0
800	0	447	200	10	0	0
1000	0	382	326	40	0	0
1200	0	194	355	102	0	0
1400	0	58	269	190	0	0
1600	0	9	145	265	0	0
1800	0	1	56	285	2	0
2000	0	0	15	239	5	0
2200	0	0	3	158	16	0
2400	0	0	0	82	38	0
2600	0	0	0	82	38	0
2800	0	0	0	33	77	0
3000	0	0	0	11	129	0
3200	0	0	0	3	182	0
3400	0	0	0	0	216	0
3600	0	0	0	0	216	0
3800	0	0	0	0	216	0
4000	0	0	0	0	181	1
4200	0	0	0	0	127	3
4400	0	0	0	0	75	8
4600	0	0	0	0	36	18
4800	0	0	0	0	15	34
5000	0	0	0	0	5	59
5200	0	0	0	0	1	91
5400	0	0	0	0	0	124
5600	0	0	0	0	0	152
5800	0	0	0	0	0	165
6000	0	0	0	0	0	160
6200	0	0	0	0	0	136
6400	0	0	0	0	0	102
6600	0	0	0	0	0	68
6800	0	0	0	0	0	39
7000	0	0	0	0	0	20
7200	0	0	0	0	0	3